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Heterobinuclear Alkyl Complexes of Rhodium and Iridium

by

Okemona Efe Oke ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry

Edmonton, Alberta
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To

God

For His boundless Grace

Abstract

The chemistry of the dppm-bridged heterobinuclear methyl complexes, $[RhIr(CH_3)(CO)_n(dppm)_2][CF_3SO_3]$ (n = 3 (**1**), n = 2 (**2**)), has been investigated. Reaction of **1** with PMe_3 or PMe_2Ph at low temperature yields $[RhIr(CH_3)(CO)_3(PMe_2R)(dppm)_2][CF_3SO_3]$ (R = Me (**3a**), Ph (**3c**)), having the phosphine moiety bound to Rh. Compounds **3a,c** rearranged to $[RhIr(CH_3)(CO)_2(PMe_2R)(dppm)_2][CF_3SO_3]$ (**4a,c**) upon warming, accompanied by facile phosphine transfer and CO loss. Compound **4a** has been characterized crystallographically. Removal of one carbonyl from **4a,c** results in phosphine transfer back to Rh from Ir, yielding $[RhIr(CH_3)(\mu\text{-}CO)(PMe_2R)(dppm)_2][CF_3SO_3]$ (**5a,c**).

A series of monomethyl derivatives with the general formulation $[RhIr(CH_3)(R)(CO)_2(dppm)_2]$ (R = H (**11**), CN (**10**), I (**13**), CH_3 (**25**), Ph (**28**), CH_2Ph (**29**)) has been synthesized by addition of the appropriate nucleophile to **2**; all but compound **13** have both anionic ligands, CH_3 and R, bound to Ir.

Reaction of **2** with C_2F_4 gives the olefin-bridged complex $[RhIr(CH_3)(CO)(\mu\text{-}CO)(\mu\text{-}C_2F_4)(CF_3SO_3)(dppm)_2]$ (**18**) whereas allene provides $[RhIr(CH_3)(CO)_2(C_3H_4)(dppm)_2][CF_3SO_3]$ (**19**) in which the olefin is η^2-bound to Ir and the methyl group has migrated to Rh. The structurally related **5c** reacts with allene to give the allene-bridged species $[RhIr(CH_3)(CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_3H_4)(PMe_2Ph)(dppm)_2][CF_3SO_3]$ (**22**).

The dimethyl and dibenzyl A-frame complexes, $[RhIr(R)_2(\mu\text{-}CO)(dppm)_2]$ (R = CH_3 (**23**), CH_2Ph (**24**)), have been obtained by halide metathesis reactions of *trans*-$[RhIrCl_2(CO)_2(dppm)_2]$ with methyl- and benzyl magnesium chloride,

respectively. Reaction of **23** with CO results in acetone formation whereas reaction with H_2 yields the dihydride species $[RhIr(CH_3)_2(H)(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]$ (**30**). Carbonylation of **30** at 0 °C yields the acetyl species, $[RhIr(COCH_3)(CH_3)(H)(\mu\text{-}CO)(\mu\text{-}H)(dppm)_2]$ (**31**), which generates $[RhIr(CO)_3(dppm)_2]$ along with acetaldehyde and methane upon warming. The trimethyl species, $[RhIr(CH_3)_3(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**34**), observed at low temperature upon alkylation of **23**, reacts with olefins to give the methyl-bridged complexes $[RhIr(CH_3)_2(L)(\mu\text{-}CH_3)(CO)(dppm)_2][CF_3SO_3]$ (L = ethylene (**37**), dimethylallene (**38**)).

Reactions of **2** and **23** with SO_2 affords the alkyl sulphonate species, $[RhIr(SO_2CH_3)(CO)_2(\mu\text{-}SO_2)(dppm)_2][CF_3SO_3]$ (**9**) and $[RhIr(SO_2CH_3)(CH_3)(CO)(\mu\text{-}SO_2)(dppm)_2]$ (**33**), respectively, whereas with the dihydrosilane Ph_2SiH_2, the agostic species, $[RhIr(CH_3)(CO)_2(H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SiPh_2H)(dppm)_2][CF_3SO_3]$ (**57**), and the methyl silyl species $[RhIr(CH_3)(CO)(H)(\mu\text{-}H)(SiPh_2Me)(dppm)_2]$ (**66**), were obtained, respectively.

The methoxy methyl complex, $[RhIr(I)(CH_2OCH_3)(CO)_2(dppm)_2]$ (**74**), prepared by oxidative addition of iodomethylmethyl ether to $[RhIr(CO)_3(dppm)_2]$, reacts rapidly with methyl triflate and trimethylsilyl triflate affording, $[RhIr(CH_2OCH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**75**) and the methylene-bridged species, $[RhIr(I)(CO)_2(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**76**), respectively. Addition of CH_2N_2 to **2** at ambient temperature did not give the targeted methylene-bridged product, but instead provided the hydrido-ethylene species $[RhIr(CO)_2(C_2H_4)(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**80**), along with the C_4 product, 1-butene.

Acknowledgement

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List of Abbreviations and Symbols

anal.	analysis
ca.	circa (approximately)
calcd.	Calculated
CP-MAS	cross-polarization with magic angle spinning
Diazald	N-methyl-N-nitroso-p-toluenesulfonamide
DMAD	dimethylacetylenedicarboxylate
dppm	bis(diphenylphosphino)methane
DFT	density functional theory
equiv	equivalent
Et	Ethyl, CH_3CH_2-
h	hour(s)
HFB	hexafluoro-2-butyne
HMQC	heteronuclear multiple quantum coherence
IR	infrared
Me	methyl, CH_3-
MeOH	methanol
mg	milligrams
min	minute(s)
mL	millilitres
mmol	millimoles
M	molar
MHz	megahertz
NMR	nuclear magnetic resonance
Ph	phenyl, C_6H_5-
ppm	parts per million
THF	tetrahydrofuran
^{t}Bu	tertiary butyl, $(CH_3)_3C$-
µL	microlitres

Crystallographic Abbreviations and Symbols

a, b, c	lengths of the x, y, and z axes, respectively, of the unit cell
deg (or °)	degrees
F_c	calculated structure factor
F_o	observed structure factor
$GOF(S)$	goodness of fit
h, k, l	Miller indices defining lattice planes, where the plane intersects the unit cell axes at 1/h, 1/k 1/l of the respective lengths a, b, and c.
R_1	residual index (a measure of agreement between calculated and observed structure factors)
wR_2	weighted residual index
V	unit cell volume
w	weighting factor applied to structure factor
Z	number of molecules per unit cell
Å	Angström(s) (1Å = 10^{-10} metres)
α, β, γ	angles between b and c, a and c, and a and b axes, respectively, of unit cell
λ	wavelength
ρ	density
σ	standard deviation

Chapter One

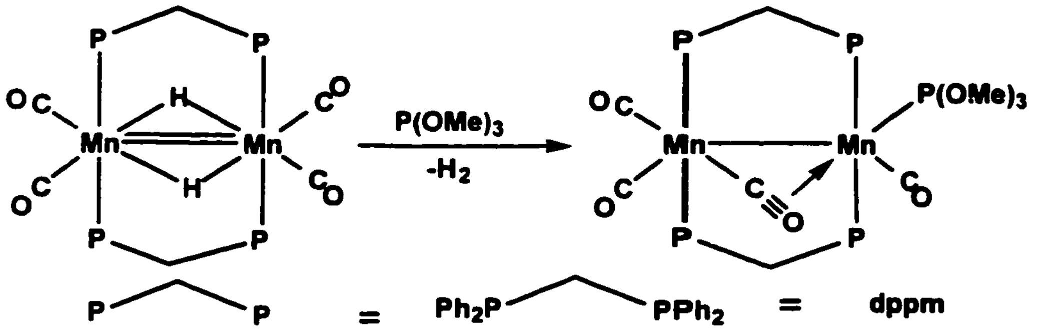
Introduction

The desire to understand more fully reactions in which simple organic molecules are transformed into more complex useful end-products is a continuing challenge to chemists. A large number of these transformations are catalyzed[1] by transition metals which bind to the substrates and become intimately involved in the catalytic cycles. An understanding of the dynamics of metal-substrate interactions is therefore central to the rational design of highly efficient catalyst systems.

Catalysts, commonly used in industrial scale processes, fall into two classes: homogeneous[2] and heterogeneous,[1c] according to the physical state of the catalysts and the reacting substrate. Homogeneous catalysts, which are normally transition metal complexes dissolved in the appropriate solvent, offer the advantages of being better understood due to the ease by which the discrete reaction steps can be monitored and analyzed by a battery of spectroscopic techniques. In addition, since a single, well-defined catalyst or catalyst precursor is used, it is capable of high selectivity toward specific functional groups in substrates. On the other hand, heterogeneous processes involving metals as catalysts often occur either on the surfaces of metals or on metal oxides and are preferred for industrial use because the catalyst can be easily recovered for re-use and generally possesses much higher thermal stability. One major drawback of heterogeneous systems, however, is the lack of specificity owing to the availability of several types of active sites on the surface.[3] Thus it has been difficult to identify the active component or reaction intermediates, and mechanistic information on some of the processes occurring on these surfaces is scarce.[4] Although a number of research protocols[4,5] have been devised to study these processes, including surface spectroscopy, probe-molecule studies and chemical trapping experiments, heterogenous catalysis remains largely a black-box science in which the reaction outcomes are adjusted by "tinkering" with the experimental conditions.

One approach to obtaining valuable information about intermediates in heterogeneous systems is through the use of well-behaved model compounds which are usually studied under more amenable homogeneous conditions. Currently, most homogeneous processes occurring at a single metal center are understood in great detail, and what has been learned about these systems has been adapted as models for heterogeneous processes.[6] However, it is now commonly accepted that polymetallic clusters[7] are probably better representations of metal surfaces in heterogeneous catalysis than their mononuclear counterparts, due to the fact that the metals are held in close proximity, mimicking to some degree the multi-metal environments of metal surfaces.[8,9] The Fischer-Tropsch process[10] effectively emphasizes this concept of "cluster-surface analogy",[7b,11] in that it implicates the coupling of an ensemble of high-energy organic fragments such as "C", "CH" and "CH_2" on the metal surfaces. The existence of these fragments, although fleeting, owing to their inherent instability, has been established on catalyst surfaces in a number of heterogenous processes,[10,12a] and they have been observed as ligands in several polymetallic[12] and bimetallic complexes.[13]

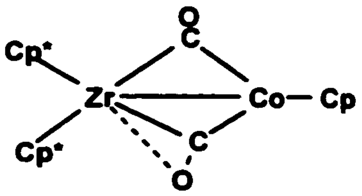
Binuclear complexes, which can be viewed as prototypical clusters containing two metals, represent the simplest multi-metal system in which the involvement of adjacent metals in the chemistry can be studied. Although the binuclear system is a poorer model of a metal surface or other heterogeneous systems than a multi-metal cluster of higher nuclearity, it does offer the advantage of ease of study. In such systems the metals can either act independently of each other, reacting essentially as two monomeric units in the activation of organic or inorganic substrates, or alternately, one metal can perturb the other thereby acting in some cooperative manner.[14] The anticipation here is that the influence of metal-metal cooperativity can result in unique chemistry not observed in related mononuclear complexes. This cooperativity effect may manifest itself in several ways. A substrate may coordinate to one metal followed by subsequent reactivity with organic fragments bound to both metals. As an example, the methylation of the vinylidene-bridged complex $[RhMn(CO)_3(\mu\text{-}C{=}CHC(O)Me)(dppm)_2]$ was reported to occur at rhodium to give an initial methyl species $[RhMn(CH_3)(CO)_3(\mu\text{-}C{=}CHC(O)Me)(dppm)_2][CF_3SO_3]$ which subsequently rearranged to the vinyl species $[RhMn(Z\text{-}C(Me){=}CHC(O)Me)(CO)_2(\mu\text{-}CO)_2(dppm)_2][CF_3SO_3]$ upon CO addition.[15e] In addition, a ligand may be coordinated to one metal with the adjacent metal serving as a sink or source for electrons[16] or molecular fragments,[10a] thereby receiving or supplying electrons or molecular fragments as dictated by the requirements of the neighbouring metal. In the example shown below,[14d] the terminal CO group on one of the Mn centers, acts as an



electron source by simultaneously binding in a π fashion to the adjacent Mn atom thereby compensating for the electronic unsaturation at this metal, which would have an unfavorable 16e configuration in its absence.

Furthermore, the combination of two or more closely held metals can often stabilize an inherently transient species[12e,14e,g] or provide bridged forms of a coordinated ligand,[14f] in which the ligand may display reactivity different than when it is terminally bound to only one metal. An example of the former is seen in the stabilization of "CH" and "CH_2" fragments by triiron clusters.[12e]

Although the reactivity and catalytic potential of homobinuclear complexes have been investigated for several years,[16] the chemistry of heterobinuclear systems (in which the two metals are different) has only recently become the object of inquiry.[17] It has been suggested[18] that two different metals, adjacent to each other, might display a different chemistry than their homobinuclear counterparts, due to the combination of the differing metal properties in the same system. This reasoning perhaps inspired the

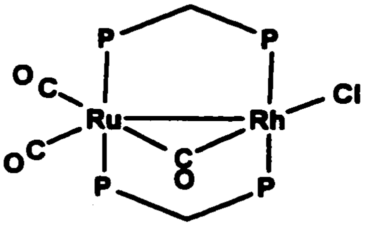


Cp* = $C_5(CH_3)_5^-$

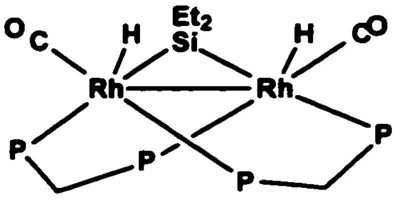
Cp = $C_5H_5^-$

use of early-late heterobinuclear complexes[18a] in the reduction of polar substrates by combining the Lewis acidity and oxophilicity of early metals (hard center) with the ability of late metals (soft center) to form strong metal-carbon bonds and to bind π acid ligands, as exemplified by Bercaw and co-workers[19] in the Zr/Co species shown above. The strategy used in such complexes was that the early metal could assist in weakening the C-O bond while the late metal could coordinate and activate dihydrogen molecules for subsequent reduction of coordinated CO. Although mixed-metal binuclear complexes have been studied largely for the possibilities of exhibiting novel chemistry, lately they have elicited a great deal of interest as homogeneous catalysts.[1e,2c] Also, mixed-metal catalysts find extensive use in industrial scale processes such as the hydrodesulfurization of coal (Co/Mo),[20] gasoline reforming (Re/Pt),[20] and catalytic converters employed in the scrubbing of exhaust from automobiles (Rh/Pt). In addition, the formation of ethylene glycol from syn gas (CO/H_2) utilizes a Ru/Rh catalyst.[21] Although Ru and Rh used individually as catalysts are known to produce oxygenates, improved selectivity was shown for the mixed-metal catalyst owing presumably to the complementary influences of the different metals.[22] Most of these systems require heterogeneous conditions, although several homogeneously catalyzed processes are known including the Wacker Process in which ethylene is oxidized by a Pd/Cu[18d,f] catalyst to give acetaldehyde, and the BP Chemicals Acetic Acid Process which employs an Ir/Ru[21] catalyst to convert a CH_3OH/CO mixture into acetic acid.

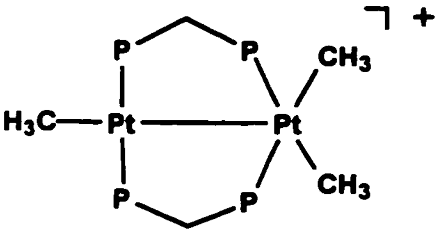
During reactions involving binuclear complexes, the integrity of the complex may be disrupted through fragmentation into mononuclear units, complicating the study of cooperativity effects. One common solution to this problem is to use bridging ligands which serve to hold both metals in close proximity while permitting some flexibility in the form of interaction between the metals and ligands. Although several bridging groups are in current use,[15,23] one of the most popular has been the diphosphine, bis(diphenylphosphino)-methane (dppm or DPM), already shown in the example above.[24] By far the most commendable features of this ligand are its affordability, its tendency to bridge rather than chelate when binding to metals, and its ready access to structural information through the use of ^{31}P and ^{1}H NMR spectroscopy.[25] In addition, the dppm ligand is a good σ donor and therefore tends to increase the electron density at the metals, thereby rendering the metals easily oxidizable.[26] Furthermore, the bulky phenyl substituents often give rise to favorable solubility and frequently allows the crystallization of the metal complexes needed for X-ray crystallography. Complexes containing two bridging dppm ligands can display a number of geometries.[27-30] In a binuclear framework, the common arrangements when two diphosphine ligands bridge the metals (examples of which are shown below) are trans,trans[28,30b] (most dppm-bridged binuclear complexes), trans,cis[27] (eg. $[Pt_2Me_3(dppm)_2][PF_6]$[15b]) and cis,cis (eg. $[Rh_2(H)_2(CO)_2(\mu\text{-}SiEt_2)(dppm)_2]$).[29a] There are also reports[29] of complexes (eg. $[Rh_2(CO)_4(\mu\text{-}SiEt_2)(dppm)(\eta^1\text{-}Ph_2PCH_2PPh_2)]$)[29a] in which one dppm ligand bridges both metals while the other either binds in an η^1 fashion, having a pendent phosphine, or is chelated to one of the metals.[30] Normally, the dppm ligands play an innocent role during the reactions but there are emerging reports where deprotonations or substitutions of the dppm methylene hydrogens,[31] insertions/cleavages of the M-P[32] or P-C[30,29a,33] bonds or orthometallation processes[27,31c] have occurred.



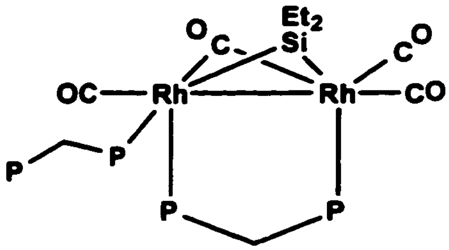
trans-trans



cis-cis



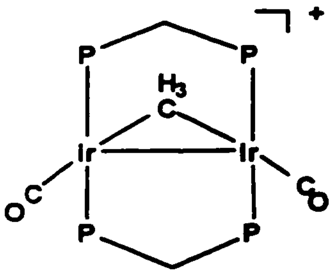
trans-cis



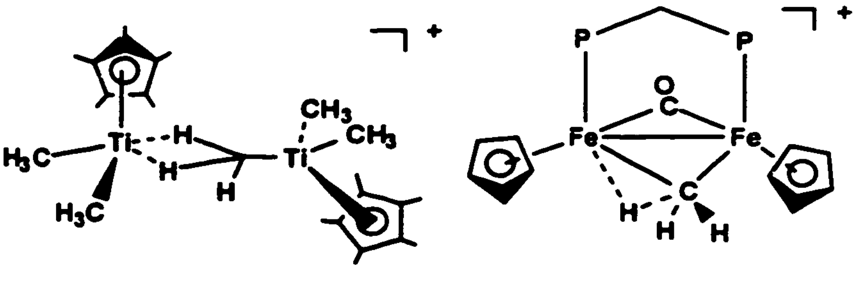
bridging-pendent

This study will concentrate on the chemistry of dppm-bridged binuclear systems incorporating the simplest organic moiety, the methyl group. Historically, metal alkyls have been implicated as key intermediates in a variety of important catalytic processes such as the carbonylation of methanol,[34] olefin hydroformylation, and hydrosilylation.[35] A notable reaction linked to the intermediacy of alkyl fragments is the hydrogenation of carbon monoxide.[22] An illustration of this is seen in the Pettit mechanism[36] for the Fischer-Tropsch reaction, in which carbon monoxide is reduced to CH_2 and CH_3 fragments and carbon chain growth is assumed to occur via the coupling of surface-bound alkyl and methylene framents, initiated by coupling of a methyl with a methylene group. The hydrogenation of olefins also involves the formation of alkyl intermediates at some stage in the catalytic cycle via insertion of the alkene molecule into the metal-hydrogen bond. Furthermore, it is also widely accepted that alkyl complexes,[35d,37] particularly those of Ti and Zr, are important intermediates during the chain-propagation stages of Ziegler-Natta polymerization of olefins. The metal-alkyl bond of the resulting polymer can be hydrogenolyzed or removed by β-hydride elimination, causing termination of chain growth.[37b,c]

It is noteworthy that some of the most significant advances in our understanding of fundamental mechanistic steps in homo- and heterogeneous catalysis has benefitted from reactions utilizing mononuclear alkyl complexes. Some of the early mononuclear alkyl complexes include coordinatively unsaturated iridium (I)[38] or rhodium (I)[39] and platinum (II)[40] species. These compounds were principally exploited to take advantage of the ability of the metals to undergo oxidative addition followed by reductive elimination reactions; these two reaction steps are pivotal in many catalytic processes. Much of the catalytic studies on metal-mediated organic transformations involving alkyl substituents have concentrated on mononuclear systems[37] with little attention having been given to binuclear complexes, in spite of the potential of such systems as mixed-metal catalysts, as discussed earlier.[1e,2c,18d,20-22] However, in the aftermath of the early studies of binuclear alkyl complexes such as [$Li_2Re_2Me_8.2Et_2O$][41] and [$Mo_2Me_4(PMe_3)_4$],[42] the pace of research involving these complexes, particularly within the Co and Ni triads, has picked up dramatically in recent years, owing in part to the possibility of cooperative activation of organic substrates by adjacent metals. As was first reported for the diplatinum complex [$Pt_2Me_4(dmpm)_2$] by Puddephatt and co-workers,[43] alkyl groups in a bimetallic core can be quite mobile, migrating from one metal to the other, paralleling similar transfers on metal surfaces. Such ligand movements are of obvious interest to us as are the factors that dictate them. Although the majority of metal complexes have the alkyl substituent binding terminally to one of the metals, there are reports of complexes in which an alkyl group (usually methyl) either symmetrically bridges both metals[44] or binds in an asymmetric[45] fashion, being σ bound to one metal while engaging in a three-center-two-electron C-H (agostic) interaction with the adjacent metal.

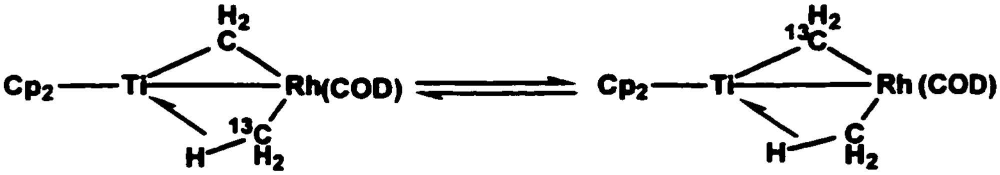


Symmetric



Asymmetric (agostic)

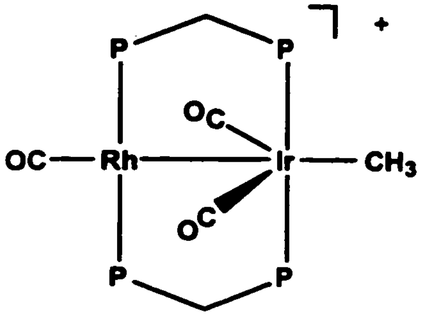
Examples of both types are shown above. Migrations of alkyl groups between adjacent metals are believed to proceed via the intermediacy of bridged alkyls.[13a,43] On the other hand, agostic interactions of the type shown above are of interest because they constitute attractive models for the activation of C-H bonds.[46] This is supported by the observation of C-H activation in several systems containing agostic C-H bonds.[47-49] As an example,[48b] hydrogen transfer between a μ-methylene and μ-methyl group was reported to occur for the mixed-metal Rh/Ti complex (shown below) after several months in solution, thus demonstrating the reversibility of C-H activation steps. More dramatic is



the facile, reversible H transfer between the hydride and the methylene group in the Ir_2 system $[Ir_2(H)(CO)_2(\mu\text{-}CH_2)(\mu\text{-}SO_2)(dppm)_2][CF_3SO_3]$ which presumably occurs via a bridged agostic methyl group in which the activation barrier to H exchange between the methylene hydrogens and the hydrido ligand is only *ca.* 6 Kcal mol^{-1}.[47b]

Interest in our group[15e,24c-e,47b] in alkyl complexes has focused mainly on dppm-bridged homo- and heterobinuclear systems having the group 9 metal, Rh, in combination with a second metal derived from groups 9 (Rh,Ir), 8 (Os), 7 (Mn) or 6 (Mo, W). One of our longstanding goals is to learn more about the involvement of adjacent metals in the activation of small molecules of catalytic relevance. In this thesis, the reactivity of a Rh/Ir framework will be investigated. Previous work on the reactivity of Rh_2 and Ir_2 systems with a variety of small molecules such as H_2, CO, ^{t}BuNC, SO_2, olefins, phosphines and alkynes had exhibited some rather interesting features[50-52] Thus it was anticipated that the heterobinuclear Rh/Ir analogues would lend themselves to some unique behaviour not shown by the Rh_2 and Ir_2 congeners. In the mixed-metal case, the greater tendency of Rh to be labile, adopt a square planar geometry and be coordinative unsaturated[53] combined with the greater basicity of Ir, its proclivity toward oxidative addition as well as its preference for high oxidation states[15b] suggested that the Rh/Ir combination could give rise to unusual reactivity that may yield useful insights into the modelling of organic transformations that occur on metal surfaces. Such model compounds are particularly useful when considering mixed-metal catalysts.

The mixed-metal monoalkyl complex $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (I), shown below, has been synthesized and structurally characterized in this research group and its reactivity with a number of small molecules has been investigated.[51b]



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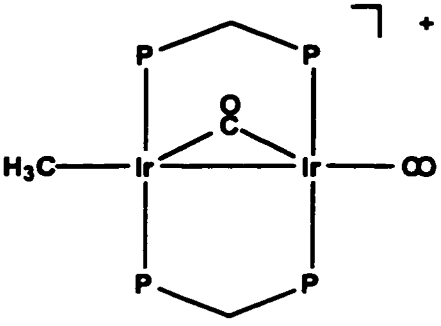


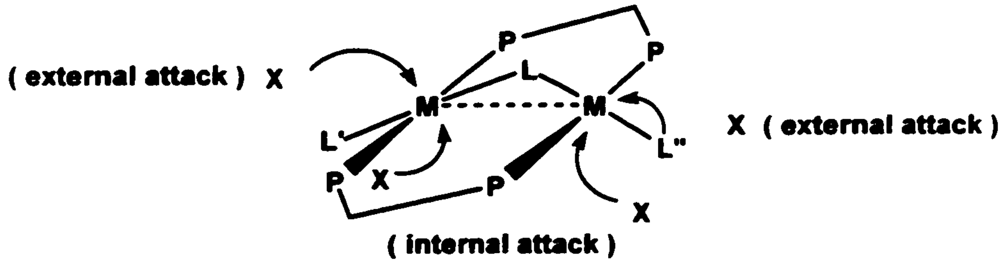
II

For example, I reacts with ${}^tBuNC$ to yield the iminoacyl species $[RhIr(CO)_2(\mu\text{-}{}^tBuN{=}C(CH_3))(dppm)_2][CF_3SO_3]$, and with SO_2 to give the acetyl species $[RhIr(COCH_3)(\mu\text{-}SO_2)(CO)_2(dppm)_2][CF_3SO_3]$. In each case, the observed product results from a migratory insertion of the methyl group. Surprisingly, in the latter reaction, no electrophilic attack of the CH_3 by SO_2 was observed. In addition, phosphine and ethylene additions to I gave CO-substituted products having the general formulation $[RhIr(CH_3)(CO)_2(L)(dppm)_2][CF_3SO_3]$ ($L = PR_3$, C_2H_4), and exposure of I to an atmosphere of dihydrogen gave the trihydride species $[RhIr(H)(CO)_2(\mu\text{-}H)_2(dppm)_2][CF_3SO_3]$ accompanied by methane and CO loss. In these reactions no intermediates leading to the final products were observed at ambient conditions. Therefore, the first goal of this study was to conduct investigations of these reactions at low temperature in attempts to establish the initial sites of ligand attack, the natures of any intermediates, and the roles each metal plays in subsequent rearrangements leading to the final products.

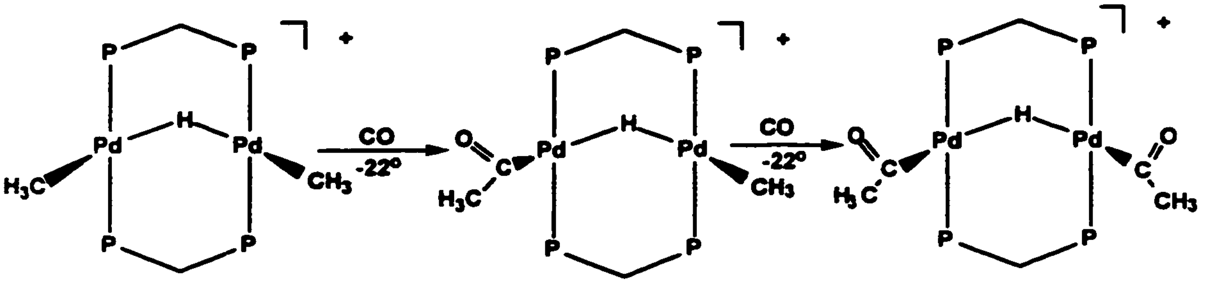
The related diiridium dicarbonyl analogue of **I**, $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**II**), shown above, has also been prepared and has revealed a wealth of chemistry,[47b] the most prominent of which involves the C-H bond activation of the methyl group upon substrate addition under relatively mild conditions. Furthermore, with unsaturated hydrocarbyl substrates subsequent C-C bond formation has also been observed.[51c] A second goal of this study was to synthesize the mixed-metal, dicarbonyl analogue $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**III**) and to study its reactivity with substrates having a range in steric and electronic properties. It was of interest to probe the functions of each metal in compound **III** in its possible insertion reactions (with, for example, CO, ^{t}BuNC, SO_2 and other unsaturated substrates) leading to the formation of C-C and C-heteroatom bonds, in its oxidative additions (with hydrogen sources such as dihydrogen, hydrosilanes and terminal alkynes), and in its reductive elimination chemistry, in the hopes of providing simple conceptual models of these transformations in mixed-metal catalysis. Related to this, it was of further interest to determine how the reactivities of the mixed Rh/Ir dicarbonyl species **III** and its homobinuclear counterpart **II** compared, bearing in mind the differing reactivity patterns reported for their tricarbonyl analogues.[51b]

A third minor goal of this study was to synthesize substituted alkyl compounds having the general formulation $[RhIr(CH_2X)(CO)_n(dppm)_2][CF_3SO_3]$ ($n = 2$ or 3) in attempts to probe possible steric and electronic effects as a result of modifying the methyl subsituent. How these effects would reflect on its subsequent reactivity, compared to those of the methyl complex **III**, was also of interest to us.

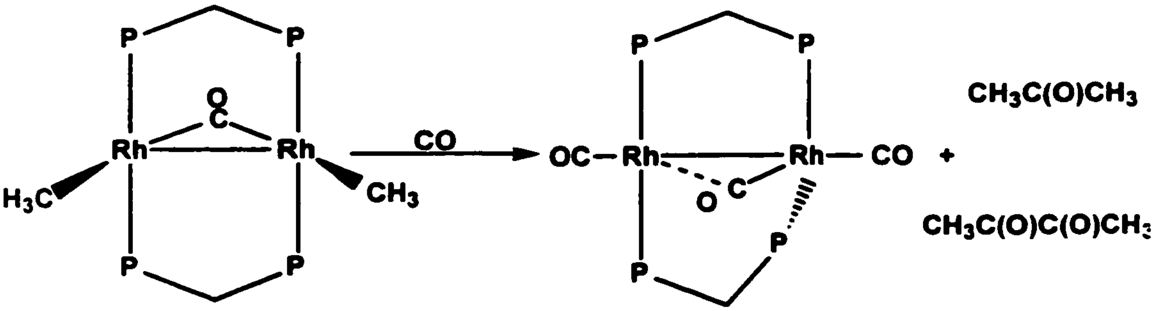
As mentioned earlier, alkyl transfers between adjacent metals have been observed[13a,43] for complexes of groups 9 and 10. These migrations are important since they make available open sites at one of the metals for further ligand coordination and reactivity. The availability of such sites at one or more metals in a binuclear framework or the lack of these are critical factors in determining the outcomes of important reaction steps in stoichiometric and catalytic studies such as oxidative-additions[54] and reductive-eliminations.[55] One system suitable for probing these factors is the so-called A-frame complex,[55a,56] having a structure in which the bridgehead ligand serves as a link between the two metal-containing square planes, thereby orienting the metal centers in a particular fashion as diagrammed below.



It has also been observed that the bridgehead ligand can direct the site of substrate attack by selectively permitting small molecules such as H_2, CO, HC≡CH and SO_2 to coordinate either in the pocket (internal attack) or outside (external attack) of the A-frame structure; these processes have been implicated in the catalytic processes such as the homogeneous hydrogenation of olefins,[56a] hydroformylation and water-gas shift reaction.[50b] The nature of the bridgehead ligand can also dictate the outcome of the subsequent reductive-elimination steps as exemplified[55a] in the low temperature carbonylation of the dipalladium A-frame complex $[Pd_2(CH_3)_2(\mu\text{-}H)(dppm)_2]$. In this reaction, the hydride ligand occupies a bridgehead site and the resulting bis(acetyl) species was proposed to reductively eliminate acetaldehyde presumably via an unobserved complex in which the eliminating fragments were mutually cis.



Interestingly, although the reactions using halogen-bridged dimers under similar conditions yielded the corresponding diacetyl species, these failed to spontanously reductively eliminate the expected acyl halide.[55a] Recently, Eisenberg and co-workers have reported[50c,d] that the carbonylation of the dialkyl A-frame complexes $[Rh_2(R)_2(\mu\text{-}CO)(dppm)_2]$ (R = CH_3, CH_2Ph) led to the formation of ketone and dione products, as depicted below for the dimethyl complex. These products were formed by distinctly different pathways; the



dione products were formed via a radical process while the ketone products resulted from a concerted intramolecular process.

The fourth goal of this study was the synthesis of the mixed-metal (Rh/Ir) dialkyl species such as $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$, with the intent of comparing its carbonylation chemistry with that of its homobinuclear Rh_2 analogue. Its subsequent reactivity toward other small molecules such as alkynes, silanes, dihydrogen, phosphines and sulfur dioxide was of additional interest.

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Chapter Two

Monomethyl Complexes : Reactions with Small Molecules

Introduction

A great deal of research effort has been expended on the studies of alkyl complexes of the groups 8, 9 and 10 (the iron, cobalt and nickel triads, respectively) in an attempt to gain a greater understanding of their thermodynamic stability,[1] mechanism of insertion reactions[2] and the roles they play in several metal-catalyzed transformations including hydroformylation,[3] hydrosilation,[4] olefin hydrogenation,[5] methanol carbonylation and carbon dioxide reduction.[6]

Although work on mononuclear alkyl complexes of these metals has resulted in an improved understanding of the involvement of metal-alkyl species in catalysis,[7] much less has been reported on binuclear derivatives, in spite of continuing interest in utilizing complexes containing adjacent metals as catalysts.[8,9] Our ongoing interest in possible cooperativity effects between adjacent metals[9e,f,10-14] and their involvement in the activation of C-H bonds of alkyl groups in dppm-bridged (dppm = $Ph_2PCH_2PPh_2$) binuclear complexes[10] has resulted in an extension of these studies to include the mixed Rh/Ir combination.[15]

Recent studies[15e,f] on the heterobinuclear alkyl complex $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**1**) with a variety of small molecules such as H_2, CO, ^tBuNC, SO_2, olefins, phosphines and with alkynes has shed some light on adjacent-metal involvement in migratory insertions, reductive eliminations and

C-C bond-forming and bond-breaking processes that are relevant to mixed-metal catalysis. One objective of this study was to further elaborate the chemistry of compound **1** and to prepare its dicarbonyl analogue [RhIr(CH_3)-($CO)_2$(dppm)$_2$][CF_3SO_3] (**2**) in the hope that the coordinative unsaturation generated on both metals would reflect a different reactivity pattern. In this chapter, particular emphasis will be placed on ligand additions to **1** and **2** with the intention of determining their initial sites of attack, subsequent ligand substitutions and rearrangements that occur, and finally the functions of each metal and how they influence these transformations.

EXPERIMENTAL SECTION

General Comments. All solvents were appropriately deoxygenated and dried by distillation over the appropriate drying agents (see Appendix) prior to use and were stored under dinitrogen. Deuterated solvents used for NMR experiments were degassed and stored under dinitrogen over molecular sieves. Reactions were carried out routinely at room temperature (unless otherwise stated) and under standard Schlenk conditions; compounds that were isolated as solids were purified by recrystallization. Hydrated rhodium trichloride was purchased from Engelhard Scientific, whereas all the phosphines and phosphites, silver trifluoromethanesulphonate (AgOTf), tert-butyl isocyanide, trimethylamine-N-oxide, 1,1-dimethylallene, Superhydride (lithium triethylborohydride, 1.0 M solution in THF), tetrabutylammonium cyanide and allyl bromide (99%) were obtained from Aldrich and were used as received. Potassium iodide was purchased from BDH Chemicals, allene was purchased from Canadian Liquid Air Ltd, tetrafluoroethylene was purchased from PCR Inc, ethylene and hydrogen were purchased from Linde, 1,2 butadiene was purchased from Fluka and carbon monoxide and sulfur dioxide were purchased from Matheson. ^{13}CO was supplied by Isotec Inc. All gases were used as received. The compounds, *trans*-$[RhIr(Cl)_2(CO)_2(dppm)_2]$[16] and $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$[10a] (**1**), were prepared as previously reported, while the compounds, $[RhIr(CH_3)(CO)_2(PR_3)(dppm)_2][CF_3SO_3]$ (**4a** R = Me, **4b** R = OPh), although previously prepared had been incompletely characterized.[17] The latter two compounds are included with full characterization in this chapter for completeness.

All routine NMR experiments were conducted on a Bruker AM-400 Spectrometer, whereas the $^{13}C\{^{31}P\}$ experiments were conducted on a Bruker AM-200 spectrometer operating at 50.32 MHz. ^{1}H-^{13}C HMQC experiments were carried out on a Varian Unity 500 MHz spectrometer while ^{1}H-^{1}H COSY experiments were performed on a Bruker AM-400 MHz Spectrometer. The solid-state $^{13}C\{^{1}H\}$ NMR spectrum was recorded on a Bruker AMR-300 spectrometer (with MAS accessory) operating at 75.5 MHz. Infra-red spectra were obtained on a Nicolet 7199 Fourier Transform or a Perkin-Elmer 883 IR Spectrometer, either as Nujol mulls on KBr plates or as solutions in KCl cells with 0.5mm-window pathlengths. Elemental analyses were performed by the microanalytical service within our department. Spectroscopic data for all compounds are given in Table 2.1, except for ^{19}F NMR data which are provided, where appropriate, with information on preparation of compounds.

Preparation of Compounds.

(a) $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (2). Compound **1** (60 mg, 0.046 mmol) was dissolved in 20 mL of CH_2Cl_2. The solution was gently refluxed under a slow dinitrogen purge at *ca.* 0.2 mLs^{-1} for 1 h, during which time the orange color of the solution deepened slightly. Removal of the solvent under

Table 2.1. Spectroscopic Parameters for the Compounds^{a}

Compounds	IR,^{b}cm^{-1}	NMR^{d}		
		δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C{^{1}H})
[RhIr(CH_3)(CO)$_2$(dppm)$_2$]-[CF_3SO_3] (**2**)	1954(ss)^{c}, 1858(bs), 1997(ms)	21.0-22.8(second order multiplet)	4.27(m,2H), 3.84(m,2H) 0.59(t,3H)	184.9(dm,$^{1}J_{RhC}$=7.0Hz,1C) 175.4(dt,$^{1}J_{RhC}$=72.8Hz,1C)
[RhIr(CH_3)(CO)$_3$(PMe$_3$)-(dppm)$_2$][CF_3SO_3] (**3a**)^{f}	-	29.6(ddm,$^{1}J_{RhP}$=121.0Hz) -19.6(m), -35.4(dt,$^{1}J_{RhP}$=147.2Hz,$^{2}J_{PP}$=29.7Hz)	4.75(m,2H),2.74(m,2H), -0.14(t,3H),0.60(d,$^{2}J_{PH}$=11.0Hz,9H)	262.7(dm,$^{1}J_{RhC}$=25.3Hz, 1C), 202.4(ddm,$^{1}J_{RhC}$=52.8Hz,1C),185.1(ddt,$^{2}J_{CC}$=$^{2}J_{RhC}$=14.0Hz,1C)
[RhIr(CH_3)(CO)$_3$(P(OPh)$_3$)-(dppm)$_2$][CF_3SO_3] (**3b**)^{f}	-	126.3(dt,$^{1}J_{RhP}$=190.3Hz), 27.2(ddm,$^{1}J_{RhP}$=144.1Hz, $^{2}J_{PP}$=48.9Hz), -21(m)	4.61(m,2H),4.94(m,2H), 0.65(t,3H)	232.8(bs,1C), 185.3(dm, $^{1}J_{RhC}$=31.2Hz,1C),186(ddm $^{1}J_{RhC}$=64.3Hz,1C)
[RhIr(CH_3)(CO)$_3$-(PPh(Me)$_2$)(dppm)$_2$]-[CF_3SO_3] (**3c**)^{f}	-	28.8(ddm,$^{1}J_{RhP}$=105.1Hz), -32.5(dt,$^{1}J_{RhP}$=128.9Hz, $^{2}J_{PP}$=35.8Hz), -17.6(m)	4.58(m,2H),2.90(m,2H), 1.06(d,$^{2}J_{PH}$=7.2Hz,6H), -0.08(t,3H)	260.2(dm,$^{1}J_{RhC}$=12.0Hz, 1C), 201.1(ddm,$^{1}J_{RhC}$=65.1Hz,1C), 187.7(bs,1C)
[RhIr(CH_3)(CO)$_3$-(PPh(OMe)$_2$)(dppm)$_2$]-[CF_3SO_3] (**3d**)^{f}	-	153.0(dt,$^{1}J_{RhP}$=157.2Hz, $^{2}J_{PP}$=53.7Hz), 27.4(ddm, $^{1}J_{RhP}$=134.0Hz), -17.0(m)	4.94(m,2H),4.62(m,2H), 3.92(d,$^{2}J_{PP}$=6.0Hz,6H), 0.41(t,3H)	233.9(dm,$^{1}J_{RhC}$=10.2Hz, 1C)190.7(ddt,$^{1}J_{RhC}$=63.9Hz $^{2}J_{PH}$ =15.1Hz,1C), 185.0 (m,1C)

Table 2.1 (contd).

Compounds	IR,^{b}cm^{-1}	NMR^d		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(CH_3)(CO)_2(PMe_3)$-$(dppm)_2][CF_3SO_3]$ **(4a)**^{n}	2028(ms), 1956 (ss)	12.6(dm,$^1J_{RhP}$=131.3Hz), 6.4(dm,$^1J_{RhP}$=126.1Hz), -23.5(m), -32.7(m), -61.2(m)	5.55(m,1H), 5.08(m,1H), 4.82(m,1H), 4.77(m,1H) 0.33(dt,$^3J_{P(DPM)H}$=8.2Hz,$^3J_{PH}$ =14.1Hz,3H), 0.23(d,9H)	182.4(dm,$^1J_{RhC}$=67.7Hz, 1C), 178.7(m,1C)
$[RhIr(CH_3)(CO)_2(P(OPh)_3)$-$(dppm)_2][CF_3SO_3]$ **(4b)**^{n}	1980(ms), 1955(ss)	58.2(m), 15.7(dm,$^1J_{RhP}$= 128.7Hz), 6.9(dm,$^1J_{RhP}$= 123.0Hz), -22.9(m), -23.9(m),	5.55(m,1H), 5.06(m,1H) 4.65(m,1H), 4.60(m,1H) 0.50(m,3H)	189.9(m,1C), 179.9 (bs, 1C)
$[RhIr(CH_3)(CO)_2(PPhMe_2)$-$(dppm)_2][CF_3SO_3]$ **(4c)**^{n}	1958(bs)	13.7(dm,$^1J_{RhP}$=130.0Hz), 6.0(dm,$^1J_{RhP}$=131.0Hz), -24.2(m), -30.5(m), -45.3(m)	5.60(m,1H), 4.97(m,1H) 4.78(m,1H), 4.70(m,1H), 0.52(d,3H), 0.48(d,3H), 0.44(dt,3H)	182.4(dm,$^1J_{RhC}$=70.0Hz, 1C), 179.9(bs,1C)
$[RhIr(CH_3)(CO)_2$-$(PPh(OMe)_2)(dppm)_2]$-$[CF_3SO_3]$ **(4d)**^{n}	1957(bs)	117.4(m), 17.2(dm,$^1J_{RhP}$= 156.8Hz), 9.6(dm,$^1J_{RhP}$= 128..7Hz), -22.1(m), -23.7 (m)	5.17(m,1H), 4.90(m,1H) 4.55(m,1H), 4.45(m,1H), 3.32(d,3H), 3.16(d,3H), -0.18(dt,3H)	182.5(bs,1C), 181.8(dm,$^1J_{RhC}$=73.4Hz 1C)

Table 2.1 (contd).

Compounds	IR,^{b}cm^{-1}	NMR^d		
		δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C{^{1}H})
[RhIr(CH_3)(μ-CO)(PMe_3)- (dppm)$_2$][CF_3SO_3] (**5a**)	1953(ss), 1747(sb)^c	25.8(ddm,$^1J_{RhP}$=131.8Hz, $^2J_{PP}$=42.4Hz), 18.3(m), -32.6(dt,$^1J_{RhP}$=138.1Hz)	4.22(m,2H), 3.41(m,2H), 0.35 (td,$^4J_{PH}$=2.0Hz,3H), 0.28(dd, $^2J_{PH}$=8.2Hz,$^3J_{RhH}$=1.0Hz,9H)	214.5(ddm,$^1J_{RhC}$=35.8Hz, $^2J_{PC}$=27.4Hz, 1C)
[RhIr(CH_3)(μ-CO)($PPhMe_2$)- (dppm)$_2$][CF_3SO_3] (**5c**)	1774(ss)^c	24.1(ddm,$^1J_{RhP}$=130.1Hz, $^2J_{PP}$ =41.3Hz), 15.2(m), -19.2 ($^1J_{RhP}$=143.0Hz, $^4J_{PP}$=6.2Hz)	4.48(m,2H), 3.65(m,2H), 0.47(td,3H), 0.60(d,6H)	212.2(ddm,$^1J_{RhC}$=36.1Hz, $^2J_{PC}$=26.2Hz, 1C)
[RhIr(CH_3)(CO)$_3$(^{t}BuNC)- (dppm)$_2$][CF_3SO_3] (**6**)^h	-	10.5(dm,$^1J_{RhP}$=137.6Hz) -16.7(m)	5.48(m,2H), 5.13(m,2H) 0.92(s,9H), -1.18(t,3H)	181.3(dt,$^1J_{RhC}$=74.0Hz, 1C) 181.9 (dt,$^1J_{RhC}$= 77.3Hz, 1C) 176.3(t,1C)
[RhIr(CH_3)(CO)$_2$(^{t}BuNC)- (dppm)$_2$][CF_3SO_3] (**7**)^g	-	11.9(dm,$^1J_{RhP}$=141.2Hz) -20.6(m)	5.15(m,2H), 4.86(m,2H), 0.93(s,9H), 0.22(t, 3H)	180.2(dt,$^1J_{RhC}$=68.9Hz, 1C) 233.3(bs,1C)
[RhIr(CH_3)(CO)$_2$(SO_2)- (dppm)$_2$][CF_3SO_3] (**8**)^i	-	31.2(dm,$^1J_{RhP}$=112.1Hz) 2.5(m)	4.17(m,2H), 3.94(m,2H), 0.68(t,3H)	179.4(dt,$^1J_{RhC}$=75.0Hz, 1C) 173.7(bs,1C)
[RhIr(SO_2CH_3)(CO)$_2$(μ- SO_2)(dppm)$_2$][CF_3SO_3] (**9**)	1976(bs),1768(w), 1230(m)^{e}1149(w)^e, 1027(m)^e	25.9(dm,$^1J_{RhP}$=109.4Hz) -3.8(m)	4.35(m,2H), 4.30(m,2H), 1.70(s,3H)	196.5(dm,$^1J_{RhC}$=30.1Hz, 1C) 168.8(bs,1C)

Table 2.1 (contd).

Compounds	IR,^{b}cm^{-1}	NMR^d		
		δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C{^{1}H})
[RhIr(CH$_3$)(CN)(CO)$_2$-(dppm)$_2$] **(10)**	2060(m)^f, 1960(m), 1932(ss)	11.4(dm,$^1J_{RhP}$=146.2Hz) -18.2(m)	5.84(m,2H), 5.38(m,2H), -0.74(t,3H)	187.2(t,1C),183.8(dt, $^1J_{RhC}$=66.8Hz,1C)
[RhIr(CH$_3$)(H)(CO)$_2$-(dppm)$_2$] **(11)**^{h}	-	15.8(dm,$^1J_{RhP}$=146.8Hz) -7.2(m)	5.22(m,4H), -1.02(t,3H) -10.08(t,1H)	182.4(dt,$^1J_{RhC}$=82.7Hz, 1C) 190.4(bs,1C)
[RhIr(CH$_3$)(I)(CO)$_2$-(dppm)$_2$] **(13)**	1931(ss), 1761(m)	33.8(dm,$^1J_{RhP}$=151.6Hz) -4.1(m)	4.48(m,2H), 4.22(m,2H), -0.63(td,3H)	212.3(dm,$^1J_{RhC}$=40.2Hz, 1C), 179.7(m,1C), 3.1 (dt,$^1J_{RhC}$=22.2Hz,1C)
[RhIr(CH$_3$)(H)(μ-H)(CO)$_2$-(dppm)$_2$][CF$_3$SO$_3$] **(14)**^{g}	-	25.7(dm, $^1J_{RhP}$=110.3Hz) -1.1(m)	4.42(m,2H), 4.07(m,2H) -0.16 (t,3H), -10.02(m,1H, $^1J_{RhH}$= 14.9Hz), -12.47(m,^{1}H,$^1J_{RhH}$ =24.1Hz,$^2J_{P(Rh)H}$=11.2Hz)	187.5(dt,$^1J_{RhC}$=75.1Hz, 1C) 174.4(t,1C)
[RhIr(CH$_3$)(H)(μ-H)(CO)$_2$-(dppm)$_2$][CF$_3$SO$_3$] **(15)**^{g}	-	30.8(dm, $^1J_{RhP}$=142.5Hz) -2.6(m)	3.92(m,2H), 3.30(m,2H), 0.28 (td,3H), -9.68 (dm, $^1J_{RhH}$= 14.6Hz,1H), -12.58(t,1H)	221.2(dm, $^1J_{RhC}$ = 30.2Hz, 1C), 168.9(t,1C)

Table 2.1 (contd).

		NMR^d		
Compounds	IR,^{b}cm^{-1}	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(CH_3)(\eta^2$- $H_2C{=}C(H)CH_2Br)(CO)_2$- $(dppm)_2][CF_3SO_3]$(**16**)^f	-	20.5 (dm, $^1J_{RhP}$=99.1Hz) -14.3 (m), -18.0(m)	4.88(m, 1H), 4.78(m, 1H) 4.19(b, 1H), 4.18(b, 1H) 3.37(b,1H), 1.41(t, 3H), 0.98 (b, 1H), 0.96(b,1H)	210.0(dm,$^1J_{RhC}$=40.7Hz, 1C), 185.9(dt,$^1J_{RhC}$= 78.0Hz, 1C)
$[RhIr(CH_3)(\mu$-$Br)$- $(CH_2CHCH_2)(CO)_2$- $(dppm)_2][CF_3SO_3]$ (**17**)	1981(bs), 1853(m)	18.1(dm,$^1J_{RhP}$=125.9Hz) -13.5(m)	4.58(m,2H), 4.21(m,2H),5.48 (m,1H),4.34(dd,$^3J_{HH(tr)}$=12.0Hz $^2J_{HH}$=1.0Hz,1H), 4.40(dd $^3J_{HH(cis)}$=8.1Hz,1H), 3.10(dt, $^3J_{HH}$=6.9Hz, 2H), -0.18(t,3H)	192.6(dm,$^1J_{RhC}$=13.6Hz, 1C) 191.7(dt,$^1J_{RhC}$= 87.0Hz,1C)
$[RhIr(CH_3)(CO)_2$- $(\mu{:}\eta^1,\eta^1C_2F_4)(dppm)_2$- $(CF_3SO_3)]$ (**18**)	2003(ss), 1745(m), 1377(sh)^e, 1154(ss)^e, 1030(m)^e	21.7(dm,$^1J_{RhP}$=141.7), 15.3(m)	3.88(m,2H), 3.55(m,2H) 1.08(b,3H)	236.5(dm,$^1J_{RhC}$=29.0Hz, 1C),186.4(bs,1C), 31.5 (t,$^2J_{PC}$=5.2Hz,1C)
$[RhIr(CH_3)C_3H_4)(CO)_2$- $(dppm)_2][CF_3SO_3]$ (**19**)	1796(bs)	32.3(dm,$^1J_{RhP}$=141.3Hz), 1.7(m)	3.34(m,4H), 0.60(tt,$^3J_{PH}$= 7.0Hz, $^4J_{HH}$=2.0Hz,2H), 1.60(b,2H), 0.56(td,3H $^2J_{RhH}$=1.9Hz)	208.5(dm,$^1J_{RhC}$=24.7Hz, 1C) 206.3(dm,$^1J_{RhC}$= 17.9Hz,1C)

Table 2.1 (contd).

		NMR^d		
Compounds	IR,^{b}cm^{-1}	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(CH_3)(CH_2C(CH_3)_2)$-$(CO)_2(dppm)_2][CF_3SO_3]$ **(20)**	1817(ms)^c 1744(ms)^c	32.1(dm,$^1J_{RhP}$=140.8Hz), 0.6(m)	3.48(m,2H), 3.22(m,2H), 1.08(t,2H), 1.18(s,3H), 0.97(s,3H), 0.48(td,3H)	209.0(dm,$^1J_{RhC}$=22.8Hz, 1C) 204.8(bs,1C)
$[RhIr(CH_3)(CH_2CC(H)$-$(CH_3)(CO)_2(dppm)_2]$-$[CF_3SO_3]$**(21a)**	-	32.7(dm,$^1J_{RhP}$=140.9Hz), 1.9(m)	3.40(m,2H), 3.38(m,2H), 4.88(tq,$^3J_{HH}$=6.0Hz,1H), 0.95 (d,3H),0.57(t,2H),0.50(td, 3H)	207.7(dm,$^1J_{RhC}$=23.2Hz,1C) 206.5(dm,$^1J_{RhC}$=18.2Hz, $^2J_{PC}$=8.8Hz,1C)
(21b)	-	32.0(dm,$^1J_{RhP}$=135.7Hz), 1.0(m)	3.44(m,2H), 3.23(m,2H), 5.52(q,1H), 1.21(d,$^3J_{PH}$= 6.3Hz,3H), 0.98(t,2H), 0.50(td,3H)	209.3(dm,$^1J_{RhC}$=25.0Hz,1C) 204.6(dm,$^1J_{RhC}$=16.0Hz,1C)
$[RhIr(CH_3)(CO)(PPhMe_2)$-$(\mu:\eta^2,\eta^2\text{-}C_3H_4)(dppm)_2]$-$[CF_3SO_3]$ **(22)**^{f}	1982(sh)	22.4(ddm,$^1J_{RhP}$=146.8Hz, $^2J_{PP}$=31.0Hz,$^2J_{PP(DPM)}$=45.9Hz), 17.2(ddm,$^1J_{RhP}$=146.8Hz), 9.5(m,$^2J_{PP}$=363.1Hz), -14.7 (m,$^2J_{PP}$= 366.6Hz),-15.4(dm, $^1J_{RhP}$=127.0Hz)	5.80(m,1H), 5.72(b,1H), 5.70(b,1H), 4.84(m,1H), 4.82(m,1H), 4.40(m,1H), 3.90(b,1H), 2.30(b,1H), 1.04(d,3H), 0.93(t,3H), 0.42(d,3H)	180.3(t,$^1J_{PC}$=9.8Hz,1C) 141.9(dm,$^1J_{RhC}$=33.2Hz,1C) 71.7(dm,$^1J_{RhC}$=30.4Hz,1C) 58.9(m,1C), 18.0(t,1C) 16.2(d,$^1J_{PC}$=20.1Hz,2C)

Table 2.1 (contd).

[a] IR abbreviations: ss = strong sharp, sb = strong broad, ms = medium sharp, m = medium, w = weak, sh = shoulder. NMR abbreviations: t = triplet, d = doublet, dt = doublet of triplets, dd = doublet of doublets, tt = triplet of triplets, ddt = doublet of doublets of triplets, ddm = doublet of doublets of multiplets, dm = doublet of multiplets, td = triplet of doublets, bs = broad singlet, m = multiplet, q = quartet, s = singlet. [b] Nujol mull except as indicated. Values quoted are ν(CO) except as indicated. [c] CH_2Cl_2 cast. [d] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4 while ^1H and $^{13}C\{^1H\}$ are referenced vs TMS. Chemical shifts for the phenyl hydrogens are not given in the ^1H NMR data. [e] ν(SO) for CF_3SO_3. [f] ν(CN) for CN. [g] 0°C. [h] -40°C. [i] -60°C. [j] -80°C.

vacuum and recrystallization from CH_2Cl_2/ether gave a bright orange solid (53 mg, 90% Yield). Anal. Calcd for $IrRhSP_4F_3O_5C_{54}H_{47}$: C, 50.51; H, 3.66. Found : C, 50.23; H, 3.45.

(b-e) Low-Temperature Reactions of Compound 1 with Phosphines and Phosphites. In an NMR tube, 30 mg (0.023 mmol) of compound **1** was dissolved in 0.6 mL of CD_2Cl_2 under N_2. The solution was then cooled to *ca.* -80 °C by immersion in a dry ice/acetone bath. PMe_3 (46 µL in 1 M THF solution) was added via a syringe. The NMR (^{31}P and ^1H) spectra showed the presence of $[RhIr(CH_3)(CO)_3(PMe_3)(dppm)_2][CF_3SO_3]$ **(3a)**. Upon gradual warming of the sample to 0 °C, **3a** was replaced by $[RhIr(CH_3)(CO)_2(PMe_3)$-$(dppm)_2][CF_3SO_3]$ **(4a)**. A similar procedure was performed for $P(OPh)_3$, $PPh(OMe)_2$ and $PPhMe_2$ for which the species **3b-d**, respectively, were observed in solution.

(f) Low-Temperature Reaction of Compound 2 with PMe_3. For the reaction of compound **2** and PMe_3, the procedure was as described above except that one equiv of PMe_3 was used for the reaction and NMR data were collected at -100 °C. Only compound **4a** was observed in solution at this temperature.

(g-j) $[RhIr(CH_3)(CO)_2(PR_2R')(dppm)_2][CF_3SO_3]$ (R = R′ = Me: (4a); R = R′ = OPh: (4b); R = Me, R′ = Ph: (4c); R = OMe, R′ = Ph: (4d)). One equiv of neat PMe_3 (97%, 15.7 µL, 0.076 mmol) was syringed into a 100 mL flask containing 100 mg (0.076 mmol) of **1** dissolved in 10 mL of CH_2Cl_2, causing the dark orange solution to turn yellow immediately. The mixture was stirred for 2 h after which the solvent was removed *in vacuo*. Recrystallization from CH_2Cl_2/ether yielded a yellow microcrystalline solid (65 mg, 68% Yield). Anal. Calcd for **4a**.

$IrRhSP_5F_3O_5C_{57}H_{56}$: C, 50.33.; H, 4.11. Found : C, 50.34.; H, 3.91. In the preparation of **4b-d**, the procedure was the same as described for **4a** except that the reactions were carried out using one equiv each of $P(OPh)_3$, $PPhMe_2$ or $PPh(OMe)_2$, respectively. Anal. Calcd for **4b**. $IrRhSP_5F_3O_8C_{72}H_{62}$: C, 54.24.; H, 3.92. Found : C, 54.19.; H, 3.96 (85 mg, 70% Yield). Anal. Calcd for **4c**. $IrRhSP_5F_3O_5C_{62}H_{58}$: C, 52.31.; H, 4.08. Found : C, 52.23.; H, 3.70 (83mg, 77% Yield). Anal. Calcd for **4d**. $IrRhSP_5F_3O_7C_{62}H_{58}$: C, 51.16.; H, 3.99. Found : C, 50.74.; H, 4.13.

(k-n) [RhIr(CH$_3$)(PR$_2$R′)(μ-CO)(dppm)$_2$][CF$_3$SO$_3$] (R = R′ = Me (5a), R = Me, R′ = Ph (5c)). A 50 mL flask was charged with **4a** (50 mg, 0.037 mmol) and a large excess of Me_3NO (14 mg, 0.187 mmol) dissolved in 10 mL of CH_2Cl_2. The resulting mixture was stirred under a slow N_2 flow for 6 h during which time the yellow color of the starting material turned deep orange. The solution was taken to dryness *in vacuo* and redissolved in *ca*. 1 mL of CH_2Cl_2. A dark brown-orange solid was precipitated upon addition of 5 mL of ether. The product was separated by filtration, washed twice with 5 mL of ether, dried under N_2 flow and *in vacuo* overnight. The procedure for preparing **5c** was similar except that the reaction time was 2 h. Microanalyses for **5a** and **5c** consistently gave variable results due to difficulties in separating the excess Me_3NO used in these reactions.

(o) Low-Temperature Reaction of Compound 1 with ^{t}BuNC. The procedure used in preparing **3a-d** was duplicated except that one equiv of neat ^{t}BuNC (2.6 μL, 0.023 mmol) was syringed into the solution at -80 °C in a dry ice/acetone bath. The orange solution darkened immediately, so was taken immediately for NMR characterization. At temperatures below -40 °C several intermediates were observed which could not be identified owing to their low concentration and overlapping signals. At -40 °C, the major species was shown to be $[RhIr(CH_3)(CO)_3(^tBuNC)(dppm)_2][CF_3SO_3]$ **(6)**. Upon warming to 0 °C a second species $[RhIr(CH_3)(CO)_2(^tBuNC)(dppm)_2][CF_3SO_3]$ **(7)** was identified. This species transformed to the final iminoacyl product[15f] upon further warming. Compounds **6** and **7** were characterized in solution by NMR techniques ($^{13}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$).

(p) Low-Temperature Reaction of Compound 2 with ^{t}BuNC. The above procedure was repeated using compound **2**. The major species identified in solution at -40 °C was compound **7** in addition to trace amounts of the final iminoacyl product.

(q) Low-Temperature Reaction of Compound 2 with SO_2. 30 mg (0.023 mmol) of compound **2** was dissolved in 0.6 mL of CD_2Cl_2 at -80 °C. Approximately one equiv of SO_2 gas (*ca.* 0.3 mL) was syringed into the solution and the NMR spectra was obtained immediately afterwards at -60 °C. The spectra showed the presence of $[RhIr(CH_3)(SO_2)(CO)_2(dppm)_2][CF_3SO_3]$ **(8)**. The sample was then warmed up to room temperature and allowed to stand at this temperature for 0.5 h, after which the NMR was taken. The spectra showed the presence of the known compound $[RhIr(CH_3)(\mu\text{-}SO_2)(CO)_2\text{-}(dppm)_2][CF_3SO_3]$.[15f] Upon addition of excess sulfur dioxide, by bubbling the gas briefly through a stirred solution of **8**, the final alkylsulfonate product **9** appeared after a 3 d period. However, if CO gas was passed through the solution containing **8** instead of SO_2, the NMR spectra showed the presence of the previously characterized acetyl species $[RhIr(COCH_3)(\mu\text{-}SO_2)(CO)_2(dppm)_2]\text{-}[CF_3SO_3]$[15f] as the major product in solution.

(r) [RhIr(SO_2CH_3)(μ-SO_2)($CO)_2$(dppm$)_2$][CF_3SO_3] (9). Sulfur dioxide gas was passed briefly (*ca.* 1 min) through a solution of compound **2** (40 mg dissolved in 5 mL of CH_2Cl_2) at -80 °C and the solution was stirred for 0.5 h. Upon a gradual warming to room temperature, the orange color slowly turned dark brown. Stirring of this solution was continued under a static atmosphere of SO_2 for 24 h, during which time the color turned purple. The solvent volume was reduced to 1 mL. Addition of 5 mL of ether caused the precipitation of a bright purple solid. Yield: 27 mg, 56%. Anal. Calcd for $IrRhS_3P_4F_3O_{10}C_{54}H_{47}$: C, 45.93; H, 3.33; S, 6.81. Found: C, 45.70; H, 3.79; S, 7.27.

(s) [RhIr(CH_3)(CN)($CO)_2$(dppm$)_2$] (10). 30 mg (0.023 mmol) of compound **2** and 7 mg (0.026 mmol) of tetrabutylammonium cyanide were placed into an NMR tube and dissolved in 0.5 mL THF-d_8, causing an immediate color change from orange to pale yellow. Compound **10** was identified by NMR spectroscopy since attempts to isolate it resulted in formation of an intractable oil.

(t) Reaction of Compound 2 with Super-Hydride. 30 mg (0.023 mmol) of **2** was dissolved in 0.5 mL of CD_2Cl_2 in an NMR tube at -80 °C. Approximately one equiv of Super-Hydride (LiH($BEt_3)_3$) (23 μL of 1 M THF solution, 0.023 mmol) was syringed into the solution. NMR data were collected immediately. The compound [RhIr(CH_3)(H)($CO)_2$(dppm$)_2$][CF_3SO_3] **(11)** was shown to be the major ^{31}P-containing species at this temperature. The sample was then gradually warmed to room temperature over a 0.5 h period causing the appearance of compound, [RhIr($CO)_2$(μ-H)(μ-η^3-(o-C_6H_4)P(Ph)CH_2PPh_2)-(dppm)][CF_3SO_3] **(12)**, the tricarbonyl species [RhIr($CO)_3$(dppm$)_2$] and a number of unidentified decomposition products. CH_4 was also identified in the ^{1}H NMR spectrum of the crude product mixture. Compound **12** was never successfully separated from the tricarbonyl and other species so was only characterized by NMR spectroscopy.

(u) [RhIr(CH$_3$)(I)(CO)$_2$(dppm)$_2$] (13). 60 mg (0.046 mmol) of **2** was dissolved in 10 mL of acetone. Slightly more than one equiv of KI (8 mg, 0.048 mmol) dissolved in 5 mL of acetone was added via an addition funnel to a stirring solution of **2** over a 0.5 h period, causing a slow color change from orange to yellow. The mixture was stirred for 1 h and the solvent volume was then removed, to give an orange-yellow residue. The product was extracted with 3 mL of CH$_2$Cl$_2$, filtered through a frit after which the solvent was removed *in vacuo* and then redissolved in 1 mL of acetone. A yellow solid precipitated upon addition of 5 mL of pentane, and was washed once with 5 mL of pentane, dried under N$_2$ stream and then *in vacuo*. Microanalysis consistently gave variable results due to contamination with [RhIr(I)$_2$(CO)$_2$(dppm)$_2$].[8g]

(v) Low-Temperature Reaction of Compound 1 with H$_2$. In an NMR tube, 30 mg (0.023 mmol) of **1** was dissolved in 0.6 mL of CD$_2$Cl$_2$ under an N$_2$ atmosphere, and the solution was cooled in an ice/salt bath. Dihydrogen was passed through the solution for ca. 3 min and the mixture was allowed to stand for 2 h at this temperature, after which the NMR spectra was obtained at 0 °C Monitoring the solution at earlier times or at lower temperatures showed only incomplete reaction. [RhIr(CH$_3$)(H)(μ-H)(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] **(14)** was the only metal containing species observed other than **1** and the final trihydride product.[18]

(w) Low-Temperature Reaction of Compound 2 with H$_2$. The procedure described above (v) was repeated except that compound **2** (30 mg, 0.023 mmol) was used. The NMR spectra (^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}) showed the presence of the dihydride species $[RhIr(CH_3)(H)(\mu\text{-}H)(CO)_2(dppm)_2][CF_3SO_3]$ **(15)** as the major species in soluion, together with **2** and the final trihydride product.[18]

(x) Low-Temperature Reaction of Compound 2 with Allyl Bromide. 30 mg (0.023 mmol) of compound **2** was dissolved in 0.6 mL of CD_2Cl_2 at -80 °C in an NMR tube. Allyl bromide (2.0 µL, 0.023 mmol) was added and the resulting mixture was agitated briefly. NMR analysis of the sample showed the presence of $[RhIr(CH_3)(CO)(\mu\text{-}CO)(\eta^2\text{-}H_2C{=}CHCH_2Br)(CO)_2((dppm)_2][CF_3SO_3]$ **(16)** and $[RhIr(Br)(CH_3)(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_2(dppm)_2][CF_3SO_3]$ **(17)** in a ratio of 1:1. Upon warming to room temperature, only compound **17** was observed.

(y) $[RhIr(Br)(CH_3)(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_2((dppm)_2][CF_3SO_3]$ (17). Compound **2** (45 mg, 0.035 mmol) was dissolved in 5 mL of CH_2Cl_2 at -80 °C in a round-bottom flask. To a stirred solution of this was added one equiv of allyl bromide (3.0 µL, 0.035 mmol) via syringe. The solution was and left to stand at this temperature for 15 min, then gradually warmed to room temperature over a 0.5 h period. The solvent volume was then reduced to *ca.* 1 mL. A bright orange product was collected upon addition of 5 mL of ether. The product was washed once with 5 mL of ether, dried under a stream of N_2 and then stored under vacuum overnight (39 mg, 80% Yield). Anal. Calcd for $IrRhBrSP_4O_5C_{57}H_{52}$: C, 48.68; H, 3.70; Br, 5.69. Found: C, 48.55; H, 3.45; Br, 6.00.

(z) $[RhIr(CH_3)(CO)(\mu\text{-}CO)(\mu\text{-}C_2F_4)(CF_3SO_3)(dppm)_2]$ (18). 50 mg (0.039 mmol) of **2** was dissolved in 10 mL of dichloromethane and an atmosphere of tetrafluoroethylene was placed over the solution. The reaction mixture was stirred for two days after which the solution was taken to dryness. Recrystallization from CH_2Cl_2/Et_2O afforded a golden yellow powder which was dried briefly under N_2 and then *in vacuo* overnight (35 mg, 65% Yield). **Note** : during the course of the preparation of **18**, we ran out of C_2F_4 (unavailable in the commercial market). As a result, a satisfactory elemental analysis could not be obtained. A typical result is provided below. Anal. Calcd for $IrRhSP_4F_7O_5C_{56}H_{47}$: C, 48.38; H, 3.39. Found: C, 47.74; H, 3.85. ^{19}F NMR: -77.3 (m, 2F), -54.8 (dm,$^2J_{RhF}$ = 22 Hz, 2F).

(aa-cc) [RhIr(CH$_3$)(η^2-H$_2$CCCRR′)(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] (R = R′ = H (19), R = R′= Me (20), R = H, R′ = Me (21a,b)). To prepare compounds **19** and **21a,b**, a solution of **2** (50 mg, 0.039 mmol in 3 mL of CH_2Cl_2) was placed under a static atmosphere of either allene or 1,2 butadiene, respectively, at -80 °C. The solution containing **19** was stirred for 0.5 h at this temperature and then slowly warmed to room temperature, whereas for **21**, the reaction mixture (at ambient temperature) was stirred for 24 h. Addition of 10 mL of ether to the mixture gave light yellow solids. Yield for **19**: 40 mg, 77%. Anal. Calcd for $IrRhSP_4O_5C_{57}H_{51}$: C, 51.66; H, 3.85. Found : C, 51.72; H, 3.65. Yield for **21**: 44mg, 84%. Anal. Calcd for $IrRhSP_4O_5C_{58}H_{53}$: C, 52.02.; H, 3.96. Found: C, 51.93.; H, 4.19. The preparation procedure for compound **20** was similar except that one equiv of 1,1-dimethylallene (3.8 µL, 0.039 mmol) was syringed into the flask containing compound **2** at room temperature and the reaction mixture was stirred for 1h. Yield for **20**: 39 mg, 75%. Anal. Calcd for $IrRhSP_4F_3O_5C_{59}H_{55}$: C, 52.37; H, 4.07;. Found: C, 52.59; H, 4.31.

(dd) [RhIr(CH$_3$)(μ-CO)(μ-η^2:η^2-CH$_2$CCH$_2$)(PPhMe$_2$)(dppm)$_2$][CF$_3$SO$_3$] (22). 30 mg (0.021 mmol) of **5c** was dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube capped with a rubber septum and cooled to -80 °C by immersing in a dry ice/acetone bath. An atmosphere of allene gas was was placed over the solution and the mixture was allowed to stand at this temperature for 10 min, after which it was slowly warmed to room temperature. The NMR spectra were taken immediately at room temperature. The only product observed in solution was **22**. Elemental analyses carried out on compound **22** consistently gave variable results owing to contamination of Me_3NO present in the starting material (*vide supra*).

X-ray Data Collection for Compound 2. Orange crystals **2** were obtained by slow diffusion of ether into a concentrated solution of the compound. Several crystals were mounted and flame-sealed in glass capillaries under solvent vapor to minimize decomposition or deterioration due to solvent loss. Data were collected at -60 °C on a Siemens P4RA diffractometer using graphite-monochromated Cu Kα radiation. Backgrounds were scanned for 25% of peak width on either side of the peak scan. Unit cell parameters at -60 °C were obtained from a least-squares refinement of 33 reflections in the approximate range $57.0° < 2\theta < 58.0°$. The cell parameters and systematic absences (h0l, h+l = odd, 0k0, k = odd) defined the space group as $P2_1/n$. Of the 6817 unique reflections collected, 6119 were considered to be observed $[F_o^2 \geq 3\sigma(F_o^2)]$. Absorption corrections to **2** were applied using ψ scans. Crystal parameters and details of data collection are given in Table 2.2.

X-ray Data Collection for Compound 4a. Diffusion of ether into a concentrated THF solution of **4a** yielded yellow crystals of the complex, several of which were mounted and flame-sealed in glass capillaries under solvent vapor to minimize decomposition and (or) solvent loss. Data were collected at -50 °C on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 24 reflections in the range $20.0° < 2\theta < 23.9°$. The monoclinic diffraction symmetry and systematic absences (h0l, h+l=odd, 0k0, k=odd) were consistent with the space group $P2_1/n$. Of 11867 unique reflections, 4211 were considered to be observed [$F_o^2 \geq 3\sigma(F_o^2)$]. Absorption corrections were applied to the data using the method of Walker and Stuart.[19,20]

Structure Solution and Refinement for Compound 2. The positions of Rh, Ir and phosphorus atoms were located using direct methods/fragment search program DIRDIF-96;[21] the remaining atoms were found using a succession of least-squares and Fourier maps. Refinement of the structure proceeded using the program SHELXL-93.[22] The hydrogen positions were calculated by assuming idealized sp^2 or sp^3 geometries about their attached carbon atoms as appropriate and were given thermal parameters 120% of the equivalent isotropic displacement parameters of the attached carbons. Initial refinements indicated unusually high thermal parameters for the atoms of the terminal and bridging carbonyls and the methyl carbon atoms. In addition, the isotropic thermal parameter for Ir was unusually high while that of Rh was unusually low. This suggested a rotational disorder in which there are two superimposed orientations for the complex as depicted below (dppm ligands omitted for clarity). The disorder of the terminal carbonyl group attached to Rh was suggested by the extreme elongation of the thermal ellipsoids of C(3) and O(3) in a direction perpendicular to the Rh-C(3) bond axis.

Subsequent difference Fourier maps indicated that the disordered methyl and carbonyl carbons were not exactly superimposed (with the exception of the oxygen atom O(1) of the bridging carbonyl which was shared between the two disordered molecules and was refined at full occupancy) but were slightly offset from each other.

Table 2.2. Crystallographic Data

A. Crystal Data

compound	$[RhIr(CH_3)(CO)_2(dppm)_2]$-$[CF_3SO_3]$ (**2**)	$[RhIr(CH_3)(CO)_2(PMe_3)$-$(dppm)_2][CF_3SO_3]$ (**4a**).2THF
formula	$C_{54}H_{47}F_3IrO_5P_4RhS$	$C_{65}H_{72}F_3IrO_7P_5RhS$
formula weight	1283.97	1504.25
crystal dimensions (mm)	0.62 X 0.42 X 0.24	0.36 X 0.21 X 0.08
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (non-standard setting of No. 14)	$P2_1/n$ (non-standard setting of No. 14)
unit cell parameters[a]		
a (Å)	13.8579 (13)	16.431 (2)
b (Å)	15.6368 (13)	23.117 (3)
c (Å)	23.6710 (14)	17.851 (2)
β (deg)	96.525 (6)	93.410 (14)
V (Å^3)	5096.1 (7)	6768.4 (13)
Z	4	4
ρ calcd (g cm^{-3})	1.673	1.476
μ (mm^{-1})	9.661	2.414

(Table 2.2 contd.)

B. Data Collection and Refinement Conditions

diffractometer	Siemens P4/RA[b]	Enraf-Nonius CAD4[c]
radiation (λ [Å])	Cu Kα (1.54178)	Mo Kα (0.71073)
temperature (°C)	-60	-50
scan type	θ–2θ	θ–2θ
data collection 2θ limit (deg)	115.0	50.0
total data collected	7133 ($0 \leq h \leq 15$, $0 \leq k \leq 17$ $-23 \leq l \leq 23$)	12274 ($-19 \leq h \leq 19$, $0 \leq k \leq 27$ $0 \leq l \leq 21$)
independent reflections	6817	11867
number of obs. (*NO*)	6119 ($F_o^2 \geq 2\sigma(F_o^2)$)	4211 ($F_o^2 \geq 2\sigma(F_o^2)$)
structure solution method	direct methods/fragment search (*DIRDIF–9*[d])	direct methods (SHELXL-93)
refinement method	full-matrix least-sqrs on F^2 (*SHELXL–93*)	full-matrix least-sqrs on F^2 (*SHELXL–93*)
absorption corr. method	semiempirical (ψ scans)	DIFABS
range of transm. factors	0.9595–0.1741	1.217–0.619
data/restraints/paramtrs	6815 [$F_o^2 \geq -3\sigma(F_o^2)$]/ 0 / 630	11858 [$F_o^2 \geq -3\sigma(F_o^2)$]/ 39[d] / 647

Table 2.2. **Crystallographic Experimental Details (continued)**

GOF(S)[e]	1.087 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.998 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[f]		
$F_o^2 > 2\sigma(F_o^2)$	**R_1 = 0.0726**, wR_2 = 0.1910	**R_1 = 0.0915**, wR_2 = 0.2258
all data	R_1 = 0.0781, **wR_2 = 0.1980**	R_1 = 0.3217, **wR_2 = 0.3249**
largest diff. peak and hole	2.474 and −3.664 e Å^{-3}	1.761 and −2.362 e Å^{-3}

[a] Obtained from least-squares refinement of 33 reflections with 57.0° < 2θ < 58.0° for **2**, and of 24 reflections with 20.0° < 2θ < 23.9° for **4a**

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Siemens.

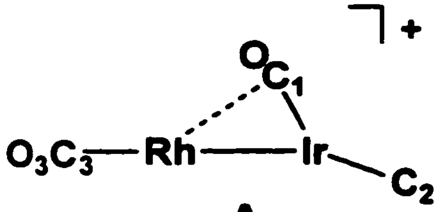
[c] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius.

[d] Restraints were applied to fix the geometries of the triflate group (S–C91 = 1.80 ± 0.01 Å; S–O91 = S–O92 = S–O93 = 1.45 ± 0.01 Å; F91–C91 = F92–C91 = F93–C91 = 1.35 ± 0.01 Å; F91–F92 = F91–F93 = F92–F93 = 2.20 ± .01 Å; O91–O92 = O91–O93 = O92–O93 = 2.20 ± .01 Å; F91–O91 = F91–O92 = F92–O91 = F92–O93 = F93–O92 = F93–O93 = 3.04 ± 0.01 Å) and the THF rings (all bond distances 1.50 ± 0.01 Å; all 1,3 distances [e.g. C101–C103] 2.45 ± 0.01 Å).

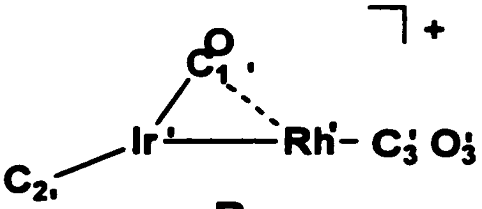
[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1404P)^2 + 22.2339P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$) for **2**.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1435P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$) for **4a**.

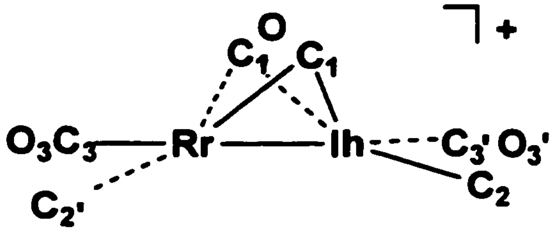
[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.



A



B



C

This together with the anomalous thermal parameters for the metals led to the model diagrammed above in which the two orientations **A** and **B** are disordered in approximately a 55:45 ratio (determined from the relative peak intensities of the ordered and disordered atoms), to give the average structure C, having the appropriate weightings (Rr = 55% Rh +45% Ir; Ih is the disorder having the higher Ir weightings). The solid lines in **C** connect atoms of the major occupant while the dashed lines connect atoms of the minor occupant. Due to the disorder there will be some degree of uncertainty about the bond distances involving the disordered atoms; however, the gross structure is clearly established. In addition, the bridging mode of the carbonyl group in the solid state was established by solid state ^{13}C NMR spectral results (*vide infra*). A similar disorder has been observed in the X-ray structure analyses for $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$,[17] $[RhM(CO)_4(dppm)_2]$ (M = Mn, Re),[23] $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$[24] and $[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$.[12d] Location of the dppm atoms proceeded well with no evidence of disorder.

Structure Solution and Refinement for compound 4a. The positions of the Rh, Ir and phosphorus atoms were obtained through use of the direct-methods program SHELXS-86.[25] The remaining non-hydrogen atoms were located using successive least-squares and difference Fourier maps. All hydrogen atoms with the exception of the THF hydrogens were included as fixed contributions but not refined. Their idealized positions were calculated from the geometries about the attached carbon atoms, using a C-H bond length of 0.95Å, and they were assigned thermal parameters 20% greater than the equivalent isotropic B's of their attached carbon atoms. Refinement was completed using the program SHELXL-93.[22] All non-hydrogen atoms of the complex cation and anion were located. In addition, two molecules of THF per formula unit of complex were also located.

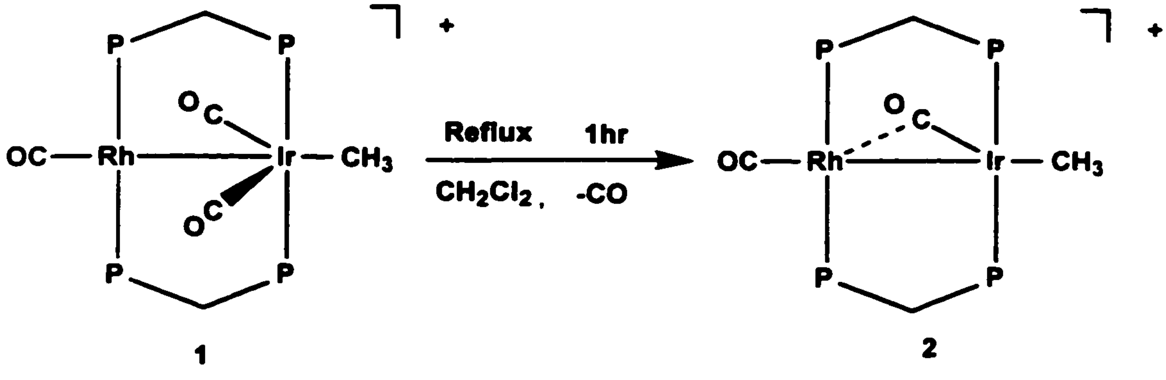
Results and Discussion

1. Preparation and Characterization of Compound 2.

Earlier studies carried out by Eisenberg and co-workers, and by members of this research group had shown that the protonation of $[Ir_2(CO)_3(dppm)_2]$, $[Rh_2(CO)_3(dppm)_2]$ and the mixed-metal analogue $[RhIr(CO)_3(dppm)_2]$ led to the formation of the hydride-bridged species $[Ir_2(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$,[8d] $[Rh_2(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$[26a,b] and $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$,[18] respectively, by apparent electrophilic attack at the metal-metal bond. The reactions of the above binuclear group 9 complexes with methyl triflate were undertaken in attempts to generate the methyl-bridged analogues of the above hydrides. However, in no case was a methyl-bridged species isolated. For the Rh_2 complex,[26c] an acyl-bridged species $[Rh_2(\mu\text{-}COCH_3)(CO)_2(dppm)_2][CF_3SO_3]$ was obtained, whereas for the Ir_2 complex[10a,24] the methylene hydride product $[Ir_2(H)(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ resulted. The reaction of the Rh/Ir complex was different from either of those of the homobinuclear species, yielding [RhIr(CH_3)(CO)$_3$(dppm)$_2$][CF_3SO_3] (**1**), having the methyl group terminally bound to Ir.[10a,15e] Further studies on the above methylene-bridged diiridium complex showed that removal of one carbonyl group caused reversal of the C-H bond cleavage step generating [Ir_2(CH_3)-(CO)$_2$(dppm)$_2$][CF_3SO_3], which has been shown to exhibit a wealth of chemistry,[24] involving C-H bond cleavage of the methyl group upon addition of selected small molecules, and in some cases followed by C-C bond formation involving unsaturated organic substrates. We therefore sought to generate the analogous mixed-metal dicarbonyl, methyl complex [RhIr(CH_3)(CO)$_2$-(dppm)$_2$][CF_3SO_3], in hopes of probing the functions of the different adjacent metals in C-H bond cleavage and C-C bond formation.

One of the carbonyl ligands of [RhIr(CH_3)(CO)$_3$(dppm)$_2$][CF_3SO_3] is labile, and refluxing in CH_2Cl_2 is sufficient to induce CO loss yielding the targeted dicarbonyl species, [RhIr(CH_3)(CO)$_2$(dppm)$_2$][CF_3SO_3] (**2**), which appears to have a structure analogous to both the dirhodium and diiridium complexes in the solid state, as shown below in Scheme 2.1. Unlike the Rh_2 and Ir_2

Scheme 2.1



analogues, which were highly fluxional in solution, displaying carbonyl exchange and migration of the methyl group from metal-to-metal, the RhIr species **2** *does not* show carbonyl exchange and the methyl group remains bound to Ir. It appears that the stronger Ir-CO and Ir-CH_3 bonds compared to Rh-CO and Rh-CH_3[27] favors the structure shown and inhibits transfer of ligands from Ir to Rh. Based on previous work, two structures seemed possible for **2**, having the methyl group either terminally bound to one metal, as in the solid-state structures of $[M_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (M = Rh,[26c] Ir[24]), or bridging the metals as in the dmpm analogue $[Ir_2(CO)_2(\mu\text{-}CH_3)(dmpm)_2][CF_3SO_3]$ (dmpm = $Me_2PCH_2PMe_2$).[28] The IR spectrum of a solid sample of compound **2** indicates that one carbonyl is terminal (1997 cm^{-1}) while the other is bridging (1858 cm^{-1}), and the location of the terminal carbonyl on Rh is supported by the stretching frequency for this carbonyl, which is 23 cm^{-1} higher than in the Ir_2 analogue, and closer to the value of 2007 cm^{-1} observed in the Rh_2 species. The possibility of the triflate anion being coordinated to either metal is ruled out by its IR spectrum, which shows stretches at 1226, 1257 and 1281 cm^{-1} consistent with an uncomplexed ion. The CP-MAS ^{13}C NMR spectra of ^{13}CO- and $^{13}CH_3$-enriched samples of **2** were obtained in order to help establish its solid-state structure. A broad (54 Hz at peak half-height) overlapping pair of doublets, each displaying coupling to Rh of 80 Hz, appear at δ 177.0 and 176.0 for the Rh-bound carbonyl. The observation of two resonances is consistent with the disorder of **2** in the solid state (see Experimental Section) in which there are two orientations of the complex and therefore two environments for each carbonyl. The second carbonyl resonance appears at δ 193.0, in a downfield position consistent with a bridging arrangement; however the breadth of this resonance (140 Hz) does not allow us to determine the magnitude of the coupling to Rh. Presumably the breadth of this resonance also masks the two environments anticipated for this carbonyl owing to disorder. The resonance for the methyl group, at δ 14.8, is far too broad (*ca.* 450 Hz) to display any useful coupling information. Taken together, the spectroscopic data suggest a structure for **2** in the solid state that resembles the two homobinuclear dppm-bridged analogues,[24,26c] having a terminal methyl group and a bridging carbonyl.

An X-ray structure determination of **2** was undertaken in order to confirm the above bonding proposal. Unfortunately, owing to a 55:45 disorder (see Experimental Section), there will be some uncertainties in the metrical parameters, and the binding nature of the carbonyl groups cannot be determined solely on the basis of the X-ray results. However, the gross solid-state structure for **2**, as shown in Figure 2.1 is consistent with the spectroscopic data in the solid state (*vide supra*), and together these data leave little doubt about the structure, in which the metals are bridged by the diphospines, in a mutually trans arrangement at both metals. The structure very much resembles those of the Rh_2 and Ir_2 analogues with a few minor differences. The assignment of the methyl group as being bound to Ir was made on the basis of the successful refinement of the structure with 55% and 45% occupancy for O(3) and O(3)', which associated O(3) with the major occupant; therefore, this occupant was considered to have the carbonyl group opposite the Rh-Ir bond axis, bound to Rh and hence it has the methyl group bound to Ir. The Rh-Ir bond distance of 2.829(7) Å (see Table 2.3) is consistent with the presence of a metal-metal bond for compound **2**, and is comparable to the distances in the Rh_2 (2.811(2) Å) and Ir_2 (2.777(5) Å) analogues. The bridging carbonyl is asymmetrically bound to the metals, being more strongly bound to Ir than Rh (Ir-C(1) bond = 1.99(2), 1.88(3) Å for the disordered units; Rh-C(1) = 2.28(2), 2.34(3) Å). This carbonyl is correspondingly more linear

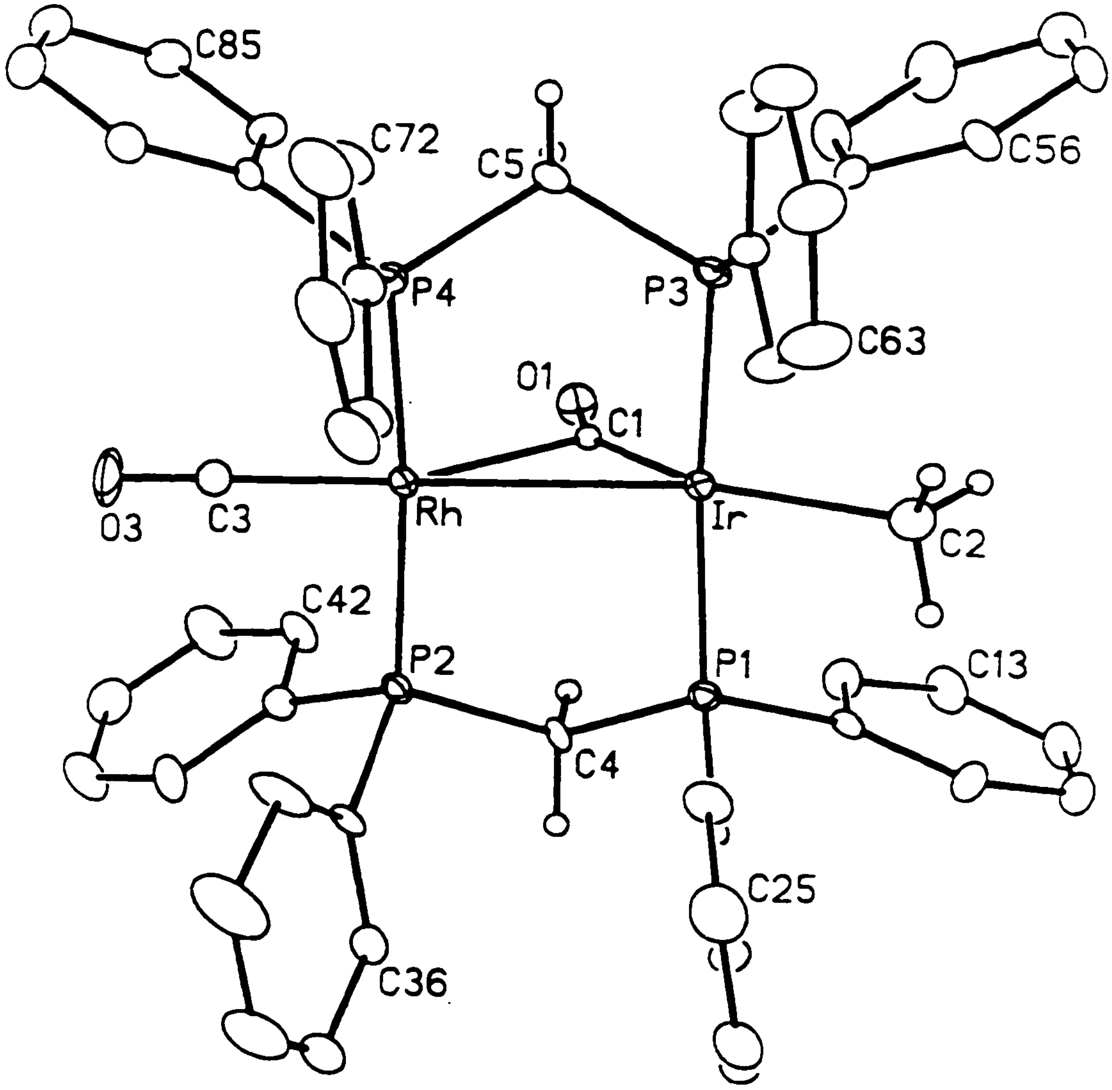


Figure 2.1. Perspective view of the $[RhIr(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]^+$ complex ion of compound **2** showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Phenyl hydrogens have been omitted.

Table 2.3. Selected Interatomic Distances and Angles for compound 2.[a]

(a) Distances (Å).

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ir	Rh	2.8290(7)	Rh'	C(1')	2.34(3)
Ir/Rh'	P(1)	2.317(2)	Rh'	C(3')	1.79(2)
Ir/Rh'	P(3)	2.319(2)	P(1)	C(4)	1.837(9)
Ir	C(1)	1.99(2)	P(2)	C(4)	1.826(9)
Ir	C(2)	2.14(3)	P(3)	C(5)	1.820(10)
Ir'	C(1')	1.88(3)	P(4)	C(5)	1.830(9)
Ir'	C(2')	2.03(3)	O(1)	C(1)	1.07(2)
Rh/Ir'	P(2)	2.311(2)	O(1)	C(1')	1.16(3)
Rh/Ir'	P(4)	2.310(3)	O(3)	C(3)	1.07(3)
Rh	C(1)	2.28(2)	O(3')	C(3')	1.13(3)
Rh	C(3)	1.84(2)			

(b) Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Rh/Ir'	Ir/Rh'	P(1)	91.15(6)	P(2)	Ir'	C(1')	91.1(8)
Rh/Ir'	Ir/Rh'	P(3)	93.15(6)	P(2)	Ir'	C(2')	87.5(7)
Rh	Ir	C(1)	53.1(6)	P(4)	Ir'	C(1')	97.9(8)
Rh	Ir	C(2)	161.0(7)	P(4)	Ir'	C(2')	86.4(7)
P(1)	Ir/Rh'	P(3)	173.57(8)	C(1)'	Ir'	C(2')	142.2(13)
P(1)	Ir	C(1)	90.4(5)	Ir/Rh'	Rh/Ir'	P(2)	92.92(6)
P(1)	Ir	C(2)	85.7(7)	Ir/Rh'	Rh/Ir'	P(4)	90.76(6)
P(3)	Ir	C(1)	96.0(5)	Ir	Rh	C(2)	44.2(5)
P(3)	Ir	C(2)	88.7(7)	Ir	Rh	C(3)	177.2(7)
C(1)	Ir	C(2)	145.5(9)	P(2)	Rh/Ir'	P(4)	170.77(8)
Rh'	Ir'	C(1')	55.4(9)	P(2)	Rh	C(1)	90.7(4)
Rh'	Ir'	C(2')	162.4(8)	P(2)	Rh	C(3)	88.7(6)

Table 2.3. (contd)

Atom1	Atom2	Atom3	Angle
P(4)	Rh	C(1)	97.8(4)
P(4)	Rh	C(3)	87.3(6)
C(1)	Rh	C(3)	138.1(9)
Ir'	Rh'	C(1')	41.3(8)
Ir'	Rh'	C(3')	172.7(9)
P(1)	Rh'	C(1')	91.5(7)
P(1)	Rh'	C(3')	88.1(8)
P(3)	Rh'	C(1')	94.8(7)
P(3)	Rh'	C(3')	87.0(8)
Ir/Rh'	P(1)	C(4)	113.7(3)
Rh/Ir'	P(2)	C(4)	113.2(3)
Ir/Rh'	P(3)	C(5)	113.0(3)
Rh/Ir'	P(4)	C(5)	113.1(3)
Ir	C(1)	Rh	82.7(6)
Ir	C(1)	O(1)	153.2(16)
Rh	C(1)	O(1)	123.9(15)
Ir'	C(1')	Rh'	83.4(10)
Ir'	C(1')	O(1)	164.3(26)
Rh'	C(1')	O(1)	112.3(22)
Rh	C(3)	O(3)	178.9(19)
Rh'	C(3'1)	O(1)	176.3(30)
P(1)	C(4)	P(2)	109.7(5)
P(3)	C(5)	P(4)	110.3(5)

[a] Primed atoms have 45% occupancy (except for O(1), which has 100% occupancy) and are related to the unprimed (55% occupancy) atoms by the rotational disorder.

with respect to Ir (Ir-C(1)-O(1): 153(2)°, 164(2)°; Rh-C(1)-O(1): 124(2)°, 112(2)°). The asymmetry in this carbonyl is reminiscent of that seen in the Rh_2 analogue[26c] but contrasts with the essentially symmetrically bridged carbonyl in the Ir_2 analogue. Moreover, the stronger bonding of the bridging carbonyl to Ir is expected on the basis of stronger bonding to the third-row metal.[27] This asymmetry is also presumably reflected in the carbonyl stretch (1854 cm^{-1}) which is higher than both the Rh_2 (1851 cm^{-1}) and Ir_2 (1832 cm^{-1}) analogues, suggesting a slight tendency towards a terminal coordination in the mixed-metal species. All other parameters for the compound are in close agreement with those of the Rh_2 and Ir_2 analogues, and in particular the terminal carbonyl is almost along the metal-metal axis in all structures (M-M-CO angles: Rh_2, av. 176°; Ir_2, av. 177°; RhIr, av. 175°) while the methyl group is significanly off this axis (M-M-CH_3 angles: Rh_2, av. 161°; Ir_2, av. 164°; RhIr, av. 162°).

In solution the structure of **2** is somewhat different than in the solid state. This is most evident from the solution IR spectrum which shows no bridging carbonyl stretch and displays only one broad peak centered at 1954 cm^{-1}, which presumably is a combination of the stretches for terminal carbonyls on each metal. The $^{31}P\{^1H\}$ NMR spectrum (see Figure 2.2) for **2** displays an unusual pattern reflecting strong second-order effects due to the proximity of the two resonances. The multiplet centered at *ca.* δ 22.0 results from the Rh-bound ^{31}P nuclei, while the peak *ca.* δ 22.4 results from the Ir-bound ^{31}P nuclei. This is the only example in this thesis where the Ir-bound phosphines do not appear upfield of the Rh-bound ones. The $^{13}C\{^1H\}$ NMR spectrum at room temperature displays peaks at δ 175.4 ($^1J_{RhC}$ = 72.8 Hz) and 184.9 assigned to carbonyl groups on Rh and Ir, respectively. The low-field peak also displays 7.0 Hz coupling in the resolution-enhanced spectrum. There was no significant change in the chemical shifts and magnitude of the coupling

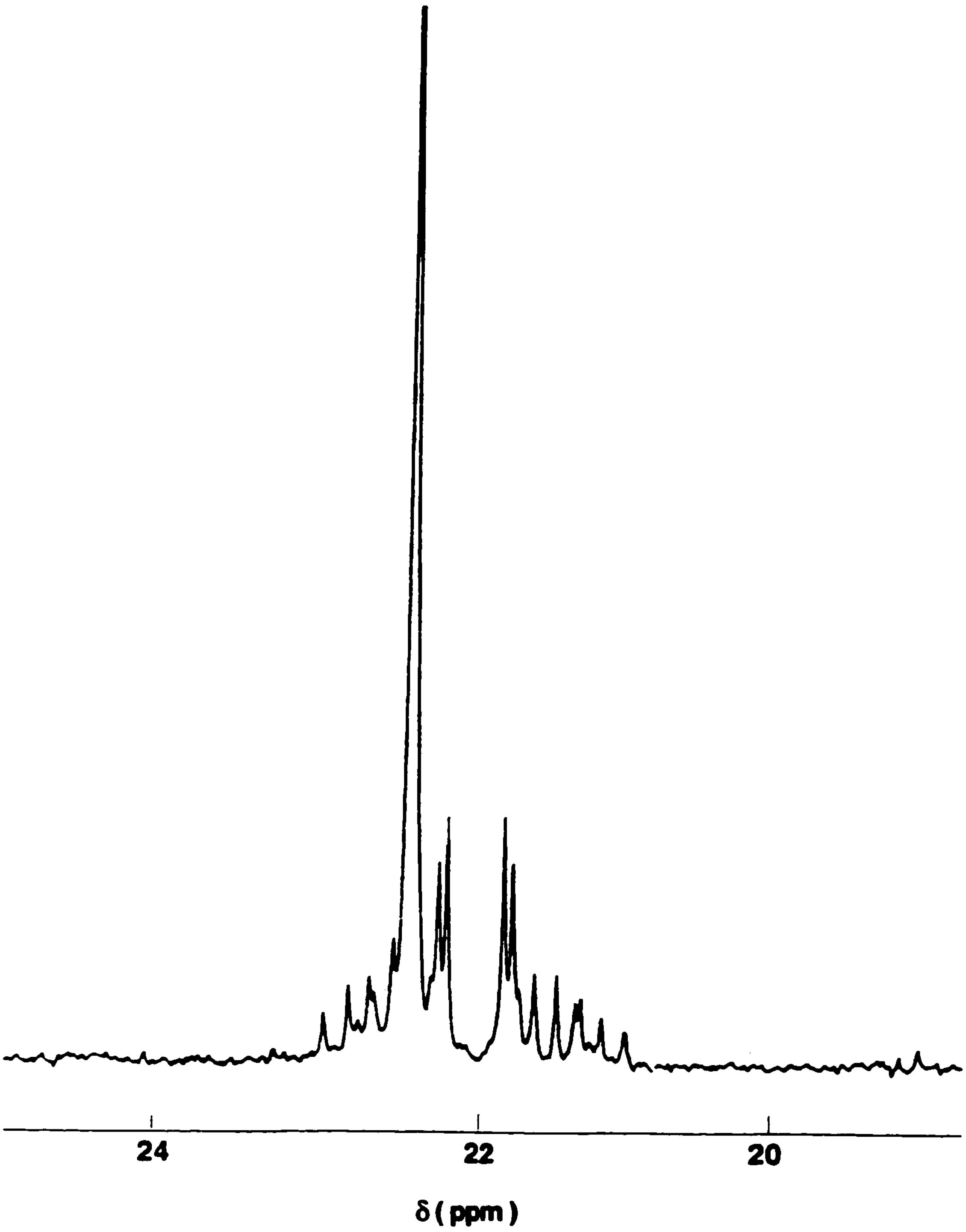
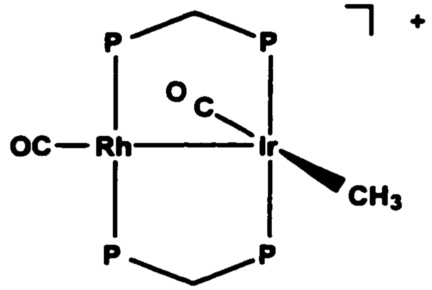


Figure 2.2. $^{31}P\{^{1}H\}$ NMR spectrum (room temperature) showing the second-order multiplet for compound **2**.

constants upon cooling the solution to -80 °C, indicating that no fluxional process which interchanges the bridging and terminal carbonyls is taking place. These spectroscopic data mirror the spectral changes between solid and solution that were observed for the diiridium analogue.[24] We therefore propose a structure for **2** in solution as shown below (labelled **2′**) much like that proposed in the Ir_2 complex. Furthermore, DFT calculations[24] for the isolated cation of $[Ir_2(CH_3)(CO)_2(H_2PCH_2PH_2)_2]^+$ (phenyl groups on dppm substituted by hydrogens to facilitate calculations) has demonstrated that a formulation analogous to **2′** is the stable conformation for the isolated cation.



2′

In **2′** the significance of the 7.0 Hz coupling exhibited by the low-field ^{13}CO resonance in the resolution-enhanced NMR spectrum is not obvious. However, its origin may be explained on the basis of two possible scenarios: it may arise from a very weak semi-bridging interaction of this carbonyl with the Rh center ($^1J_{RhC}$) while remaining essentially terminally bound to Ir or it could result from a two-bond coupling ($^2J_{RhC}$) through the Rh-Ir bond. We favor the former formulation since we have no other examples of mixed RhM (M = Ir, Ru, Os, Mn, Re, Mo, W) complexes in our group[11-15] in which Rh coupling was observed in a carbonyl bound to the adjacent metal, unless involved in some form of semi-bridging interaction with Rh. The low-field shift of the Ir-bound carbonyl argues for a weak interaction with the adjacent Rh center (purely terminal carbonyls on Ir usually appear upfield in the range δ160-180[15d,17]), as will be seen throughout this thesis. Furthermore, the DFT calculations[24] on $[Ir_2(CH_3)(CO)_2(H_2PCH_2PH_2)_2]^+$ indicated that the carbonyl *trans* to CH_3 was tipped in slightly towards the adjacent metal presumably reflecting a weak interaction with it. In the methyl region of the $^{13}C\{^1H\}$ NMR spectrum, a triplet resonance was observed at δ 17.8 ($^2J_{PC}$ = 6.3 Hz) and is consistent with this group being bound to Ir. The assignment of the methyl group on Ir is supported by results from the ^1H NMR spectrum which displays a triplet signal at δ 0.59 for this group, which collapses to a singlet upon irradiation of the Ir-bound ^{31}P nuclei. Overall, we take the view that the formulation **2′** best describes the solution structure for compound **2**, and that in the solid state, the Ir-bound CO group tilts slightly toward the Rh center, thereby engaging in a semi-bridging interaction with this metal as diagrammed in Scheme 2.1. In subsequent schemes, compound **2** will be shown having the solid-state formulation, although nothing will be implied from this about the actual structure of the species reacting.

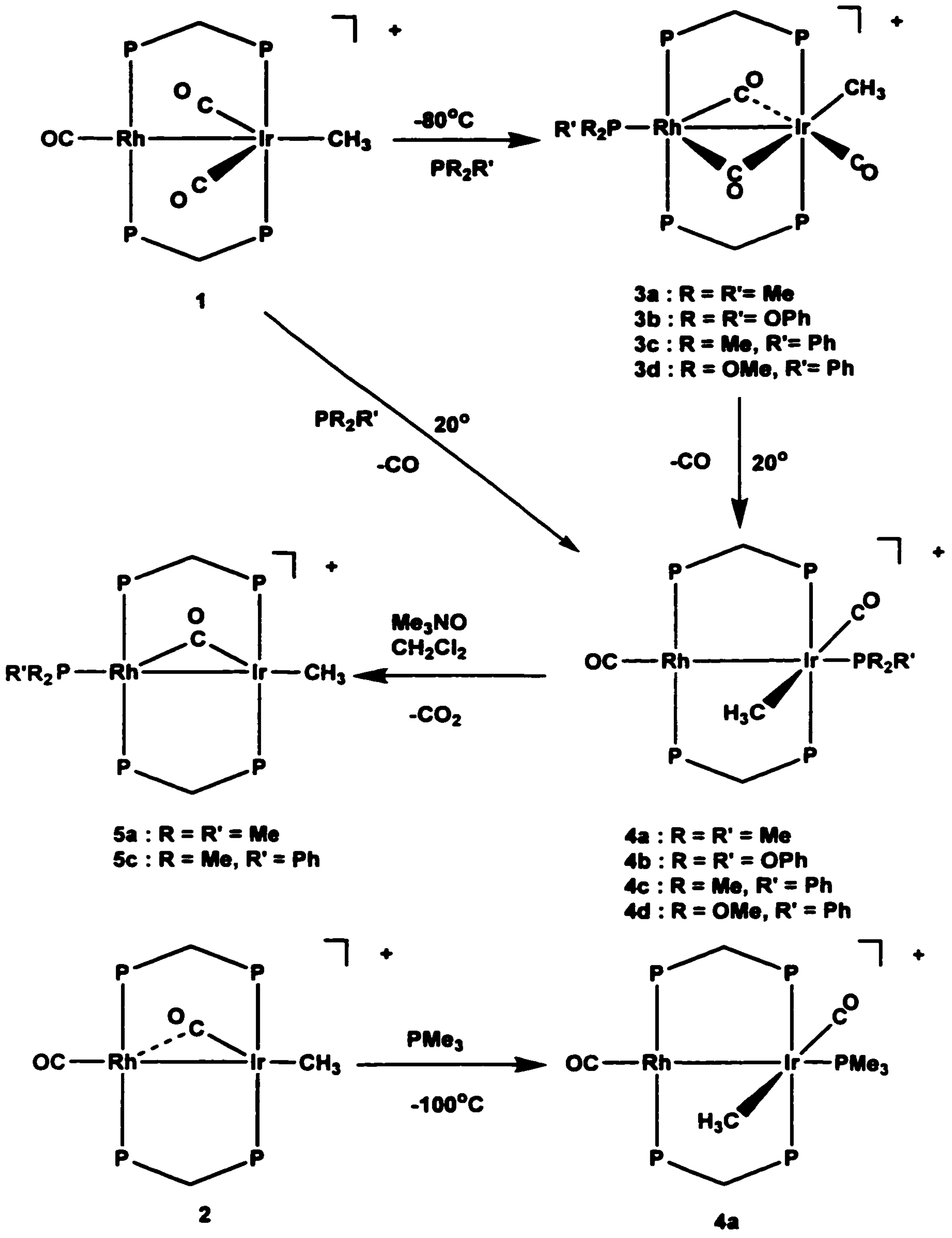
2. Reactivity studies

Compounds **1** and **2** are the two precursor molecules in the chemistry to be described in this chapter. In compound **1**, the Rh/Ir centers are 16e/18e, respectively, whereas in **2** both metals have 16e configurations. The results of the reactivity of compounds **1** and **2** with a number of ligands, having different steric and electronic properties, such as neutral donor ligands (PR_3, ^tBuNC), π-acids (SO_2), anionic nucleophiles (H^-, I^-, CN^-), H_2 and olefins (ethylene, allenes, allyl bromide) are herein presented. We are interested in determining the sites of ligand attack, the subsequent rearrangements of the ligands following coordination, and the influences of the different metals on the chemistry. It was also of interest to determine whether a bridging methyl group[29,30] can be observed by varying the steric and electronic environments (PR_3, nucleophiles); such μ-CH_3 groups would model the C-H bond activation processes in the Ir_2 analogues. In addition, the possibility of insertion processes of ligands such as ^tBuNC, olefins and SO_2 are investigated and we will also attempt to establish oxidative-addition/reductive elimination pathways. The reactions of **1** with a number of substrates were previously described[10a,17] and in general resulted in substitution of a carbonyl ligand to give products of the general form $[RhIr(CH_3)(L)(CO)_2(dppm)_2][CF_3SO_3]$ (L = PR_3, ^tBuNC, SO_2, C_2H_4). However, in the initial study little was determined about the initial site of substrate attack, the natures of the intermediates leading to the final products and the functions of each metal in effecting these transformations.

(a) Neutral η^1-binding ligands (σ donors and π acids).

Compound **1** reacts with PMe_3 at ambient temperature, as shown in Scheme 2.2, giving $[RhIr(CH_3)(CO)_2(PMe_3)(dppm)_2][CF_3SO_3]$ (**4a**) in which both the methyl and PMe_3 groups are coordinated to Ir. The structurally analogous products, $[RhIr(CH_3)(CO)_2(PR_3)(dppm)_2][CF_3SO_3]$ (**4b-d**), were also obtained by addition of the appropriate phosphine or phosphites to **2**, and are spectroscopically similar to **4a** (*vide supra*). Although this reaction proceeded smoothly with a number of phosphines listed, no reaction was observed with PPh_3 even after prolonged reaction times; presumably the approach of this bulky substrate is sterically hindered by interaction with the phenyl groups of the dppm ligands. The compounds $[RhIr(CH_3)(CO)_2(PR_3)(dppm)_2][CF_3SO_3]$ (R = Me : **4a** and R = OPh: **4b**) have been previously synthesized in our group,[17] although their characterizations were incomplete. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of **4a** displays broad unresolved resonances, in a 2:2:1

Scheme 2.2


1
-80°C
PR$_2$R'
3a : R = R'= Me
3b : R = R'= OPh
3c : R = Me, R'= Ph
3d : R = OMe, R'= Ph
PR$_2$R'
20°
-CO
-CO
20°
Me$_3$NO
CH$_2$Cl$_2$
-CO$_2$
5a : R = R' = Me
5c : R = Me, R' = Ph
4a : R = R' = Me
4b : R = R' = OPh
4c : R = Me, R' = Ph
4d : R = OMe, R' = Ph
PMe$_3$
-100°C
2
4a

intensity ratio. Upon cooling to -40 °C this pattern transforms to a complicated pattern of five resonances characteristic of an ABCDMX spin system (X = Rh), in which each phosphorus nucleus is chemically distinct. Although the asymmetry between the Rh and Ir ends of the complex is expected, the inequivalence of the two dppm ^{31}P nuclei on a given metal is a surprise; in the structure shown for compounds **4**, the two phosphines on a given metal are expected to be equivalent. The low-temperature $^{31}P\{^1H\}$ NMR spectrum for **4a** exhibits resonances for the Rh-bound ^{31}P nuclei as complex multiplets at δ 12.6 and 6.4, showing a Rh-P coupling of 131.1 and 126.0 Hz, respectively, and showing mutual coupling of 311 Hz. The large coupling between pairs of ^{31}P nuclei on this metal indicates that these nuclei have a mutually trans arrangement. By comparison, values close to 321–337 Hz have been reported for *trans*-$[Rh(X)(CO)(PH^tBu_2)_2]$[31] and within the range 300–400 Hz have been reported for a series of trans P-M-P couplings.[32] This "trans coupling" is also intermediate to those observed at the Rh centers for $[RhMn(CO)_4(\mu\text{-}SMe)\text{-}(dppm)_2][CF_3SO_3]$ (296 Hz)[33] and $[RhOs(CO)_4(Ph_2PCHPPh_2)(dppm)][CF_3SO_3]$ (321 Hz)[14b] in which both compounds again display complex $^{31}P\{^1H\}$ NMR spectra, in these cases characteristic of an ABCDX spin system, and have been shown to have trans-phosphine arrangements. The ^{31}P resonances due to the Ir-bound dppm ligands appear at δ -23.5 and δ -32.7, showing mutual coupling of 361 Hz, again consistent with a trans arrangement. An additional doublet of triplets resonance appears at δ -61.2 and is assigned to the PMe_3 group bound to Ir. The positions of the different ^{31}P resonances are typical, with the Rh-bound phosphine groups tending to appear downfield from those of Ir, as will be observed throughout this thesis. The monodentate phosphine moiety is bound to Ir, as shown by its small coupling to Rh which is about one tenth of what is expected for one-bond coupling (*vide supra*). Surprisingly, spin tickling experiments demonstrate that the resonance for the monodentate phosphine group displays coupling of 17 Hz to the two Rh-bound dppm ^{31}P nuclei ($^{3}J_{RhP}$) and also a through-metal-metal interaction to Rh of 14 Hz but shows no coupling to the adjacent Ir-bound dppm ^{31}P nuclei. This is unexpected and can be contrasted to the observation for $[Ir_2Cl_2(CO)(PMe_3)(\mu\text{-}DMAD)(dppm)_2]$[34] of 18.5 Hz coupling between PMe_3 and the adjacent dppm ^{31}P nuclei and only 1.8 Hz to the ^{31}P nuclei on the remote metal. We have no explanation for the observation of larger remote P-P couplings through adjacent P-P coupling; the opposite is generally true. However, selective ^{31}P decoupling experiments carried out on the related species $[IrRu(CO)_2(PMe_3)(\mu\text{-}CH_2)(dppm)_2][BF_4]$[35] demonstrate that the PMe_3 group displays approximately equal couplings (*ca.* 9 Hz) to all four dppm ^{31}P nuclei, while remaining bound to the Ir center. The proton signal for the Ir-bound methyl group of **4a** appears as a doublet of triplets at δ 0.33 and is shown by selective ^{31}P decoupling experiments to couple to the ^{31}P nucleus ($^{3}J_{PH}$ = 14.1 Hz) of PMe_3 and to both Ir-bound dppm ^{31}P nuclei (*ca.* 8.2 Hz). As expected, no coupling of these protons to the Rh-dppm ^{31}P is observed. In addition, the PMe_3 protons appear as a doublet at δ 0.23, having the appropriate integration with those of the Ir-bound methyl group. The $^{13}C\{^{1}H\}$ NMR spectrum of a ^{13}CO-enriched sample shows a doublet of multiplets at δ 182.4 ($^{1}J_{RhC}$ = 67.7 Hz) and a broad resonance at δ 178.7, indicating the presence of one terminal CO ligand on each metal.

Based on the proposed structures inferred from the NMR data it is still not obvious why the ABCDMX pattern in the $^{31}P\{^{1}H\}$ NMR spectrum should result. In order to establish the source of asymmetry at each metal giving rise to the observed $^{31}P\{^{1}H\}$ NMR spectrum of **4a**, its geometry was established crystallographically. A perspective view of **4a** (the triflate anion is omitted for clarity) is shown in Fig 2.3, confirming unequivocally that the PMe_3 group is

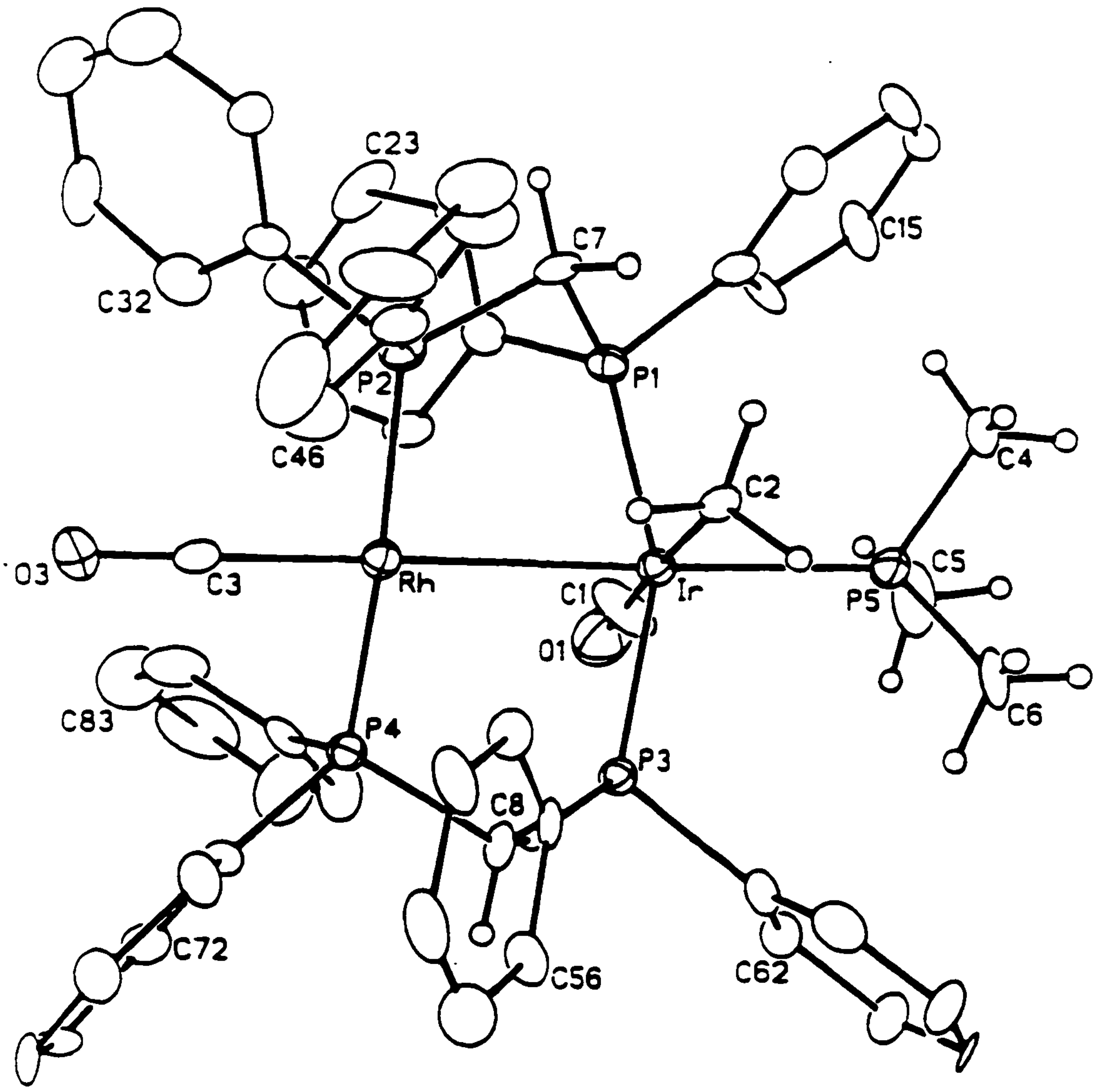


Figure 2.3. Perspective view of the $[RhIr(CO)_2(CH_3)(PMe_3)(dppm)_2]^+$ complex cation (**4a**) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the dppm methylene, trimethylphosphine and Ir-bound methyl groups, and are not shown for the dppm phenyl groups.

terminally bound to Ir. The observed Rh-Ir distance of 2.859(2) Å (see Table 2.4) is only *ca.* 0.1 Å longer than was observed (2.743(1) Å) for compound 1,[15f] indicating an essentially normal metal-metal contact. It is also shorter than that observed (2.950(2) Å) for the imino-acyl species $[RhIr(CO)_2(\mu\text{-}^tBuN{=}CCH_3)(dppm)_2][CF_3SO_3]$[15f] for which there is no metal-metal contact. This formulation is supported by the relatively small intra-ligand P-C-P angles (103.8(12)° and 105.4(11)°) observed for the dppm ligands, indicating compression along the Rh-Ir axis, and can be contrasted with values of 114.4(3)° and 114.9(3)° reported for $[RhIr(H)_2(CO)_2(\mu\text{-}Cl)(dppm)_2][BF_4]$[15b] for which there is no Rh-Ir bond (separation = 3.0651(5) Å). The PMe_3 group coordinates essentially along the Rh-Ir axis, with an Ir-P distance (2.414(7) Å), which is slightly longer than the Ir-P distances of 2.331(7) Å and 2.328(6) Å for the dppm groups, consistent with this ligand being positioned opposite a metal-metal bond which has been shown to have a high trans influence.[36] The geometry at Rh is approximately square planar, in which the Ir center occupies one of the coordination sites opposite a carbonyl group, with the dppm ligands (P(2) and P(4)) in a mutually trans alignment. The Ir center can be viewed as distorted octahedral having the CH_3 and CO groups mutually trans, the PMe_3 group essentially opposite the Rh-Ir bond, and the dppm ligands again in an approximately trans arrangement. The major deviations from an idealized octahedral geometry results from the bending back of P(1) and P(3) (P(1)-Ir-P(3) = 157.3(2)°) in order to minimize unfavorable steric interactions with the PMe_3 group, as revealed in Figure 2.3, showing the close contacts between the PMe_3 group and the dppm phenyl groups 1 and 6. This also results in the Rh-Ir-P(3) (78.2(2)°) and Rh-Ir-P(1) (79.2(2)°) angles deviating from the idealized value of 90°, with rings 2 and 5 being forced towards the Rh end of the molecule. The twisting of the dppm groups to avoid the PMe_3 ligand also results in a twisting

Table 2.4. Selected Interatomic Distances and Angles for compound **4a**
(a) Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ir	Rh	2.859(2)	P1	C7	1.81(2)
Ir	P1	2.331(7)	P2	C7	1.84(2)
Ir	P3	2.328(6)	P3	C8	1.87(2)
Ir	P5	2.414(7)	P4	C8	1.85(2)
Ir	C1	1.85(3)	P5	C4	1.77(2)
Ir	C2	2.31(3)	P5	C5	1.79(3)
Rh	P2	2.320(7)	P5	C6	1.71(3)
Rh	P4	2.299(6)	O1	C1	1.14(3)
Rh	C3	1.83(3)	O3	C3	1.13(3)

(b) Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Rh	Ir	P1	79.2(2)	Ir	Rh	P2	91.2(2)
Rh	Ir	P3	78.2(2)	Ir	Rh	P4	91.7(2)
Rh	Ir	P5	175.7(2)	Ir	Rh	C3	173.6(10)
Rh	Ir	C1	94.1(12)	P2	Rh	C3	87.3(8)
Rh	Ir	C2	90.1(6)	P2	Rh	P4	174.9(2)
P1	Ir	P3	157.3(2)	P4	Rh	C3	90.3(8)
P1	Ir	P5	100.5(2)	Ir	P1	C7	110.1(8)
P1	Ir	C1	88.9(11)	Rh	P2	C7	113.7(7)
P1	Ir	C2	90.2(6)	Ir	P3	C8	110.1(9)
P3	Ir	P5	102.2(2)	Rh	P4	C8	114.1(8)
P3	Ir	C1	90.8(10)	Ir	P5	C4	119.2(8)
P3	Ir	C2	91.9(6)	Ir	P5	C5	112.2(10)
P5	Ir	C1	90.2(12)	Ir	P5	C6	120.9(9)
P5	Ir	C2	85.5(6)	C4	P5	C5	102.3(14)
C1	Ir	C2	175.4(12)	C4	P5	C6	100.4(13)

Table 2.4 (contd).

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Rh	Ir	P1	79.2(2)	P2	Rh	C3	87.3(8)
Rh	Ir	P3	78.2(2)	P2	Rh	P4	174.9(2)
Rh	Ir	P5	175.7(2)	P4	Rh	C3	90.3(8)
Rh	Ir	C1	94.1(12)	Ir	P1	C7	110.1(8)
Rh	Ir	C2	90.1(6)	Rh	P2	C7	113.7(7)
P1	Ir	P3	157.3(2)	Ir	P3	C8	110.1(9)
P1	Ir	P5	100.5(2)	Rh	P4	C8	114.1(8)
P1	Ir	C1	88.9(11)	Ir	P5	C4	119.2(8)
P1	Ir	C2	90.2(6)	Ir	P5	C5	112.2(10)
P3	Ir	P5	102.2(2)	Ir	P5	C6	120.9(9)
P3	Ir	C1	90.8(10)	C4	P5	C5	102.3(14)
P3	Ir	C2	91.9(6)	C4	P5	C6	100.4(13)
P5	Ir	C1	90.2(12)	C5	P5	C6	98.5(16)
P5	Ir	C2	85.5(6)	Ir	C1	O1	177.4(30)
C1	Ir	C2	175.4(12)	Rh	C3	O3	174.9(32)
Ir	Rh	P2	91.2(2)	P1	C7	P2	105.4(11)
Ir	Rh	P4	91.7(2)	P3	C8	P4	103.8(12)
Ir	Rh	C3	173.6(10)				

of the P(1)-Ir-P(3) unit with respect to P(2)-Rh-P(4) by about 40°, as shown in Figure 2.4, in which the cation is viewed approximately along the Rh-Ir axis. This staggered arrangement at both metals results in different environments for P(2) (adjacent to $C(2)H_3$) and P(4) (adjacent to C(1)O(1)), which renders P(1) and P(3) inequivalent and accounts for the different chemical environments of all dppm phosphorus nuclei as observed in the low-temperature solution formulation (static structure) for **4a** in which all phosphorus nuclei are inequivalent. The fluxionality observed in the ^{31}P NMR spectra is believed to involve a twisting of the complex around the Rh-Ir axis across opposite faces of the $RhIrP_4$ framework; these motions become averaged at higher temperatures as seen in the ^{31}P spectrum at 20 °C. A similar fluxionality has been observed in related systems.[15d]

Compound **4a** is stoichiometrically analogous to the phosphine adduct of the diiridium species, $[Ir_2(H)(CO)_2(PMe_3)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$[24] the X-ray structure of which has also been determined. The principal difference between the Rh/Ir and Ir_2 species is that the methyl group in **4a** remains intact and terminally bound to Ir whereas one C-H bond has been cleaved in the Ir_2 analogue. On examining the X-ray structure of **4a**, it is clear that movement of the methyl group towards Rh should be possible, leading to activation of one of its C-H bonds. The apparent reluctance for this to occur may be related to the lower tendency[37] of the second-row Rh center in **4a** to undergo oxidative addition of the C-H bond of the methyl group compared to Ir and the weaker Rh-C/Rh-H *vs* Ir-C/Ir-H bond strengths[27] in the resulting C-H activated product.

We were interested in the initial site of phosphine attack in compound 1, for which two scenarios seemed possible if the reaction were associative. Either phosphine attack occurs at the unsaturated Rh center, followed by CO loss and migration of the phosphine to Ir, or transfer of a carbonyl from Ir to Rh

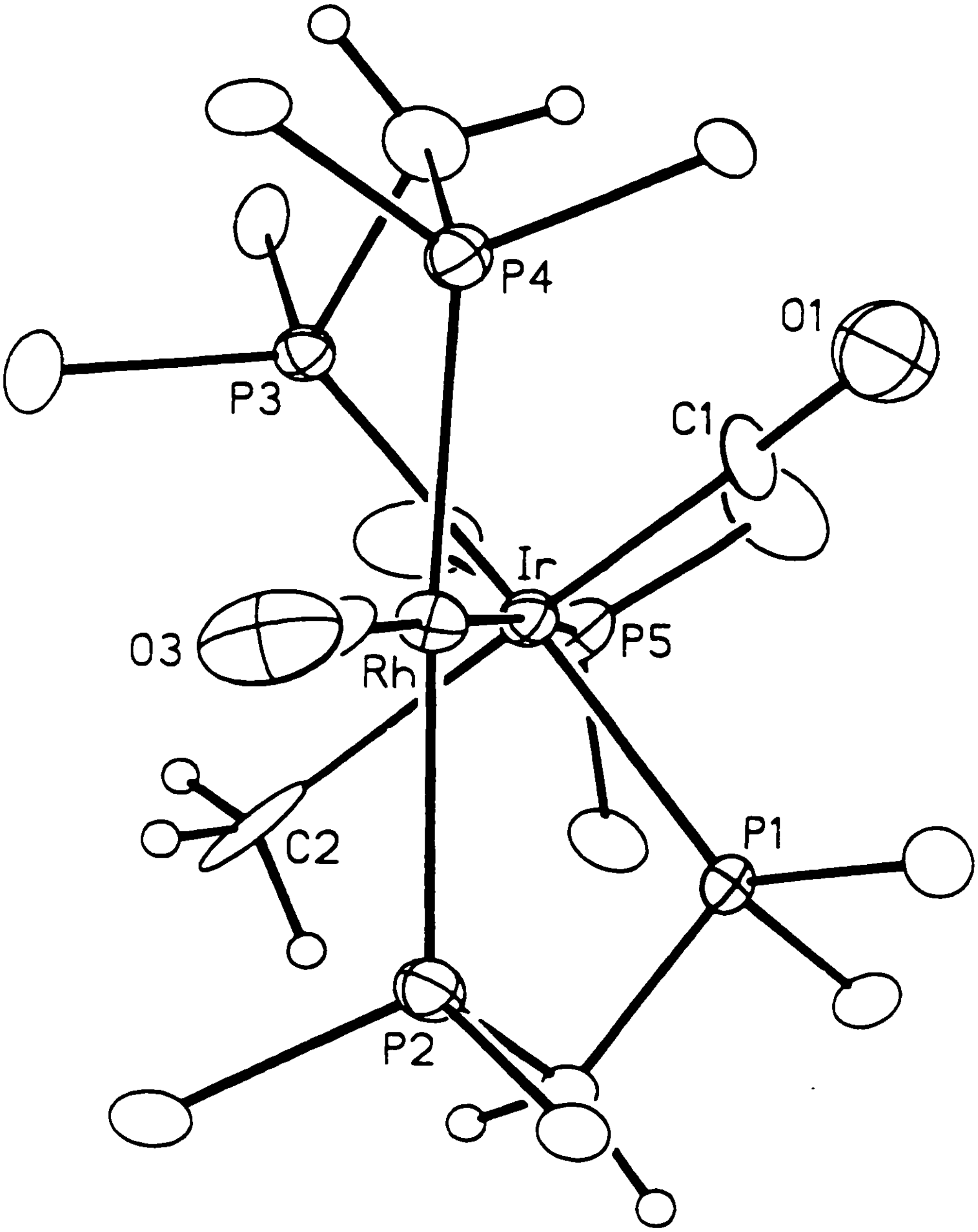


Figure 2.4 Alternate view of the complex **4a**, with all but the *ipso* carbons of the dppm phenyl rings omitted.

could occur, followed by phosphine attack directly at Ir and loss of a carbonyl ligand. If the reaction of **1** with phosphines is monitored at -60 °C or lower, the first species observed in each case is the tricarbonyl phosphine adduct [RhIr(CH_3)($CO)_3$(PR'R_2)(dppm)$_2$][CF_3SO_3] (**3**) in which the phosphine ligand is coordinated to Rh as shown in Scheme 2.2. As for compounds **4**, the very closely related spectral parameters for the different phosphine complexes (**3**) suggest that all have analogous structures, so again only the spectroscopy for the PMe_3 adduct (**3a**) is discussed in detail. The $^{31}P\{^1H\}$ resonance for the PMe_3 group of **3a** appears as a doublet of triplets at δ -35.4, and the coupling of 147.2 Hz to Rh clearly establishes this group as being bound to Rh. It is also noteworthy that this resonance is *ca.* 20 ppm downfield of the PMe_3 signal observed in compound **4a**, in which this group is shown to be bound to Ir, and parallels the trends in ^{31}P chemical shifts for the dppm resonances (Rh end downfield from Ir). The ^1H NMR spectrum shows the methyl protons as a triplet at δ -0.14, consistent with this group being terminally bound to Ir. The $^{13}C\{^1H\}$ NMR spectrum of compound **3a** shows three equal intensity peaks; a doublet of multiplets at δ 262.7 ($^1J_{RhC}$ = 25.3 Hz), a doublet of doublets of multiplets at δ 202.4 ($^1J_{RhC}$ = 52.8 Hz) and a doublet of doublets of triplets resonance at δ 185.1. The high-field resonance is assigned to an essentially Ir-bound CO group, while the low-field resonance is attributed to a bridging CO group. The resonance at δ 202.4 is proposed to be from a CO ligand primarily bound to Rh while engaged in a weak interaction with the Ir center, as indicated by its low-field character. Movement of one Ir-bound carbonyl to a bridging position in which a more crowded environment at Rh results, as shown in Scheme 2.2, although not expected based on steric arguments, may occur in order to help alleviate some of the excess electron build-up on Rh brought about by coordination of the basic PMe_3.[7c] A similar situation has previously been observed in a related diiridium system in which ligand addition at one metal caused a carbonyl on an adjacent metal to move to a bridging site.[9e] Upon warming the sample of **3a** to -40 °C, peaks due to the final dicarbonyl product begin to appear, and at -20 °C, **4a** is shown to be the predominant species in solution. Apparently, rearrangement accompanied by CO loss results in transfer of PMe_3 from Rh to Ir. Although PMe_3 transfer could occur by phosphine dissociation from Rh and subsequent recoordination at Ir, we favor a direct transfer through a PMe_3-bridged species, much in the same fashion as methyl groups migrate between metal centers.[29] No phosphine-bridged complexes are known but a related trialkylstibane-bridged analogue, $[Rh_2Cl_2(\mu\text{-}Sb^iPr_3)(\mu\text{-}CPh_2)]$, has been structurally characterized.[38] Similar phosphine transfer[39] in multimetal systems *via* a bridged intermediate[39a,b] has been proposed, and the possibility of phosphine-bridged complexes in clusters has also been suggested.[40] Although in a mixed Ru_2W cluster, intermetallic phosphine transfer was proposed to proceed by a dissociative pathway,[39c] we have no evidence to support such pathway in the present study.

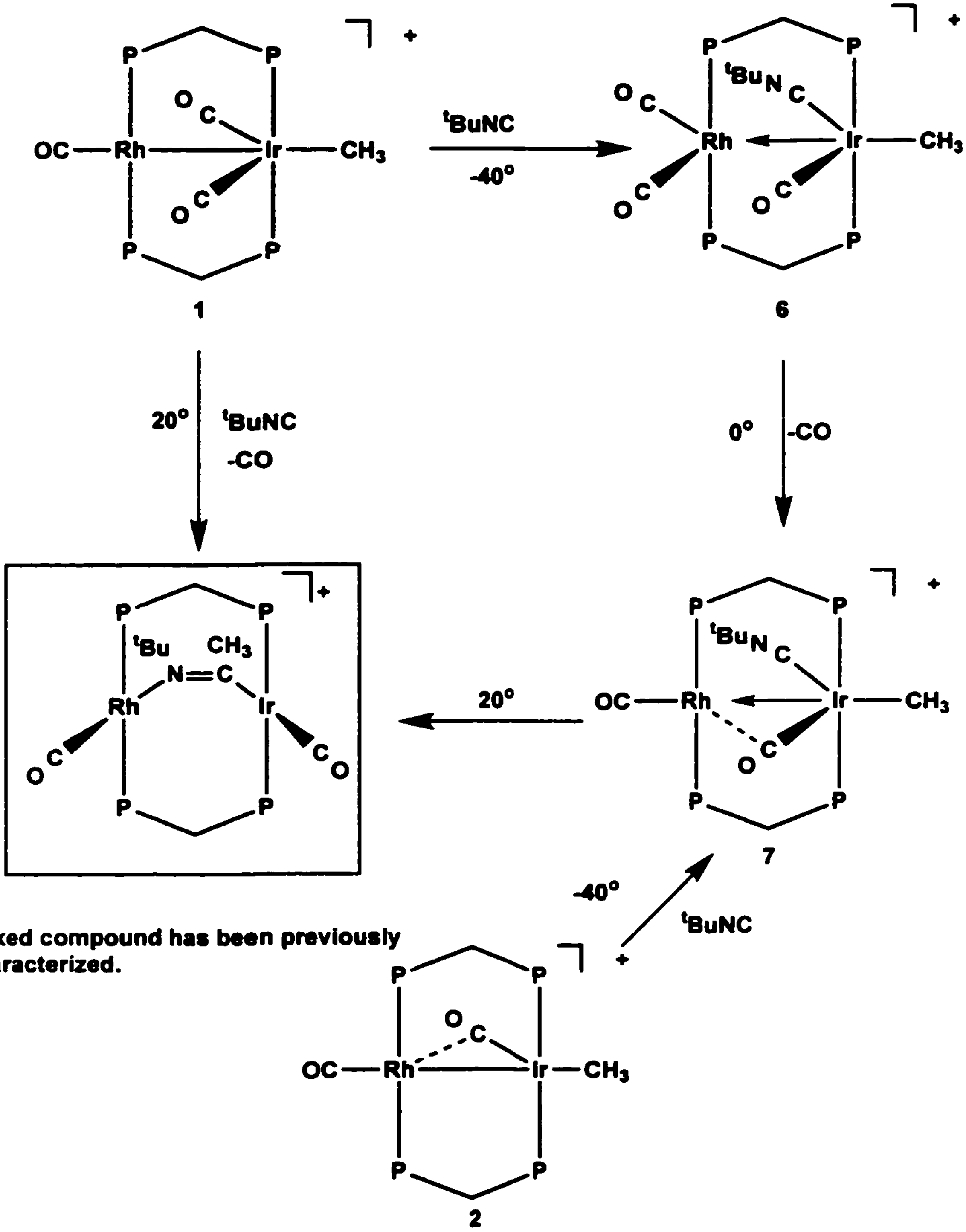
It seems that the initial site of phosphine coordination in **1**, yielding **3a** at low temperature, appears to be dictated by the coordinative unsaturation at Rh. It was then of interest to determine how the reaction of **2**, in which *both* metals are unsaturated, would compare. Treatment of a solution of compound **2** with one equiv of PMe_3, at -100 °C, followed by gradual warming of the reaction mixture to ambient conditions, yielded compound **4a** as the sole product. At all temperatures investigated only **4a**, in which attack of the phosphine has apparently occurred at Ir, was observed. Given the solid-state structure of **2**, in which the geometry at each metal is rather similar, it is difficult to envision that attack at Ir should be as kinetically favored as implied by the lack of attack at Rh observed at -80 °C. However it should be recalled that the structure of **2** (i.e. **2'**) in solution is quite different. Although both metals in **2′** have square-planar geometries, that at Rh, defined by Ir, a carbonyl and the Rh-bound phosphorus atoms is essentially perpendicular to the square plane at Ir, defined by the methyl, the carbonyl and phosphine ligands. With such a geometry, attack at Rh requires the incoming group to approach essentially perpendicular to the $RhIrP_4$ core. Such an approach should be inhibited by the four phenyl rings on either side of the $RhIrP_4$ plane and by the carbonyl and methyl groups on Ir. Conversely, attack at Ir requires the ligand to approach from the end of the complex, an approach that may be favorable, with fewer interactions with the dppm phenyl groups, and no interference from the adjacent metal.

The failure of the Rh/Ir complex **2** to undergo C-H cleavage of the methyl group upon reaction even with the basic PMe_3 group, led us to increase the basicity of the metals by substituting one of the carbonyls in **2** with PMe_3 with the intent of subsequently adding additional PMe_3 to this species. It was hoped that an analogue of compound **4a** having two PMe_3 ligands would be a candidate for subsequent C-H activation. Heating compound **4a** in refluxing THF failed to give the desired reaction, with only starting material being recovered after 2 h. However, reaction with excess Me_3NO in CH_2Cl_2 for 6 h succeeded in labilizing one of the carbonyls, giving the targeted monocarbonyl species $[RhIr(CH_3)(\mu\text{-}CO)(PMe_3)(dppm)_2][CF_3SO_3]$ (**5a**), which on the basis of its $^{31}P\{^1H\}$ NMR spectral results (*vide supra*) indicates that migration of the PMe_3 group from Ir back to Rh has occurred. The ^1H NMR spectrum shows the methyl protons as a triplet of doublets at δ 0.35. Selective ^{31}P decoupling experiments establish that the doublet is due to a long-range coupling of the methyl protons to the PMe_3 phosphorus nucleus (bound to Rh) while the triplet arises from coupling to the Ir-bound dppm ^{31}P nuclei. The $^{13}C\{^1H\}$ NMR spectrum shows only one carbonyl resonance as a doublet of doublets of multiplets at δ 214.5 with a Rh-C coupling of 35.8 Hz and an additional coupling of 27.4 Hz to the PMe_3 group, in agreement with a symmetrically bridging carbonyl group. This is supported by a solution IR spectrum which shows a strong absorption band at 1746 cm^{-1}. Surprisingly, the Nujol mull of compound **5a** shows a terminal CO stretch at 1953 cm^{-1} but no stretch corresponding to the bridging mode, suggesting that the carbonyl group is terminally bound in the solid state. The structures of the analogous compounds, **2** and **5a**, present an interesting dichotomy; although both solution structures differ from the structures in the solid state, both do so in opposite ways. The solid-state structure of **2** is similar to the solution structure of **5a**, and *vice versa*. In solution, the dicarbonyl species **2** has both carbonyls terminally bound, whereas one is bridging in the solid state. For **5a**, the carbonyl ligand bridges in solution and is terminal in the solid state. We view the solid-state structures as anomalies, with intermolecular packing forces having a major influence on the structure. For **2** the solution structure, in which each low-valent metal has one carbonyl attached, seems to be the electronically favored situation, and certainly this is borne out by DFT calculations on an Ir_2 analogue.[24] Compound **5a**, on the other hand, with only one carbonyl ligand, is expected to favor a bridging mode in which the ligand can function as a π acid to *both* metals.

The transformation of **4a** to **5a** has involved phosphine transfer from Ir to Rh. We favor a transient (albeit unobserved) phosphine-bridged intermediate, although we cannot rule out the phosphine migration proceeding via ligand dissociation and recoordination. The alternative reaction pathway would necessarily generate an intermediate, in which there is severe coordinative unsaturation at both metal centers (having only one carbonyl and methyl group in addition to the bridging dppm ligands), thus opening up such intermediate to several decomposition pathways. Interestingly, the above phosphine transfer occurs in a direction opposite to that observed earlier for the conversion of **3a-d** to **4a-d**, indicating that arguments of metal-phosphine bond strengths should be viewed with caution. On the basis of bond strengths and kinetic labilities,[27,41] we would anticipate a stronger Ir-P bond compared to a Rh-P bond and a less labile Ir center compared to Rh, but in addition we must consider other bonds present including metal-methyl and metal-carbonyl bonds, such that taken together, the product adopts the most thermodynamically stable structure. Compound **4c** also reacts with Me_3NO affording the analogous monocarbonyl species $[RhIr(CH_3)(\mu\text{-}CO)(PPhMe_2)(dppm)_2][CF_3SO_3]$ (**5c**). Compounds **5a** and **5c** display similar chemical shifts in their $^{31}P\{^1H\}$ and ^1H NMR spectra, apart from the chemical shifts of the $PPhMe_2$ and PMe_3 groups, attesting to the similarities of their structures. It should be recalled that the related diiridium species $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ undergoes facile C-H activation of the methyl group upon addition of L (L = SO_2, CO, PR_3, ^tBuNC).[24] Part of the rationalization for this may lie in the greater tendency of the third-row Ir metal to stabilize the resulting methylene-bridged hydride product with the accompanying increase in oxidation state.[37] Compound **5a** is analogous to **2** and to the diiridium species shown above, so it was hoped that the more basic PMe_3 group of **5a** may facilitate C-H activation in this species. Not surprisingly, the addition of CO to compound **5a** did not yield the desired C-H activated product as was shown for the Ir_2 species, resulting instead in the formation of the starting material **4a**, the PMe_3 group having migrated back to Ir from Rh. In addition, treatment of **5a** with an additional equiv of PMe_3 also did not lead to C-H bond cleavage, instead leading to fragmentation of the "$RhIr(dppm)_2$" framework. Such fragmentation could result from either M-P or C-P cleavage process.[42,43] The former process, which involves displacement of one or more dppm ligands from the bimetallic framework by PMe_3 groups, has been previously observed for the dirhodium species $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(dppm)_2]$.[44]

Compound **1** also reacts with ^tBuNC at room temperature to give the known species $[RhIr(CO)_2(\mu\text{-}C(CH_3){=}N^tBu)(dppm)_2][CF_3SO_3]$,[17] the product of an apparent isocyanide insertion into the Ir-methyl bond. However, it is not clear at which metal the initial site of substrate attack occurred and at which metal migratory insertion had occurred. Therefore low-temperature experiments appeared warranted. The reaction with ^tBuNC was carried out at -80 °C, and slowly warmed while observing NMR spectral changes (^1H, ^{13}C and ^{31}P). Between -80 °C and -40 °C, the major product observed is a tricarbonyl species **6**, shown in Scheme 2.3. Its $^{13}C\{^1H\}$ NMR spectrum indicates that two carbonyls (overlapping at δ 181.3 and 181.9) are bound to Rh ($^1J_{RhC}$ = 74.0 and 77.3 Hz, respectively) with only one (δ 176.3) on Ir. The methyl group is shown by ^1H NMR with selective ^{31}P decoupling, to be bound to Ir, and the protons of the tert-butyl group are observed as a singlet at δ 0.92. In the absence of ^{13}C-labelled ^tBuNC, we were unable to observe the resonance for the isocyanide carbon, so the site of coordination of this group is unknown. It is assumed to be bound to Ir, as shown, on the basis of similarities to related mixed-metal species previously characterized in this research group.[13a] The site of ^tBuNC attack on compound **1** should be at the unsaturated Rh center as was observed in the phosphine addition; however, such an adduct was not identified. At -80 °C several unidentified intermediates were observed but their low concentration and overlap of signals precluded their identification. As the reaction mixture is warmed to *ca.* 0 °C, compound **6** disappears to be replaced by $[RhIr(CH_3)(CO)_2(^tBuNC)(dppm)_2][CF_3SO_3]$ (**7**) which is shown by $^{13}C\{^1H\}$ NMR to be a dicarbonyl species, having one CO (δ 180.2, $^1J_{RhC}$ = 68.9 Hz) terminally

Scheme 2.3

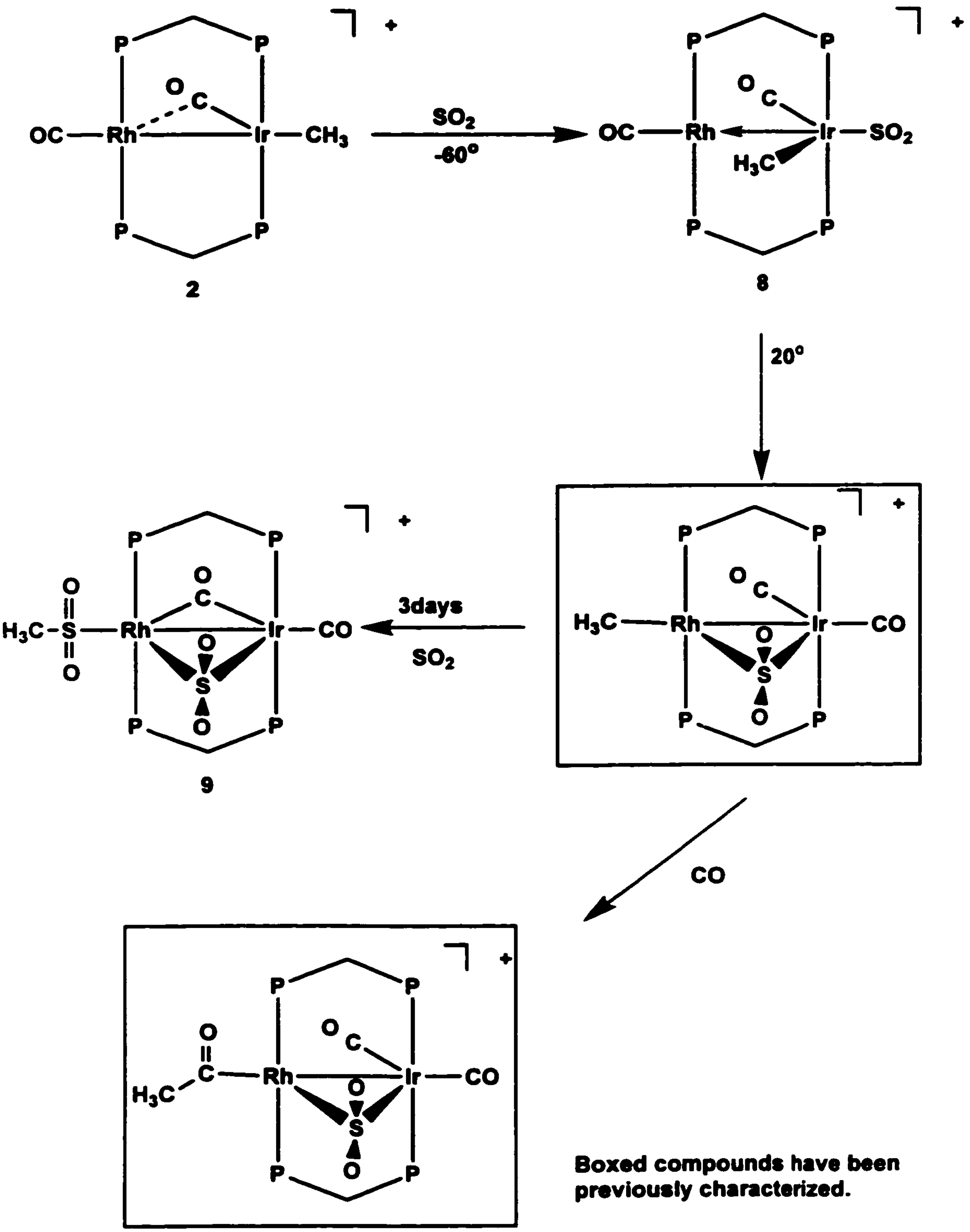


Boxed compound has been previously characterized.

bound to Rh, and by ^{1}H NMR to have the methyl group still on Ir. The low-field ^{13}C resonance for the second carbonyl (δ 233.3) suggests a bridging mode, in which interaction with Rh must be weak, since no resolvable Rh coupling is observed in this slightly broadened resonance (20 Hz at half-height). Again, the ^{t}BuNC group is assumed to be bound to Ir, yielding a species analogous to **1**, apart from the proposed semi-bridging carbonyl interaction in **7**. Upon further warming, **7** transforms to the iminoacyl-bridged product,[17] which has been previously characterized both by spectroscopy and X-ray crystallography. Although migratory insertions are known to occur more readily at Rh than Ir,[37] we see no evidence for a rearrangement bringing the isocyanide and methyl groups to Rh; instead it appears that the coupling of the isocyanide and methyl groups occurs on Ir. The ease of migratory insertion, transforming **7** to the iminoacyl-bridged product, is in contrast to the failure of the isoelectronic tricarbonyl precursor **1** to undergo a similar migration involving one of the carbonyls but is consistent with the greater tendency for isocyanides to insert.[44] Compound **2** also reacts with isocyanide at -40 °C to give mainly **7** which slowly transforms to the imino-acyl species at room temperature. Again, we observe a startlingly different pattern of reactivity for the Ir_2 and Rh/Ir systems. Addition of ^{t}BuNC to the related diiridium dicarbonyl methyl species caused the activation of the C-H bond of the methyl group, a pattern also observed for the phosphine-addition reactions. In all of these cases, the diiridium methylene hydride complexes appear to be the thermodynamically stable products. In the mixed-metal Rh/Ir system, migratory insertion occurred for both compounds **1** and **2** indicating a lower barrier for this process compared to C-H bond activation of the methyl group.

In addition to migratory insertion of alkyl groups with ligands such as carbonyls and isocyanides, sulphur dioxide is also known to insert into metal-alkyl bonds.[2c] However, the insertion of sulfur dioxide into metal-carbon bonds appears not to occur by migratory insertion, but instead proceeds via an electrophilic attack at the metal-carbon bond. Previous investigation in our group on the reaction of SO_2 with compound **1** has shown that the reaction did not give the anticipated SO_2-inserted product; instead an acetyl complex was formed.[15f] It was of interest to determine whether compound **2**, which is coordinatively unsaturated at *both* metals would behave similarly. Exposure of **2** to SO_2 gas at room temperature, in contrast, gave the S-bound sulfinate product $[RhIr(SO_2CH_3)(\mu\text{-}SO_2)(CO)_2(dppm)_2][CF_3SO_3]$ (**9**) in which the methylsulfinate moiety is apparently bound to Rh as inferred spectroscopically. The ^1H NMR spectrum of **9** shows the S-sulfinate methyl proton resonating as a singlet at δ 1.70 (with no discernable Rh-H or P-H coupling as expected for this group). This resonance is significantly downfield when compared to those of the analogous Ir-bound (δ 0.22 for $[RhIr(CH_3)(CO)_2(^tBuNC)(dppm)_2][CF_3SO_3]$ (**7**)) and Rh-bound (δ 0.35 for $[RhIr(CH_3)(CO)_2(C_2H_4)(dppm)_2][CF_3SO_3]$[10a]) methyl groups, respectively, in agreement with it being bound to the strongly electron-withdrawing SO_2 group. The $^{13}C\{^1H\}$ NMR spectrum of **9** displays two carbonyl resonances, one corresponding to a bridging carbonyl (δ 196.5, $^1J_{RhC}$ = 30 Hz) and the other to a carbonyl bound to Ir (δ 168.8), in agreement with the IR spectrum which shows carbonyl stretches at 1768 and 1976 cm^{-1}. Bands in the IR spectrum at 1230, 1149 and 1027 cm^{-1} are assigned to the SO_2 groups. The absorption band at 1230 cm^{-1} is close to the asymmetric SO stretch (1255 cm^{-1}) reported for $[Rh(I)_2(SO_2CH_3)(PPh_3)_2]$[45a] and for organocobaloximes (in the range 1220 and 1230 cm^{-1})[45b] and is assigned to the asymmetric S-O stretch for the S-bonded sulfinate group of species **9**. The same argument could be used to assign the band at 1027 cm^{-1} to the symmetric S-O stretch for the S-bonded sulfinate group on the basis of its similarity to low frequency

Scheme 2.4



Boxed compounds have been previously characterized.

band at 1055 cm^{-1} reported for $[Rh(I)_2(SO_2CH_3)(PPh_3)_2]$ and 1060-1070 cm^{-1} for organocobaloximes as well as 1063 cm^{-1} reported for a sulfene species.[46] The band at 1149 cm^{-1} is assigned to the asymmetric S-O stretch of either the bridging SO_2 or the triflate group. The S-O symmetric stretch for the μ-SO_2 group could not be found, although based on values of 1055 and 1070 cm^{-1} observed for the related species $[Ir_2(CH_3)(CO)_3(\mu\text{-}SO_2)(dppm)_2][CF_3SO_3]$[17] and $[RhIr(CO)_2(COCH_3)(\mu\text{-}SO_2)(dppm)_2][CF_3SO_3]$,[15f] respectively, it is likely buried beneath the band at 1027 cm $^{-1}$. Although the spectroscopic data do not unambigously establish the binding mode of the SO_2 ligand, the preponderance of SO_2-bridged species involving late metals,[47] including one recently characterized by X-ray crystallographic means in our group[24] and the low SO stretch[48] at 1027 cm^{-1} lead us to formulate the structure for compound **9** as diagrammed in Scheme 2.4. The above formulation, containing two molecules of SO_2, is supported by elemental analyses.

When the reaction of **2** with one equiv of SO_2 is carried out *ca.* -60 °C, the intermediate $[RhIr(CH_3)(CO)_2(SO_2)(dppm)_2][CF_3SO_3]$ (**8**) is observed in solution. This species transforms to the previously characterized product $[RhIr(CH_3)(\mu\text{-}SO_2)(CO)_2(dppm)_2][CF_3SO_3]$[15f] upon warming the sample to room temperature. In the ^1H NMR spectrum of **8**, the methyl group appears as a triplet at δ 0.68 which was shown by selective ^{31}P decoupling experiments to be still bound to Ir, while the $^{13}C\{^1H\}$ NMR shows two peaks: a doublet of triplets at δ 179.4 with a Rh-C coupling of 75.0 Hz and a broad resonance at δ 173.7, assigned to the carbonyl groups on Rh and Ir, respectively. The similarity of the spectral data of **8**, particularly for the ligands bound to Ir, with those of the analogous intermediate $[RhIr(CH_3)(CO)_3(SO_2)(dppm)_2][CF_3SO_3]$ in the SO_2 reaction with **1** at -60 °C[15f], leads us to propose that both intermediates are structurally similar with the exception of an additional Rh-bound CO ligand in the latter species.

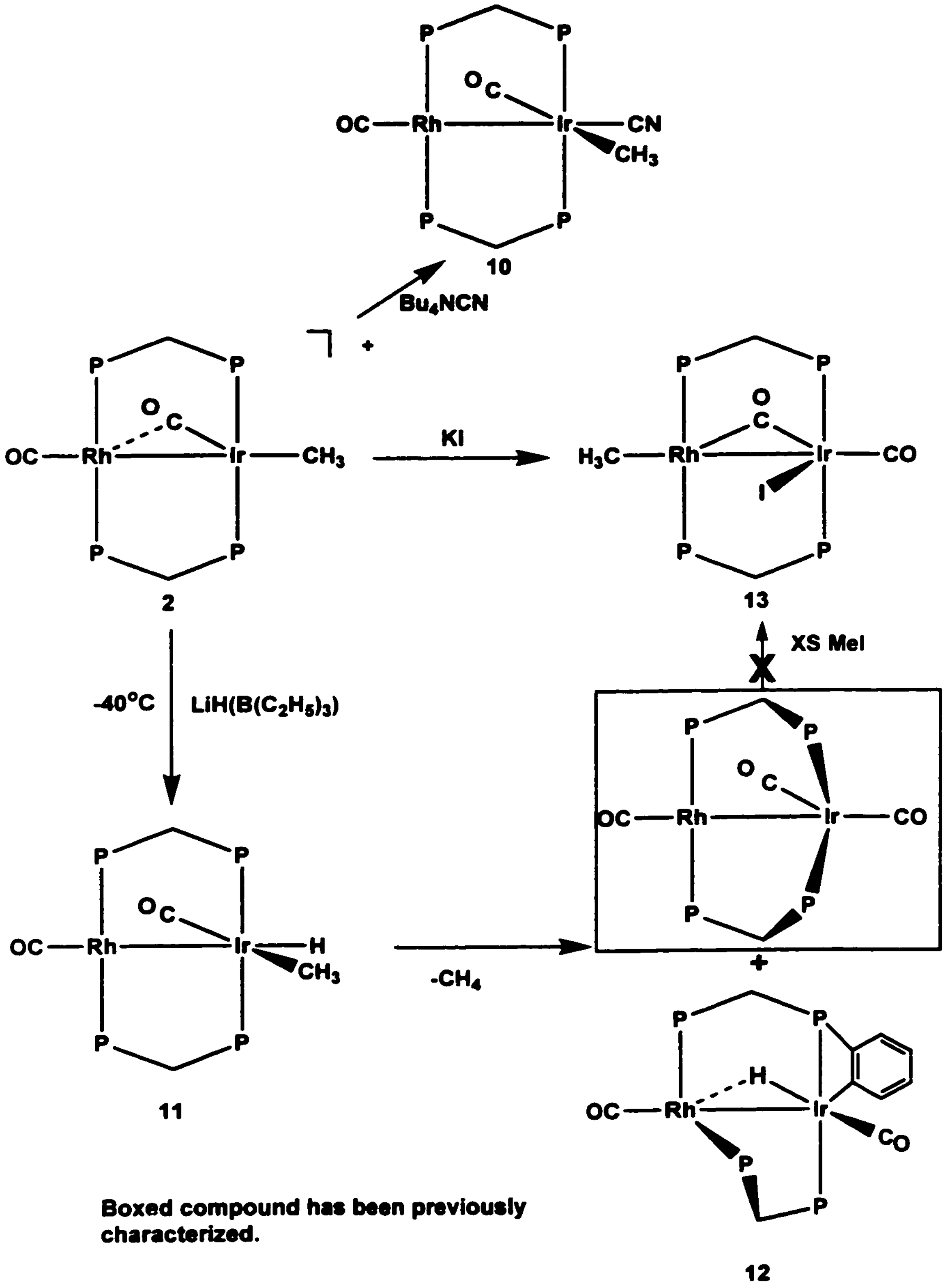
Thus for the tricarbonyl species, the ^{13}C NMR spectrum displays carbonyl resonances at δ 178.4, 175.2 ($^1J_{RhC}$ = 63.4 Hz) and 194.9 ($^1J_{RhC}$ = 56.3 Hz) in which the former two values are reasonably close to those shown by compound **8** (δ 179.4 and 173.7). That both proposed intermediates differ only in the geometry at Rh is also seen in the large chemical shift difference for the ^{31}P nuclei bound to Rh for both intermediates, with the tricarbonyl species resonating approximately 10 ppm upfield (δ 20.9) relative to the chemical shift for the dicarbonyl species (δ 31.2), while the corresponding chemical shifts for the Ir-bound dppm ^{31}P nuclei differ little (δ -1.8 *vs* 2.5), supporting the idea that the environments at Ir are essentially the same. A terminal coordination mode is proposed for the SO_2 group in compound **8** similar to one formulated for the analogous tricarbonyl intermediate on the basis of their spectral similarities as alluded to earlier. This view is reinforced by the observation that both species transform to a common SO_2-bridged product $[RhIr(CH_3)(CO)(\mu\text{-}SO_2)(dppm)_2][CF_3SO_3]$ upon warming the sample to ambient conditions. We argue against a bridging SO_2 group in compound **8** since this should inhibit methyl transfer from Ir to Rh, accompanied by CO transfer in the reverse direction, as was observed in subsequent conversions (*vide supra*). Upon addition of excess SO_2 to a solution of $[RhIr(CH_3)(CO)_2(\mu\text{-}SO_2)(dppm)_2][CF_3SO_3]$, slow conversion to the final alkylsulfinate product **9** occurs, whereas addition of CO to the same intermediate gives the acetyl species $[RhIr(CO)_2(COCH_3)(\mu\text{-}SO_2)(dppm)_2][CF_3SO_3]$, shown in Scheme 2.4, with no evidence of compound **9** being formed. Compounds **9** and the acetyl species are rather similar apart from the bridging carbonyl in **9**. Clearly, in both cases the Rh-CH_3 bond is susceptible to further reactivity, either via migratory insertion (CO) or by direct electrophilic attack (SO_2).

(b) Reactions with anionic ligands.

As a follow-up on the reactivity observed above for **1** and **2** with neutral ligands, the reactivity of **2** with anionic nucleophiles was investigated in the hope of determining if factors other than availability of coordination sites could influence the roles the metals play in reactivity. With tetrabutylammonium cyanide, reaction of **2** proceeds smoothly to give the neutral methyl cyano complex [RhIr(CH_3)(CN)($CO)_2$(dppm$)_2$] (**10**). As with many of the previous reactions, this product has the methyl group and the added ligand (CN^- anion) bound to Ir, as evidenced by the methyl resonance which appears as a triplet at δ -0.74 in the ^{1}H NMR spectrum, showing no Rh coupling. The ^{13}C NMR spectrum displays a triplet at δ 187.2 and a doublet of triplets resonance at δ 183.8 ($^1J_{RhC}$ = 66.8 Hz), assigned to the terminally bound CO groups on Ir and Rh, respectively. This is supported by the IR spectrum which displays two absorption bands at 1960 and 1932 cm^{-1} due to the two terminal carbonyl moieties while the cyanide stretch appears at 2084 cm^{-1}. This is within the range (2000-2090 cm^{-1}) reported for cyanide groups bound to other transition metals.[49] Although, in the absence of ^{13}C{^{1}H} NMR data for the CN ligand, its position on Ir cannot be verified, the spectral parameters are similar to those of related neutral dialkyl complexes (see Chapter 3), for which the coordination sites of the alkyl groups (both on Ir) can be clearly established on the basis of ^{1}H{^{31}P} experiments. The slight down-field shift of the Ir-bound carbonyl of **10** again suggests a weak semibridging interaction, as in the precursor **2**.

Compound **2** also reacts with hydride sources, such as superhydride, at room temperature, although several products are obtained which are difficult to characterize due to overlapping peaks. At -40°C (and lower) several products are again observed, but the major product is identified as [RhIrH(CH_3)($CO)_2$-(dppm$)_2$] (**11**). Compound **11** shows the methyl resonance as a triplet at

Scheme 2.5



Boxed compound has been previously characterized.

δ -1.02 and the hydride resonance, also a triplet, at δ -10.08 in the ^{1}H NMR spectrum; the lack of Rh coupling and the selective ^{31}P-decoupling experiments establish that both ligands are bound to Ir. The $^{13}C\{^{1}H\}$ NMR spectrum shows the presence of two carbonyl groups as expected : a doublet of triplets at δ 182.4 with a Rh-C coupling of 82.7 Hz and a broad peak at δ 190.4, assigned to Rh- and Ir-bound terminal carbonyl groups, respectively. As with compounds **2** and **10**, the down-field $^{13}C\{^{1}H\}$ chemical shift for the Ir-bound carbonyl suggests a weak semibridging interaction.

Upon warming the sample to ambient conditions two major compounds result in addition to minor unidentified species. The one product is the well-known, tricarbonyl species, $[RhIr(CO)_3(dppm)_2]$,[18] which has resulted from methane loss from **11** and scavenging of a carbonyl group, presumably from the decomposition products. The other major product is $[RhIr(CO)_2(\mu\text{-}H)(\mu_2\text{-}\eta^3\text{-}(o\text{-}C_6H_4)PPhCH_2PPh_2)(dppm)]$ (**12**), resulting from methane loss and subsequent orthometallation of one of the dppm phenyl groups. If a sample of **11** is allowed to warm under an atmosphere of CO, the major product obtained is the tricarbonyl complex. Also observed in the ^{1}H NMR spectrum is a singlet at δ 2.03 ascribed to dissolved methane, the other product of reductive elimination. Compound **12** displays a complex 4-resonance pattern in the ^{31}P NMR spectrum that is characteristic of an ABCDX spin system, having the Rh-bound ^{31}P resonances at δ 6.7 and 5.6 while those of the Ir-bound ^{31}P signals appear at δ -18.6 and -33.7, respectively. Although the Ir-bound phosphines display ^{31}P-^{31}P coupling of 367.3 Hz, characteristic of a *trans* alignment, no large ^{31}P-^{31}P coupling is observed for the other resonances, suggesting a cis arrangement[50] at Rh. The large difference in the Ir-bound phosphines and the high-field shift of one resonance, typical of a strained 4-membered ring,[51] suggests that orthometallation has occurred at the third-row metal.[52] The

$^{13}C\{^1H\}$ NMR spectrum is characteristic for a species having a terminal carbonyl on each metal. The ^1H NMR spectrum indicates the presence of a bridging hydride (δ -11.92, multiplet) which, on the basis of a weak Rh coupling (*ca.* 5.0 Hz), is assumed to be more tightly bound to Ir. Consistent with the low symmetry suggested for the molecule, the dppm methylene hydrogens appear as four distinct resonances at δ 5.36, 5.02, 4.18 and 4.08, respectively. Although the spectroscopic data available are insufficient to unambigously define the geometry, the close similarity of the spectral parameters to those of $[IrOs(CO)_3(H)_2(\mu\text{-}\eta^3\text{-}(o\text{-}C_6H_4)P(Ph)CH_2PPh_2)(dppm)]$[9f] suggests a related geometry, and a tentative structural proposal for **12** is shown in Scheme 2.5.

The above reaction is consistent with the reductive elimination of methane from **11**, generating a coordinatively unsaturated transient "$[RhIr(CO)_2(dppm)_2]$" which either scavenges CO, leading to tricarbonyl formation, or undergoes orthometalation of one of the Ir-bound dppm phenyl groups. This proposal is not unreasonable since this latter species is not obtained in the presence of other reacting substrates such as CO, yielding mainly the tricarbonyl species instead. A similar sequence of steps leading to methane evolution, ultimately affording an orthometalated complex, has been observed in related RhOs systems in our group.[14a]

Compound **2** also reacts with KI to give the neutral iodomethyl species $[RhIr(CH_3)(I)(CO)_2(dppm)_2]$ (**13**), as shown in Scheme 2.5. However, the reaction did not proceed cleanly and was often contaminated with traces of the previously characterized diiodide species $[RhIr(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$[8g] from which it could not be separated. Unlike compounds **10** and **11**, in which the added nucleophile and the methyl groups are on Ir, compound **13** has the methyl substituent on Rh, having migrated from Ir, as seen by the ^1H NMR spectrum in which the methyl protons, at δ -0.63, show 1.5 Hz coupling to Rh together with coupling to the Rh-bound phosphines. In the $^{13}C\{^1H\}$ NMR spectrum one carbonyl appears at δ 212.3 with a coupling of 40.2 Hz to Rh, consistent with a bridging group, and the other, on Ir, appears at δ 197.7. The binding of the methyl group to Rh is conclusively established by the $^{13}C\{^1H\}$ NMR spectrum of a $^{13}CH_3$-enriched sample which shows the methyl carbon at δ 3.1 displaying coupling of 22.2 Hz to Rh. No additional species were observed upon repeating this reaction at lower temperatures; clearly the rearrangement that brings the methyl group from Ir to Rh is facile. The structure for **13** is based on that of the isoelectronic diiodo analogue $[RhIr(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$,[8g] and this geometry is in keeping with iodide attack on **2′** at the site on Ir opposite the Rh-Ir bond (as in attack by H^- and CN^{-1}), assuming that a merry-go-round rearrangement of ligands occurs with CH_3 movement to Rh accompanied by CO movement to the bridging site. It is not clear why apparent attack of the iodide anion at Ir is accompanied by methyl group migration in this case, in contrast to what is observed in the cyanide anion reaction. Although an iodo methyl species analogous to that of the cyanide reaction was not observed, we believe it was probably formed, albeit transiently. Such an intermediate has been postulated by Van Koten and co-workers in a related system to rationalize a 1,2 methyl migration step leading to their final product.[53]

Compound **13** is the anticipated product (or an isomer thereof) of oxidative addition of MeI to $[RhIr(CO)_3(dppm)_2]$, followed by CO loss. A derivative of **13** is also expected for the reaction with the related ICH_2SiMe_3. But surprisingly, no reaction was observed using these reagents. This is in contrast to the facile oxidative addition of CH_3I to the diiridium analogue $[Ir_2(CO)_3(dppm)_2]$ which did give the anticipated $[Ir_2(I)(CH_3)(CO)_3(dppm)_2]$.[54] It also contrasts with the reaction of MeOTf and $[RhIr(CO)_3(dppm)_2]$ to give compound **1** consistent with MeI being a weaker electrophile in these reactions. It is quite conceivable that the nucleophilicity of the tricarbonyl $[RhIr(CO)_3(dppm)_2]$ could be enhanced by conducting the reaction in the presence of Me_3NO to remove a carbonyl, or by replacing one CO group by PMe_3 prior to addition of MeI, but neither of these has been attempted.

(c) Oxidative-addition reactions with H_2.

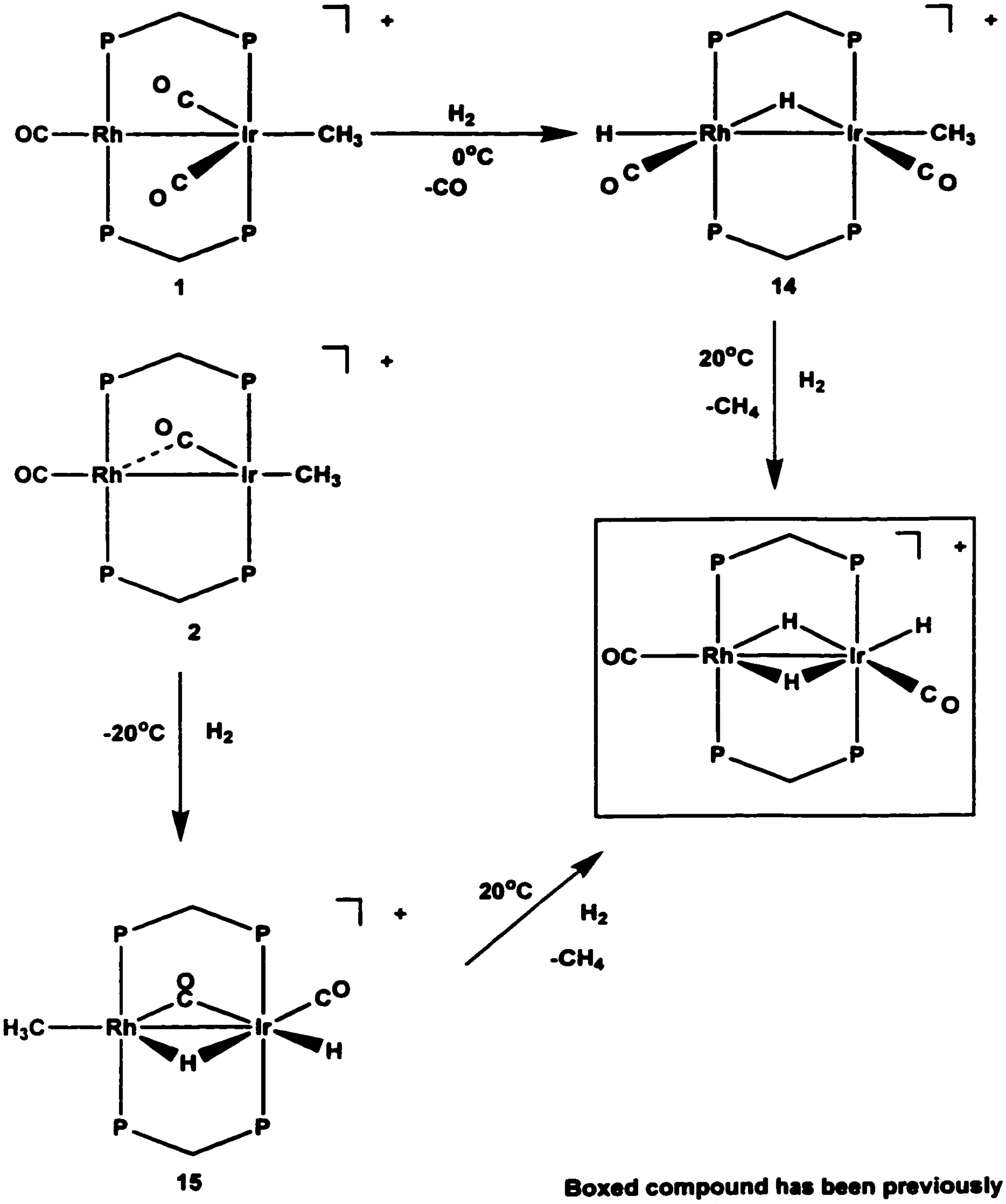
As alluded to in Chapter 1 of this thesis, methane is one of the by-products of the hydrogenolysis of compound **1**. It was of interest, amongst other considerations, to determine the role of the different metals in the reductive elimination of methane. Surprisingly, little has been established about the natures of hydrido-alkyl intermediates in the elimination of alkanes from adjacent metals. In a related dipalladium system, methane evolution from $[Pd_2(H)(CH_3)(\mu\text{-}Cl)(dppm)_2]^+$ and loss of both methane and ethane from $[Pd_2(H)(CH_3)_2(\mu\text{-}Cl)(dppm)_2]^+$ occurred under mild conditions,[55] whereas the related platinum complexes $[Pt_2(CH_3)_2(\mu\text{-}H)(dppm)_2]^+$ and $[Pt_2(H)(CH_3)(\mu\text{-}H)(dppm)_2]^+$ did not lose methane, even upon heating.[56] Although methane elimination was observed in two dirhodium A-frame complexes[25c] $[Rh_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]^+$ and $[Rh_2(CO_2)(\mu\text{-}CH_3CO)(dppm)_2]^+$, upon reaction with H_2, the hydrido-methyl intermediates were not observed, and only monohydride products were recovered. Similarly, the reductive elimination of methane from the mixed-metal species $[MRe(CH_3)(CO)_4(dppm)_2]^+$ (M = Rh, Ir) was found in a previous study[13a] to occur readily upon reaction with H_2 but no hydrido-methyl intermediate was observed down to -80 °C. Although, at -60 °C a hydride-bridged methyl complex was observed upon reaction of the above Ir/Re compound with a hydride source, and the species eliminated methane at ambient temperature, no analogous intermediates were observed for the

Rh/Re case, with the reaction proceeding over a 3 day period. Also the oxidative addition reactions of the related mononuclear alkyl complexes of Rh[57] and Ir[7c] with H_2 are known, so it was of interest to establish the site of substrate attack in the mixed binuclear framework.

Reaction of **1** with H_2 at ambient temperature yields the known trihydride species $[RhIr(H)(CO)_2(\mu\text{-}H)_2(dppm)_2][CF_3SO_3]$[18] through methane and CO evolution as shown in Scheme 2.6, while the reaction at 0 °C gives the dihydrido-methyl intermediate $[RhIr(H)(CH_3)(CO)_2(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**14**). The ^1H NMR spectrum of **14** displays two hydride resonances (δ -10.02, -12.47) in addition to that of the methyl group (δ -0.16), which is still bound to Ir. Selective phosphorus decoupling experiments allow us to establish that the hydride ligand at higher field is terminally bound to Rh with a coupling of *ca.* 24.1 Hz to this metal, while the other is bridging, having $^1J_{RhH}$ = 14.9 Hz. Only two carbonyl resonances are observed in the $^{13}C\{^1H\}$ NMR spectrum, with one CO bound to each metal. This product has a geometry consistent with attack at the coordinatively unsaturated Rh center. However, attempts to observe the initial product of H_2 addition, which is presumed to preceed CO loss, failed with no reaction being noted at temperatures lower than 0 °C; only **14** and the trihydride species were observed on slowly warming the sample under H_2 from lower temperatures.

It was of interest to establish whether reductive elimination of methane would occur from Ir or whether migration of the methyl group to Rh would occur with elimination occurring from this center. In the only alkyl intermediate observed, the methyl group remains bound to Ir, with one hydrido ligand in a bridging position. This geometry can easily give rise to methane loss via transfer of the bridging hydride to iridium, followed by reductive elimination from this metal. Although elimination should occur more readily from the second-

Scheme 2.6



Boxed compound has been previously characterized.

row metal, it appears in this case to be occurring from Ir. This parallels a previous study on a related RhOs compound,[14a] in which reductive elimination of methane also occurred from the third-row metal (Os) in preference to Rh.

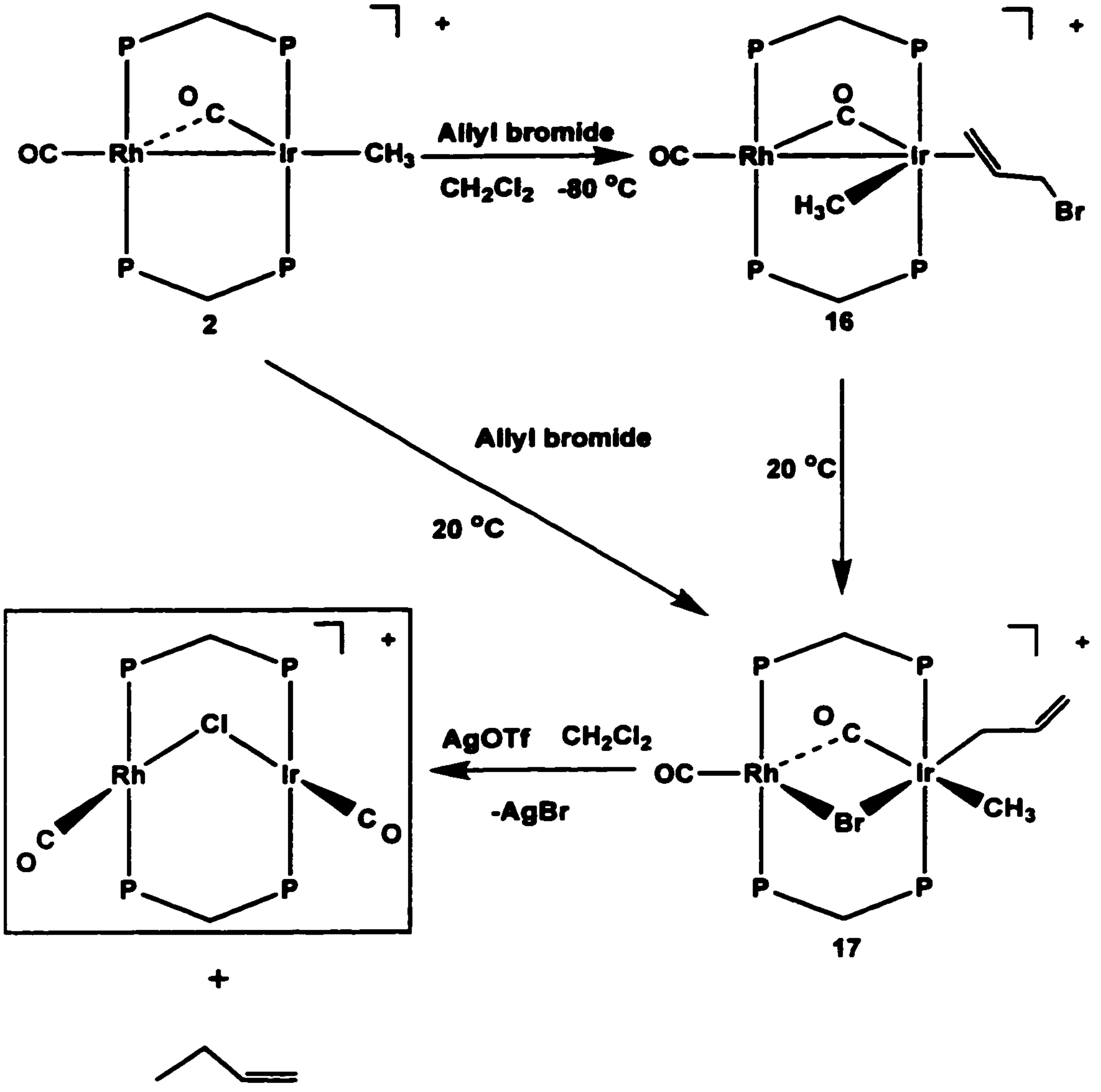
The oxidative addition of H_2 to **2** at -20°C, by contrast, occurs at one of the open coordination sites on Ir, yielding the stoichiometrically analogous hydrido-methyl species $[RhIr(H)(CH_3)(CO)(\mu\text{-}CO)(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**15**), accompanied by methyl transfer to Rh as revealed by its triplets of doublet resonance at δ 0.23 ($^2J_{RhH}$ = 1.7 Hz) in the ^1H NMR spectrum. This spectrum also shows the presence of a bridging hydride at δ -9.68 ($^2J_{P(Ir)H}$ = 11.1 Hz, $^2J_{P(Rh)H}$ = 3.7 Hz, $^1J_{RhH}$ = 14.6 Hz), which is more tightly bound to Ir, in addition to a triplet, at δ -12.58, consistent with a terminal hydride on Ir. The $^{13}C\{^1H\}$ NMR spectrum for **15** is consistent with the presence of a bridging (δ 221.2, $^1J_{RhC}$ = 30.1 Hz) and terminal carbonyl (δ 168.9) group. Under an atmosphere of H_2, compound **15** converts slowly to the known trihydride $[RhIr(H)(CO)_2(\mu\text{-}H)_2(dppm)_2][CF_3SO_3]$,[18] upon warming accompanied by methane evolution; no other intermediates were observed. The proposed geometry at Ir in which the carbonyls are placed adjacent to each other was inferred from the absence of *trans* coupling ($^2J_{CC}$) between these ligands in the $^{13}C\{^1H\}$ NMR spectrum of the ^{13}CO enriched compound. This arrangement is also consistent with an end-on attack of the added H_2 at Ir, opposite the Rh-Ir bond, assuming the solution structure of **2′**. A merry-go-round rearrangement of ligands involving transfer of the methyl and carbonyl (Rh) groups, should provide **15**, having the proposed formulation as outlined in Scheme 2.6. Based on the absence of other observable intermediates in this reaction, it is suggested that reductive elimination of methane occurs from Rh, presumably via transfer of the bridging hydride to this metal.

(d) Reactions with olefins

Olefin insertion into a metal-alkyl bond is an important step in catalytic polymerization processes.[37] We have therefore undertaken the reactions of **1** and **2** with a number of olefins in order to determine whether migratory insertions involving the methyl and olefin ligands would occur. In a previous study,[10a] it was shown that compound **1** reacted with ethylene to give $[RhIr(CH_3)(C_2H_4)(CO)_2(dppm)_2][CF_3SO_3]$, in which the methyl group has migrated from Ir to Rh; no evidence of migratory insertion and C-C bond formation was observed. Compound **2** also reacts with ethylene at -80 °C giving the ethylene adduct $[RhIr(CH_3)(C_2H_4)(CO)_2(dppm)_2][CF_3SO_3]$, together with the starting material.

Compound **2** reacts cleanly with allyl bromide at ambient temperature to afford the oxidative-addition product $[RhIr(CH_3)(\eta^1\text{-}C_3H_5)(\mu\text{-}Br)(CO)_2(dppm)_2]$-$[CF_3SO_3]$ (**17**), as shown in Scheme 2.7. The ^1H NMR spectrum shows the methyl group resonating as a triplet at δ -0.18, suggesting it is still Ir-bound, while the allyl protons give rise to signals typical of an allyl moiety coordinated in an η^1-fashion.[11,14b,58] The $^{13}C\{^1H\}$ NMR spectrum displays resonances consistent with terminal and semibridging carbonyls. Compound **17** is surprisingly robust; refluxing in CH_2Cl_2 for extended periods resulted in no reaction. Attempts to induce η^1- to η^3-allyl rearrangement via decarbonylation of **17** led only to decomposition. Similarly, removal of the bromide ligand with a silver salt did not give the expected product, but instead produced the known A-frame product $[RhIr(CO)_2(\mu\text{-}Cl)(dppm)_2][CF_3SO_3]$,[15b] together with 1-butene. The presence of free 1-butene was confirmed in the ^1H NMR by adding an authentic sample to the sample and observing an increase in intensities of the butene proton resonances. It seems that removal of the bromide anion induces reductive elimination of the allyl and methyl moieties as 1-butene.

Scheme 2.7



Boxed compound has been previously characterized.

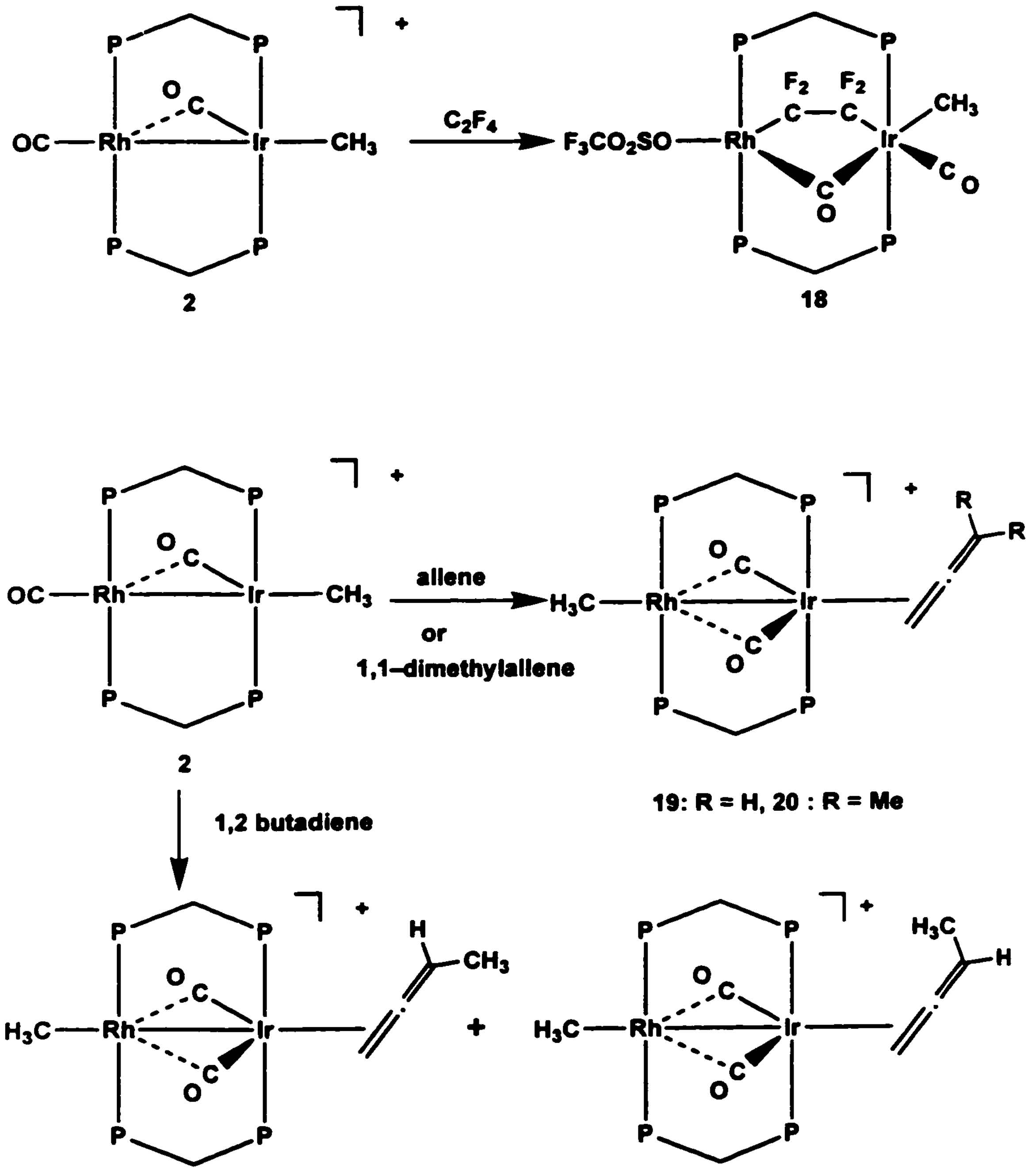
Reductive elimination is known to be facilitated by either oxidation or by anion loss to give a cationic species.[37a] The formation of the chloro-bridged A-frame species presumably occurs by chloride abstraction from the CH_2Cl_2 solvent by the transient dication "$[RhIr(CO)_2(dppm)_2][CF_3SO_3]_2$". Repeating the reaction in a non-chlorinated solvent such as THF resulted only in a number of decomposition products. Presumably, the solvated adduct is either unstable or the dicationic species "$[RhIr(CO)_2(dppm)_2][CF_3SO_3]_2$" is too reactive in the absence of strongly coordinating nucleophiles. The formation of a species corresponding to the coordinated triflate complex "$[RhIr(CO)_2(dppm)_2(CF_3SO_3)_2]$" or the η^2-butene complex "$[RhIr(CO)_2(\eta^2\text{-}C_4H_8)(dppm)_2][CF_3SO_3]_2$" could not be confirmed, as only the known A-frame species was identified in solution. It is not certain whether elimination of the allyl and methyl groups as 1-butene occurred from Ir upon bromide abstraction or whether migration of both the methyl and allyl groups from Ir to Rh occurred followed by elimination from this metal.

Compound **2** reacts with allyl bromide at -80 °C, presumably at one of the open coordination sites on Ir, to give the olefin adduct $[RhIr(CH_3)(CO)(\mu\text{-}CO)(\eta^2\text{-}H_2C{=}CHCH_2Br)(dppm)_2][CF_3SO_3]$ (**16**), in an approximate ratio of 1:1 with compound **17**. Compound **16** converts quantitatively to **17** upon warming to ambient temperature. The ^{31}P NMR spectrum for compound **16** indicates two resonances for the inequivalent Ir-bound ^{31}P nuclei, consistent with an asymmetry in the environments for these phosphines which derives from an asymmetry of the coordinated olefin. The $^{13}C\{^1H\}$ NMR spectrum for **16** conforms with the presence of a terminal (δ 185.9, $^1J_{RhC}$ = 78.0 Hz) and bridging carbonyl (δ 210.0 $^1J_{RhC}$ = 40.7 Hz), while the ^1H NMR spectrum indicates that the methyl group remains bound to Ir, as evidenced by its triplet signal at δ 1.41. Broad peaks at δ 4.18, 3.37, 0.98 and 0.96 also observed in the ^1H

NMR spectrum were assigned to the protons of the allyl bromide ligand, and were confirmed by 2D $^1H/^1H$ COSY experiments. The isoelectronic alkynyl species $[RhIr(CO)_2(\mu\text{-}C_2Ph)(dppm)_2][BF_4]$ has been shown[58] to react with allyl bromide in an analogous manner, first forming the olefin adduct at low temperature, followed by oxidative addition of the allyl and bromo fragments at Ir. However, in this case a subsequent migration of the allyl moiety to the alkynyl group occurred to give an allyl vinylidene moiety.

While there is ample evidence for ethylene insertion,[59] only a few reports have emerged on the related tetrafluoroethylene insertions.[60,61] Exposure of a solution of **2** to an atmosphere of tetrafluoroethylene produces $[RhIr(CH_3)(\mu\text{-}C_2F_4)(CO)_2(dppm)_2(CF_3SO_3)]$ (**18**), in which the olefin adopts an $\mu_2\text{-}\eta^1{:}\eta^1$ bridging mode. Again, no evidence of migratory insertion was observed. Characterization of compound **18** was relatively straight forward. The ^1H NMR spectrum showed the Ir-bound methyl protons as a broad peak at δ 1.18. This latter resonance is flanked by an additional doublet ($^3J_{HC}$ = 5.5 Hz) if the CO groups are labelled, suggesting a trans disposition between the methyl and one CO group (in all previous examples, the methyl protons do not exhibit significant coupling to the ^{13}CO group when they are mutually cis). Further confirmation for the binding site of the methyl group is derived from the $^{13}C\{^1H\}$ NMR spectrum in the methyl region which showed a triplet at δ 31.5 with a 5.2 Hz coupling to the Ir-bound dppm ^{31}P nuclei. The low-field shift of this signal, while being quite anomalous for an Ir-bound methyl carbon (which generally tend to resonate at higher fields than Rh-bound methyls), is not without precedent and has been observed earlier (*vide supra*) for the solution structure of compound **2** in which the methyl and carbonyl groups on Ir are also assumed to be trans to each other. Definitive evidence for the bridging mode for the olefin group in **18** is obtained from the ^{19}F NMR spectrum and $^{19}F\{^{31}P\}$

Scheme 2.8



2

18

2

19: R = H, 20 : R = Me

21a

21b

decoupling experiments. The high-field ^{19}F resonance is found to couple only to the phosphorus nuclei on Ir whereas the other resonance displays coupling to the Rh-bound ^{31}P nuclei. In the ^{19}F NMR spectrum with broad-band ^{31}P decoupling the only coupling observed is that of the low-field resonance to Rh (see Figure 2.5). The $^{13}C\{^1H\}$ NMR spectrum in the carbonyl region shows two resonances at δ 236.5 and 186.4, with the former displaying an additional Rh-C coupling of *ca.* 28.0 Hz, consistent with a bridging carbonyl group. It is suggested that the triflate group occupies a coordination site on Rh, opposite the Rh-Ir bond. Triflate coordination would confer a trigonal bipyramid geometry to Rh, and is required since all other ligands are either bridging (one carbonyl and the tetrafluoroethylene ligand) or terminally bound to the Ir center (carbonyl and methyl groups). This formulation receives support from the IR spectrum which shows an absorption band at 1377 cm^{-1}, assigned to the asymmetric S-O stretch of the coordinated triflate group. This absorption is shifted to a higher wavenumber compared to those observed for ionic triflate groups which generally appear in the range 1235-1288cm^{-1}.[62] The bonding mode observed for the tetrafluoroethylene ligand is not unexpected since in this position it can simultaneously form metal-carbon σ bonds with both metals, resulting in a dimetallacyclobutane bonding mode. Fluoro-substituted alkyl groups have been shown to have strong metal-carbon bonds.[63] Unlike the ethylene adduct of **2** which loses ethylene readily, compound **18** resists C_2F_4 loss and is stable in air for weeks. The failure of the C_2F_4 ligand to insert into the metal-methyl bond is probably related to the relatively strong Ir-CH_3 and metal-carbon bonds of the bridging C_2F_4 group, particularly at the Ir end.

Addition of cumulenes such as allene, 1,2-butadiene and 1,1-dimethylallene to **2** yields η^2-allene products, much as with ethylene; again these reactions are accompanied by methyl group migration from Ir to Rh. The

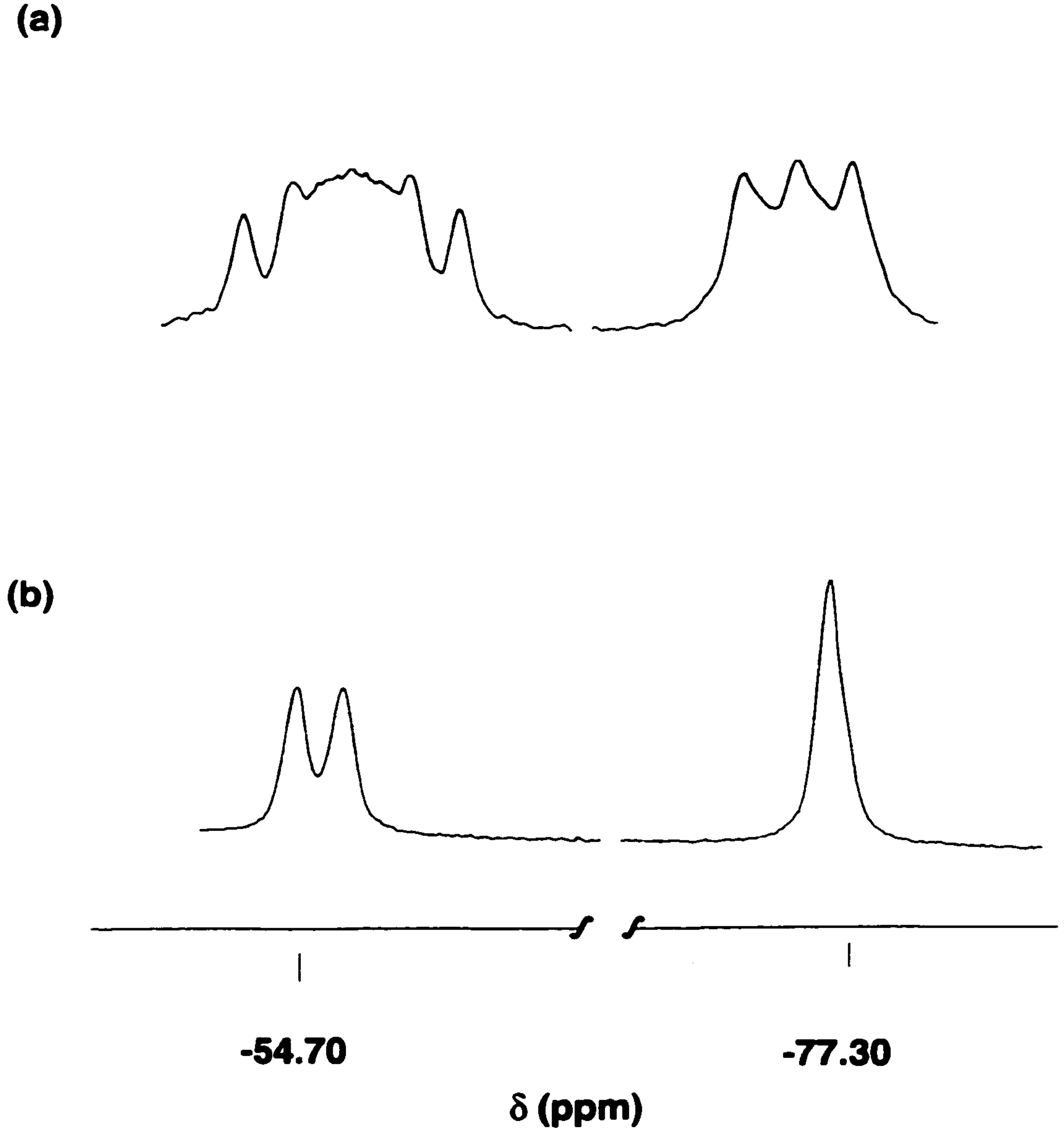


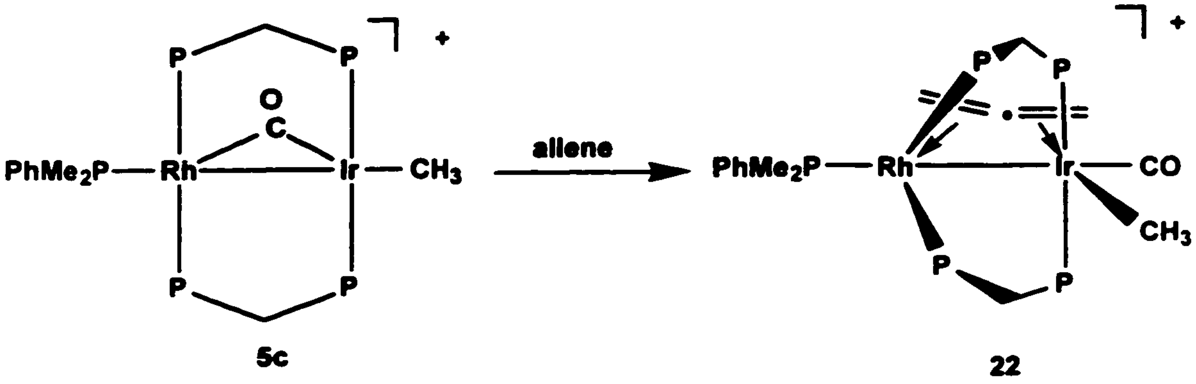
Figure 2.5 (**a**) $^{19}F\{^1H\}$ and (**b**) broad-band $^{19}F\{^1H,^{31}P\}$ NMR spectra for compound **18** at room temperature.

^1H NMR spectrum for the allene adduct $[Rh_2(CH_3)(CO)_2(C_3H_4)(dppm)_2][CF_3SO_3]$ (**19**) displays the methyl protons as a triplet of doublets at δ 0.56 with a Rh-H coupling of 2 Hz while the geminal allene protons display a triplet resonance at δ 0.60 with no resolvable geminal $^2J_{HH}$ coupling but a 7.0 Hz coupling to the Ir-bound ^{31}P nuclei. The non-coordinated allene protons appear as an unresolved broad resonance at δ 1.60 with no P-H coupling. It is proposed that the allene is coordinated to Ir such that its carbons lie in the equatorial plane perpendicular to the Rh-P and Ir-P bonds, as opposed to the out-of-plane mode, which is less favored owing to steric repulsions between the allene protons and the dppm phenyl groups. This viewpoint has been taken for the proposed formulations of other η^2-bound allene compounds in our group, including one, the structure of which has been crystallographically determined.[12c,15d,24] The dppm methylene protons appear as a multiplet at δ 3.34. integrating as four protons, possibly a result of an accidental overlap of the two sets of inequivalent methylene protons. The $^{13}C\{^1H\}$ NMR spectral parameters for **19** closely resemble those of the ethylene adduct,[10a] suggesting an analogous bonding mode for the carbonyl groups. The η^2 -bonding mode adopted by the allene ligand is in contrast with the results obtained for the related diiridium allene adduct[64] in which the unusual μ-η^1,η^3 bonding mode was adopted. After 2-3 d, a second isomer of **19** appears, in which the allene is proposed to bridge both metals in an η^2:η^2 fashion (this species was previously identified but was not fully elucidated).[17]

The reaction of **2** with 1,1-dimethylallene proceeds in the same fashion yielding the structurally analogous species $[RhIr(CH_3)(H_2CCCMe_2)(CO)_2(dppm)_2][CF_3SO_3]$ (**20**). The $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^1H NMR spectra for **20** are similar to those of **19**, with the exception that in the ^1H NMR spectrum, the two methyl groups of the noncoordinated end of the allene appear as distinct singlet peaks at δ 0.97 and 1.18 and integrate as 1:1 with the Rh-bound methyl group. Unlike compound **19** which transforms to an isomeric species upon standing in solution, **20** resists further conversion even after weeks in solution. Presumably, further rearrangement of the allene to a bridging mode is unfavorable owing to the repulsions that would occur between the two methyl substituents and the ligands bound to the second metal. 1,2-butadiene also reacts with compound **2** in a similar fashion as was described for the other cumulenes, except that two isomeric species **21a** and **21b** were obtained in a ratio of 82:18. Again, the spectral parameters for **21a,b** resemble those of the other initial cumulene adducts suggesting similar geometries. Unfortunately, the available data do not allow an unambiguous assignment of the two isomers. This notwithstanding, it is suggested that the more abundant isomer, designated **21a** in Scheme 2.8, has the methyl group on the substituted end of the allene in an exo position, pointing away from the semi-bridged carbonyl groups on the basis of steric arguments. The minor isomer with the methyl substituent in an endo position would be expected to be disfavored owing to steric interactions with the adjacent carbonyl groups on Ir. The isomer ratio remains constant even after 2-3 d at ambient temperature.

The phosphine complex $[RhIr(CH_3)(PPhMe_2)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**5c**), described earlier, is isoelectronic with **2**, and thus it was of interest to compare their reactivities towards allene. Unlike **2** which produces an η^2-olefin adduct upon exposure to allene, compound **5c** reacts cleanly with allene at room temperature to give a single product $[RhIr(CH_3)(PPhMe_2)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_3H_4)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**22**), in which the olefin bridges the metals, as diagrammed in Scheme 2.9.

Scheme 2.9



At ambient temperature, NMR spectrum for **22** is broad and uninformative. The ^1H NMR spectrum at this temperature also shows the dppm methylene protons as a broad featureless peak centered at δ 4.78 while the $PPhMe_2$ methyl protons appear as a doublet at δ 0.80, integrating in a 2:1 ratio with those of the Ir-bound methyl group, which appears as a triplet at δ 0.93. The ^1H NMR spectrum also displays multiplets at δ 4.80 and 3.00, assigned to allene protons coupled to Rh- and Ir-bound dppm ^{31}P nuclei respectively; these assignments were confirmed by selective ^{31}P decoupling experiments. However, at -60 °C the phosphine methyl groups show up as two distinct peaks at δ 1.04 and 0.42, suggesting that at ambient temperature, they are exchanging, while each of the four allene protons shows up as a distinct multiplet. The dppm methylene protons also appear as four peaks at low temperature, again consistent with an asymmetric environment. The $^{31}P\{^1H\}$ NMR spectrum at -60 °C for compound **22** displays five resonances, consistent with an ABCDMX spin system (X = Rh): a doublet of multiplets at δ 22.4 and 17.2, multiplets at δ -9.5 and -14.7, and a doublet of multiplets at δ -15.4. This last resonance is assigned to the $PPhMe_2$ group bound to Rh on the basis of its coupling of 127.0 Hz to Rh and its relatively up-field chemical shift, while the first two resonances show additional coupling to Rh (*ca*. 146.8 Hz each), and are assigned to the Rh-bound ^{31}P nuclei of the dppm groups. These ^{31}P nuclei show only a mutual coupling of *ca*. 45.9 Hz to each other. The small magnitude of this coupling suggests a cis arrangement of the dppm groups about the Rh center. On the other hand, the $^{2}J_{PP}$ of 366.6 Hz for the Ir-bound dppm ^{31}P nuclei clearly indicates a trans disposition for these groups. A similar cis,trans configuration has been observed in several dppm-bridged transition-metal complexes.[65] Presumably the Rh-bound dppm groups adopt a cis disposition, in order to accommodate the allene and the monodentate phosphine groups. It is not clear why the allene ligand does not bind terminally to Ir in an η^2 fashion as was the case with the related allene adduct **19** and observed in other allene complexes in our group.[12c,15d,24] However, it should be recalled that even the η^2-allene compound **19** rearranges to give a species proposed to be analogous to **22**; so it may be that the conversion of **5c** to **22** proceeds via an unobserved η^2-allene intermediate analogous to **19**. The $^{13}C\{^1H\}$ NMR spectrum of **22** shows a triplet resonance at δ 180.3, consistent with a terminally bound CO group on Ir. Acquisition of $^{13}C\{^1H\}$ NMR data overnight enabled us to observe two multiplets at δ 141.9 ($^1J_{RhC}$ = 33.2 Hz) and 71.7 ($^1J_{RhC}$ = 30.4 Hz) and a broad resonance at δ 58.9, attributed to the central allene carbon and the allene carbon atoms bound to Rh and Ir, respectively. These allene chemical shifts are in the expected upfield region relative to those observed for free allene (δ 200-214), with the low-field resonance being in accord with quartenary carbon shifts observed in other metal allene complexes.[66-68] Further support for the coordination mode for the allene ligand comes from HMQC $^1H/^{13}C$ correlation analyses which show correlations between the resonances at δ 71.7 and 58.9 in the $^{13}C\{^1H\}$ NMR spectrum with those at δ 4.80 and 3.00 in the ^1H NMR spectrum at 20 °C. The available data are consistent with the proposed geometry for the allene ligand as has been reported for several transition-metal allene complexes.[59,66,67] The alternative bonding modes, involving the η^2- and μ-η^1:η^3-bound allene, have also been observed on a number of occasions.[15d,66b,66c,69] However, the spectroscopic data are inconsistent with any of these. Unfortunately, X-ray quality crystals could not be grown as the compound decomposed in the absence of an atmosphere of allene.

Conclusions

The reactivities of compounds $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**1**) and $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with a selection of small molecules were investigated in order to probe the functions of the different adjacent metals in C-H bond cleavage and C-C bond formation. At the outset, it was reasoned that the coordinative unsaturation at both metals in **2** in contrast to the situation in **1** where only the Rh center is coordinatively unsaturated together with the fact that compounds **1** and **2** have 18e/16e and 16e/16e configurations at Ir and Rh, respectively could reflect different chemistries.

In all cases investigated, the reaction of **1** with small molecules results in the substitution of one carbonyl ligand by the added substrate to give products that are identical to those of substrate addition to **2**. At low temperatures, a number of intermediates in the reactions of **1** were observed, although only for phosphines and dihydrogen were the initial products of addition at the unsaturated Rh center identified. By contrast, the reaction of **2** with substrates appears to occur exclusively at Ir.

Compound **2** reacts with a number of hard and soft nucleophiles, such as KI, cumulenes and ethylene to afford species in which methyl migration from Ir to Rh has occurred, with the site of substrate attack being apparently at

Ir. Although we did not succeed in isolating or observing a methyl-bridged complex in these systems, the facile migration described implies a methyl-bridged species as a probable intermediate. Such alkyl-bridged species are important precursors[28] in subsequent C-H activation of the alkyl group by the adjacent metal, as was observed in the analogous diiridium system.[17,28] The failure of these RhIr species to undergo C-H bond cleavage of the methyl group as occurred for the Ir_2 analogues can be rationalized in terms of the weaker Rh-C/Rh-H *vs* Ir-C/Ir-H bond strengths,[27] favoring retention of the intact CH_3 group in the RhIr compounds. These bond strengths are presumably also responsible for the lack of fluxionality in **2**, in contrast to the facile methyl and carbonyl migrations occurring between metals in the Rh_2 and Ir_2 analogues. In the mixed-metal species the stronger Ir-CH_3 *vs* Rh-CH_3 and Ir-CO *vs* Rh-CO bonds favor the structure in which the ligands remain on their respective metals.

It is also clear that subtle electronic and possibly steric effects dictate whether the methyl group ends up being bound to Rh or Ir. This view is borne out by the fact that in the reaction of **2** with nucleophiles such as superhydride (low temperature) and cyanide anion, no analogous methyl group migration from Ir to Rh was observed, although the site of substate attack on the metal appeared to be at Ir, as in the previous cases. In the case of the reaction with KI, however, methyl transfer occurs. We assume that methyl, rather than iodide, migration to Rh may reflect a more favorable Ir-I bond. Furthermore, the accommodation of the methyl and hydrido or cyano ligands, presumably in a cis geometry, may reflect the absence of significant steric repulsions between these groups, taking into account their small sizes.

One unexpected finding of this study is that reductive elimination of methane from the hydrido-methyl species **14** and migratory insertion of the methyl onto an isocyanide group giving rise to the imino-acyl species $[RhIr(CO)_2(\mu\text{-}C(CH_3)=N^tBu)(dppm)_2][CF_3SO_3]$, both appear to occur at the less labile Ir center. Furthermore, the oxidatively-induced elimination of 1-butene from **17** also appears to occur from Ir, as evidenced by the absence of intermediates in which either of the eliminated fragments are bound to Rh. These results seem to reinforce our earlier views of a somewhat more labile Ir center in the Rh/Ir system compared to Ir_2 systems, possibly from the subtle influence of the adjacent Rh. As a consequence, the behaviour of these Rh/Ir systems in some of their reactions approach that exhibited by analogous dirhodium complexes.[26a,c,70]

In this study we strove to understand the roles of the different metals in the reactions of the two mixed Rh/Ir methyl complexes **1** and **2** with a variety of substrates. The initial sites of attack (at either Rh or Ir) can be rationalized on the basis of either the site of unsaturation (Rh) in **1**, or in the case of compound **2**, based on its structure in solution, in which substrate approach appears to be favored at a site on Ir remote from the Rh center. In much of this chemistry, the rearrangements that occur appear to be driven by the stronger bonds involving the third-row metal, and in some cases, by steric congestion at this metal.

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Chapter 3

Dimethyl and Trimethyl Complexes : Carbonylation and Related Reactions

Introduction

In Chapter 2, it was demonstrated that the monomethyl species $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) reacted with nucleophiles such as $Li(HBEt_3)$ and tetrabutylammonium cyanide to give hydrido-methyl and cyano-methyl products, respectively, in which the anionic ligands occupy mutually cis positions at iridium. Unfortunately, both compounds were unstable to isolation so their subsequent chemistry was not followed. The former species, for example, was stable in solution only at temperatures below -40 °C. One logical extension of this chemistry is to employ hydrocarbyl nucleophiles in attempts to generate dialkyl complexes. The resulting dialkyl species should be less susceptible toward reductive elimination of the alkanes compared to the hydrido-methyl species and therefore more amenable to reactivity studies in which we could further investigate the influence of the different metals in the chemistry.

One aspect of interest in the chemistry of RhIr complexes containing two hydrocarbyl fragments relates to the binding of the hydrocarbyl fragments to the different metals since it might be anticipated that a Rh-bound fragment should display subtle (or even significant) differences in reactivity compared to an Ir-bound fragment. It was also anticipated that the increased electron density on the metals from the presence of two alkyl groups[1] should predispose such complexes toward enhanced reactivity with electrophiles and π-acids such as CO and SO_2, with the corollary benefit of inducing insertion processes.

Particularly relevant is the possibility of adjacent-metal involvement in the formation of dialkyl, acyl-alkyl and acyl-hydride species and the subsequent reductive elimination of alkanes, ketones and aldehydes.[2] In this chapter, routes to dialkyl, alkyl-benzyl, alkyl-aryl, dibenzyl and trialkyl complexes will be described as will the results of the carbonylation of the dimethyl and trimethyl complexes and related reactions with unsaturated substrates. Since these binuclear systems can be regarded as the simplest conceptual models[3] of mixed-metal catalysts, learning more about their reactivities may lead to a greater understanding of how surface-bound alkyl, acyl and hydride groups on metal surfaces couple in the termination steps of catalytic processes to form alkanes, ketones and aldehydes. Such models may also shed some light on the factors that dictate the outcomes of the above processes and on the functions of each metal in effecting these transformations.

Experimental Section

General Comments. General experimental conditions were as described in Chapter 2. Phenyl and benzyl magnesium chloride (2 M in THF solution) were purchased from Aldrich while $[RhIrCl_2(CO)_2(dppm)_2]$[4] and $[RhIr(CH_3)(CO)_2\text{-}(dppm)_2][CF_3SO_3]$ (**2**)[5] were prepared as previously reported. Spectroscopic data for the compounds are found in Table 3.1.

Preparation of Compounds.

(a) $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (23). 200 mg (0.168 mmol) of $[RhIrCl_2(CO)_2(dppm)_2]$ was dissolved in 150 mL of dry THF at -78 °C. To a

Table 3.1 Spectrocopic Parameters for the Compounds[a]

		NMR[d]		
Compounds	IR,[b,c] cm^{-1}	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ **(23)**	1715 (ms)	31.9 (dm, $^1J_{RhP}$=154.0Hz) 21.5 (m)	3.86 (m, 2H), 3.53 (m, 2H), -0.35 (td, $^2J_{RhH}$=2.0Hz, 3H), 0.22 (t, 3H)	230.8 (dm, $^1J_{RhC}$=29.3Hz, 1C)
$[RhIr(CH_2Ph)_2(\mu\text{-}CO)\text{-}(dppm)_2]$ **(24)**	1713 (ms)	29.3 (dm, $^1J_{RhP}$=160.5Hz) 18.1 (m)	3.62 (m, 2H), 3.38 (m, 2H), 2.57 (t, 2H), 1.82 (td, 2H)	230.1 (dm,$^1J_{RhC}$=30.5Hz, 1C)
$[RhIr(CH_3)_2(CO)_2(dppm)_2]$ **(25)**[f]	1985 (m), 1943 (bs)	12.1 (dm, $^1J_{RhP}$=151.5Hz) -14.9 (m)	5.41 (m, 2H), 5.22 (m, 2H), -0.24 (t, 3H), -1.39 (m, 3H)	185.7 (t, 1C), 182.6 (dt, $^1J_{RhC}$=67.8Hz,1C)
$[RhIr(CH_3)_2(CO)_3(dppm)_2]$ **(26)**[g]	-	6.9 (dm, $^1J_{RhP}$=153.3Hz) -7.8 (m)	4.97 (m, 2H), 4.64 (m, 2H), 0.40 (b, 3H), -1.18 (b, 3H)	204.8 (dt,$^1J_{RhC}$=77.4Hz, 1C) 190.2 (dt,$^1J_{RhC}$=60.2Hz, 1C) 184.3 (t, 1C), -7.7 (t, $^2J_{PC}$= 6.2Hz, 1C), -9.0 (t, $^2J_{PC}$= 6.9Hz, 1C)
$[RhIr(CH_3)(Ph)(CO)_2\text{-}(dppm)_2]$ **(28)**	-	10.9 (dm, $^1J_{RhP}$=149.2Hz) -17.9 (m)	5.50 (m, 2H), 5.22 (m, 2H), -0.41 (t, 3H)	185.2 (t, 1C), 182.0 (dt, $^1J_{RhC}$=66.8Hz, 1C)

Table 3.1 (contd).

		NMR^d		
Compounds	IR,^{b,c}cm^{-1}	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(CH_3)(CH_2Ph)(CO)_2$-$(dppm)_2]$ **(29)**	-	11.7 (dm, $^1J_{RhP}$=131.9Hz) -19.8 (m)	5.45 (m, 2H), 5.10 (m, 2H), 1.38 (t, 2H), 0.14 (t, 3H)	184.3 (t, 1C), 182.2 (dt, $^1J_{RhC}$= 66.8Hz, 1C)
$[RhIr(CH_3)_2(\mu$-$H)(H)(CO)$-$(dppm)_2]$ **(30)**	1816 (m)^c	35.1 (dm, $^1J_{RhP}$=148.0Hz) 8.7 (m)	3.64 (m, 2H), 3.23 (m, 2H), -0.82 (t, 3H), -0.19 (td, 3H) -10. 65 (dm, $^1J_{RhH}$=14.0Hz, 1H), -13.3 (t, 1H)	231.1 (dm, $^1J_{RhC}$=19.8Hz 1C)
$[RhIr(COCH_3)(CH_3)(\mu$-$H)$-$(H)(CO)(dppm)_2]$ **(31)**^{f}	1742 (ss)^c, 1626 (m)^c	24.6 (dm, $^1J_{RhP}$=166.1Hz) 10.5 (m)	3.63 (m, 2H), 3.18 (m, 2H), 0.97 (s, 3H), -1.02 (t, 3H), -11.83 (dm, $^1J_{RhH}$=20.1Hz, $^2J_{P(Ir)H}$=13.8Hz, $^2J_{P(Rh)H}$= 18.2Hz,1H), -13.58 (t, 1H)	277.5 (ddm, $^1J_{RhC}$=29.0Hz, $^2J_{CC}$=9.8Hz, 1C), 227.2 (ddm, $^1J_{RhC}$=24.4Hz, 1C)
$[RhIr(CH_3)_2(\mu$-$SO_2)(CO)$-$(dppm)_2]$ **(32)**^{h}	-	32.7 (dm, $^1J_{RhP}$=149.9Hz) 5.9 (m)	4.22 (m, 2H), 3.48 (m, 2H), -0.22 (td, 3H), -0.43 (t, 3H)	171.3 (t, 1C)
$[RhIr(SO_2CH_3)(CH_3)$-$(\mu$-$SO_2)(CO)(dppm)_2]$ **(33)**	1987 (ss), 1406 (ms)^e, 1130 (bs)^e 1090 (ms)^e 1024(m)^e	33.2 (dm, $^1J_{RhP}$=144.9Hz) 4.2 (m)	3.96 (m, 2H), 3.24 (m, 2H), 1.51 (s, 3H), 0.60 (t, 3H)	177.8 (t, 1C)

Table 3.1 (contd).

Compounds	IR,^{b,c}cm^{-1}	NMR^{d}		
		$\delta(^{31}P\{^{1}H\})$	$\delta(^{1}H)$	$\delta(^{13}C\{^{1}H\})$
$[RhIr(CH_3)_3(CO)(dppm)_2]$-$[CF_3SO_3]$ (**34**)^{h}	-	26.1 (dm, $^{1}J_{RhP}$=138.9Hz) 22.9 (m)	4.05 (m, 2H), 3.77 (m, 2H), 0.98 (b, 3H), 0.15 (b, 3H), 0.13 (b, 3H)	211.5 (dm, $^{1}J_{RhC}$=36.8Hz, 1C), 7.4 (dt, $^{1}J_{RhC}$= 22.4Hz, 1C), -11.5 (t, 1C), -18.3 (t, $^{2}J_{PC}$=2.7Hz, 1C)
$[RhIr(CH_3)_3(CO)_2(dppm)_2]$-$[CF_3SO_3]$ (**36**)	1783 (bs)	29.8 (dm, $^{1}J_{RhP}$=139.9Hz) -2.5 (m)	3.33 (m, 4H), 0.82 (td, 3H), -0.13 (t, 6H)	214.8 (dm, $^{1}J_{RhC}$=20.3Hz, 1C), 24.1 (dt, $^{1}J_{RhC}$=22.8Hz, 1C), -9.6 (t, 2C)
$[RhIr(CH_3)_2(\mu$-$CH_3)$-$(C_2H_4)(CO)(dppm)_2]$-$[CF_3SO_3]$ (**37**)^{f}	1965 (bs)^{c}	27.8 (dm, $^{1}J_{RhP}$=107.3Hz) -11.9 (m)	3.73 (m, 2H), 3.24 (m, 2H) 2.59 (b, 2H), 2.22 (b, 2H), 0.28 (dm,$^{2}J_{RhH}$=3.0Hz, 3H), -0.06 (t, 3H), -0.08(t, 3H)	203.2 (dm, $^{1}J_{RhC}$=20.2Hz, 1C)
$[RhIr(CH_3)_2(\mu$-$CH_3)$-$(\eta^{2}$-$H_2CCC(CH_3)_2)(CO)$-$(dppm)_2][CF_3SO_3]$ (**38**)^{f}	1959 (bs)	20.1 (dm, $^{1}J_{RhP}$=111.1Hz) -15.9 (m)	3.84 (m,2H), 3.30 (m, 2H), 2.15 (dm, $^{2}J_{RhH}$=2.5Hz 2H), 1.23 (s, 3H), 0.98 (s, 3H), 0.16 (dm,3H), 0.05 (t, 3H), -0.06(t, 3H)	200.1 (bs, 1C), 21.3 (dm $^{1}J_{RhC}$=11.0Hz, 1C), -9.9 (t, $^{2}J_{PC}$=4.9Hz, 1C), -20.7 (b, 1C)

Table 3.1 (contd).

[a] IR abbreviations: ss = strong sharp, sb = strong broad, ms = medium sharp, m = medium, w = weak, sh = shoulder. NMR abbreviations: t = triplet, d = doublet, dt = doublet of triplets, dd = doublet of doublets, tt = triplet of triplets, ddt = doublet of doublets of triplets, ddm = doublet of doublets of multiplets, dm = doublet of multiplets, td = triplet of doublets, bs = broad singlet, m = multiplet, q = quartet, s = singlet. [b] Nujol mull except as indicated. Values quoted are ν(CO) except as indicated. [c] CH_2Cl_2 cast. [d] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4 while ^1H and $^{13}C\{^1H\}$ are referenced vs TMS. Chemical shifts for the phenyl hydrogens are not given in the ^1H NMR data. [e] ν(SO) for CF_3SO_3. [f] 0°C. [g] -40°C. [h] -80°C.

stirred solution was added methyl lithium (840 µL, 1 M solution in THF), causing an immediate color change from light orange to deep red. The reaction mixture was stirred for 0.5 h, and then slowly warmed to room temperature, after which stirring was continued for 3 h. The excess MeLi was destroyed with florisil, filtered through a frit and concentrated to *ca.* 3 mL. A burgundy powdery solid precipitated from solution upon addition of 15 mL of freshly distilled *n*-pentane. The product was recrystallized from THF/pentane, dried briefly under a stream of dinitrogen gas and then *in vacuo*. Yield: 135 mg, 72%. Microanalysis repeatedly gave poor results due to high air and moisture sensitivity of **23**. A typical result is given below: Anal. Calcd for $IrRhP_4OC_{53}H_{50}$: C, 56.74.; H, 4.49. Found : C, 55.85.; H, 3.91.

(b) [RhIr(CH$_2$Ph)$_2$(µ-CO)(dppm)$_2$] (24). The procedure is the same as described above except that 100 mg (0.084 mmol) of [RhIrCl$_2$(CO)$_2$(dppm)$_2$] and benzyl magnesium chloride (420 µL, 2 M solution in THF) were used and the mixture was stirred for 4 h at room temperature. The volume was reduced to one half of its original, filtered through a frit and 50 mL of pentane was added, causing the precipitation of a dull yellow solid. The extremely air-sensitive solid was recrystallized from benzene/*n*-pentane and dried under N_2. Microanalysis was not carried out due to its extreme moisture sensitivity together with the fact that the product could not be isolated free from co-crystallized THF.

(c) [RhIr(CH$_3$)$_2$(CO)$_2$(dppm)$_2$] (25). Method (i). 30 mg (0.027 mmol) of compound **23** was dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube capped with a rubber septum at 0 °C. Approximately one equiv of CO gas was added via a gas-tight syringe. The sample was allowed to stand at this temperature for 0.5 h, after which it was subjected to three freeze/pump/thaw cycles to expel any residual CO present. NMR experiments were carried out at 0 °C. The orange product could be isolated by transferring the solution to a flask, removing the solvent *in vacuo* and recrystallizing from THF/ether. Yield : 12 mg, 39%. Anal. Calcd for $IrRhP_4O_2C_{54}H_{50}$: C, 56.36; H, 4.35. Found : C, 56.37; H, 4.10. Method (ii). 20 mg (0.0156 mmol) of $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) was dissolved in 0.6 mL of THF-d_8 in an NMR tube at -78 °C. A slight excess $AlMe_3$ (17 µL, 1 M soln in toluene) was syringed into the sample and the mixture was allowed to stand at this temperature for 2 h. NMR analysis carried out at room temperature showed **25** as the only product. However, attempts to isolate the species prepared by this method led to the formation of several decomposition products. The use of *trans*-$[RhIrCl_2(CO)_2(dppm)_2]$ instead of **2** under identical experimental conditions also gave similar results except that two equiv of $AlMe_3$ were required.

(d) $[RhIr(CH_3)(Ph)(CO)_2(dppm)_2]$ (28). 50 mg (0.039 mmol) of $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) was dissolved in 10 mL of THF at -78 °C. Phenyl magnesium chloride (78 µL, 1 M solution in THF) was added using a syringe. The mixture was stirred for 0.5 h, and then gradually warmed to room temperature. The excess Grignard reagent was washed with 5 mL of methanol, filtered and the solvent removed under vacuum. Recrystallization from THF/ether gave a dull orange solid. The NMR spectra (^1H, ^{13}C and ^{31}P) also showed the presence of an unidentified species formed in a 1:1 ratio with **28**. The use of phenyl lithium, instead of the Grignard reagent did not give this latter species but the reaction was never complete, with a substantial amounts of the starting material being recovered.

(e) $[RhIr(CH_3)(CH_2Ph)(CO)_2(dppm)_2]$ (29). The procedure was as described for **28**, except that one equiv of benzyl magnesium chloride was used instead. The NMR spectra (^1H, ^{13}C and ^{31}P) also showed the presence of the tricarbonyl species [RhIr(CO)$_3$(dppm)$_2$] and other unidentified decomposition products in addition to the targeted product.

(f) [RhIr(CH$_3$)$_2$(H)(μ-H)(CO)(dppm)$_2$] (30). 30 mg (0.027 mmol) of compound **23** was dissolved in 1 mL of CD$_2$Cl$_2$ at -78 °C. Hydrogen gas was slowly passed through the solution at *ca.* 0.1 mLs^{-1} for a period of 5 min. The solution was then slowly warmed to room temperature under H$_2$ purge and stirred until the deep red color turned pale yellow (~ 3 min). This solution was syringed into an NMR tube under an atmosphere of hydrogen and NMR analysis was carried out immediately. Attempts to isolate **30** led to decomposition so its structure is based on its solution spectroscopy.

(g) [RhIr(COCH$_3$)(CH$_3$)(H)(μ-H)(CO)(dppm)$_2$] (31). The procedure described above for **30** was repeated. Once the pale yellow solution was obtained, the sample was transferred via a syringe to an NMR tube. The tube was then immersed in a dry ice/acetone bath to bring the sample temperature to -78 °C and CO gas was passed through the solution briefly. NMR data (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) collected at 0 °C after allowing the solution to stand at this temperature for 2 h showed **31** as the major product in addition to variable amounts of **30** and the tricarbonyl species. Upon warming to room temperature, compound **31** reacted further with CO to form the tricarbonyl species [RhIr(CO)$_3$(dppm)$_2$], acetaldehyde and methane. The presence of methane and acetaldehyde were confirmed by their resonances in the ^{1}H NMR spectrum.

(h) [RhIr(SO$_2$CH$_3$)(CH$_3$)(CO)(μ-SO$_2$)(dppm)$_2$] (33). 50 mg (0.044 mmol) of compound **23** was dissolved in 3 mL of THF. A static atmosphere of SO$_2$ gas was placed over the stirred solution, causing an immediate color change from deep red to brown. A brown solid precipitated upon addition of 5 mL of pentane. The dark brown solid was washed with two 5 mL aliquots of pentane, dried under a N_2 stream, then *in vacuo*. Yield: 31 mg, 56%. Anal. Calcd for $IrRhS_2P_4O_5C_{53}H_{50}$: C, 50.89; H, 4.00; S, 5.12. Found : C, 50.95; H, 3.78.; S, 5.08.

(i) Reaction of Compound 23 with Methyl Triflate. In an NMR tube, 30 mg (0.027 mmol) of **23** was dissolved in 0.5 mL of CD_2Cl_2 at -78 °C. To this was added one equiv of methyl triflate (3 µL, 0.027 mmol). The NMR spectra (^1H, ^{13}C and ^{31}P) taken immediately showed compound $[RhIr(CH_3)_3(CO)(dppm)_2][CF_3SO_3]$ (**34**) as the sole product present in solution. At -60 °C, a new trimethyl species formulated as $[RhIr(CH_3)_3(CO)(dppm)_2(CF_3SO_3)]$ (**35**) was identified in solution, in addition to compound **34**. At higher temperatures, the concentration of this species increased at the expense of **34** such that at 0 °C, this species was present as the major species in addition to variable amounts of the monomethyl species $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$[4] (**2**) and ethane. The signal of ethane appears as a singlet at δ 0.82 in the ^1H NMR spectrum.

(j) $[RhIr(CH_3)_3(CO)_2(dppm)_2][CF_3SO_3]$ (36). 50 mg (0.044 mmol) of **23** was dissolved in 2 mL of CH_2Cl_2 at -78 °C. One equiv of methyl triflate (5 µL, 0.044 mmol) was added via a syringe. This was stirred for 5 min and an atmosphere of CO was then placed over the solution. The reaction mixture was stirred for 0.5 h and then taken to ambient temperature over a 15 min period. The orange product was precipitated and washed twice with 5 mL of ether, dried under dinitrogen gas stream and then *in vacuo*. Yield : 35 mg, 62%. Anal. Calcd for $IrRhSP_4O_5F_3C_{56}H_{53}$: C, 51.18; H, 4.07. Found : C, 51.41; H, 4.08.

(k-l) Reactions of $[RhIr(CH_3)_3(CO)(dppm)_2][CF_3SO_3]$ with ethylene and 1,1–dimethylallene. Compound **34** was prepared *in situ* as described previously. Approximately 0.3 mL of ethylene gas was syringed into the NMR tube at -78 °C by means of a gas-tight syringe. The mixture was briefly agitated and allowed to stand at this temperature for 0.5 h, after which NMR spectra were taken at 0 °C. The NMR spectra (^1H, ^{13}C and ^{31}P) showed the presence of $[RhIr(CH_3)_2(\mu\text{-}CH_3)(C_2H_4)(CO)(dppm)_2][CF_3SO_3]$ (**37**) as the major product, in addition to **35**. In the absence of an atmosphere of the gas, compound **37** gradually lost ethylene with time, converting to **35** and other decomposition products, and so was not isolated. However, under ethylene pressure **37** reacted further, giving rise to a number of uncharacterized products. The preparation of the analogous dimethylallene adduct $[RhIr(CH_3)_2(\mu\text{-}CH_3)\text{-}(H_2CCC(CH_3)_2)(CO)(dppm)_2][CF_3SO_3]$ (**38**), follows the same procedure as described above for **37** except that one equiv of 1,1–dimethylallene was used instead of ethylene. Compound **38** also slowly lost dimethylallene in solution under ambient temperature but was stable in solution at 0 °C and in the solid under a dinitrogen atmosphere. Anal. Calcd for $IrRhSP_4F_3O_4C_{60}H_{61}$: C, 53.22; H, 4.51. Found : C, 53.34; H, 4.06.

Experiments to Characterize Low-Temperature Intermediates.

(a) Reaction of Compound 23 with CO. The procedure for preparing compound **25** was repeated except that CO gas was added at -78 °C and the NMR analysis was carried out at -40 °C. The major species in solution was $[RhIr(CH_3)_2(CO)_3(dppm)_2]$ (**26**) and the minor species is proposed to be the acetyl methyl tricarbonyl complex $[RhIr(COCH_3)(CH_3)(CO)_3(dppm)_2]$ (**27**). Compounds **26** and **27** can also be obtained by cooling a solution of **25** to -40 °C and adding 1 mL of CO gas at this temperature.

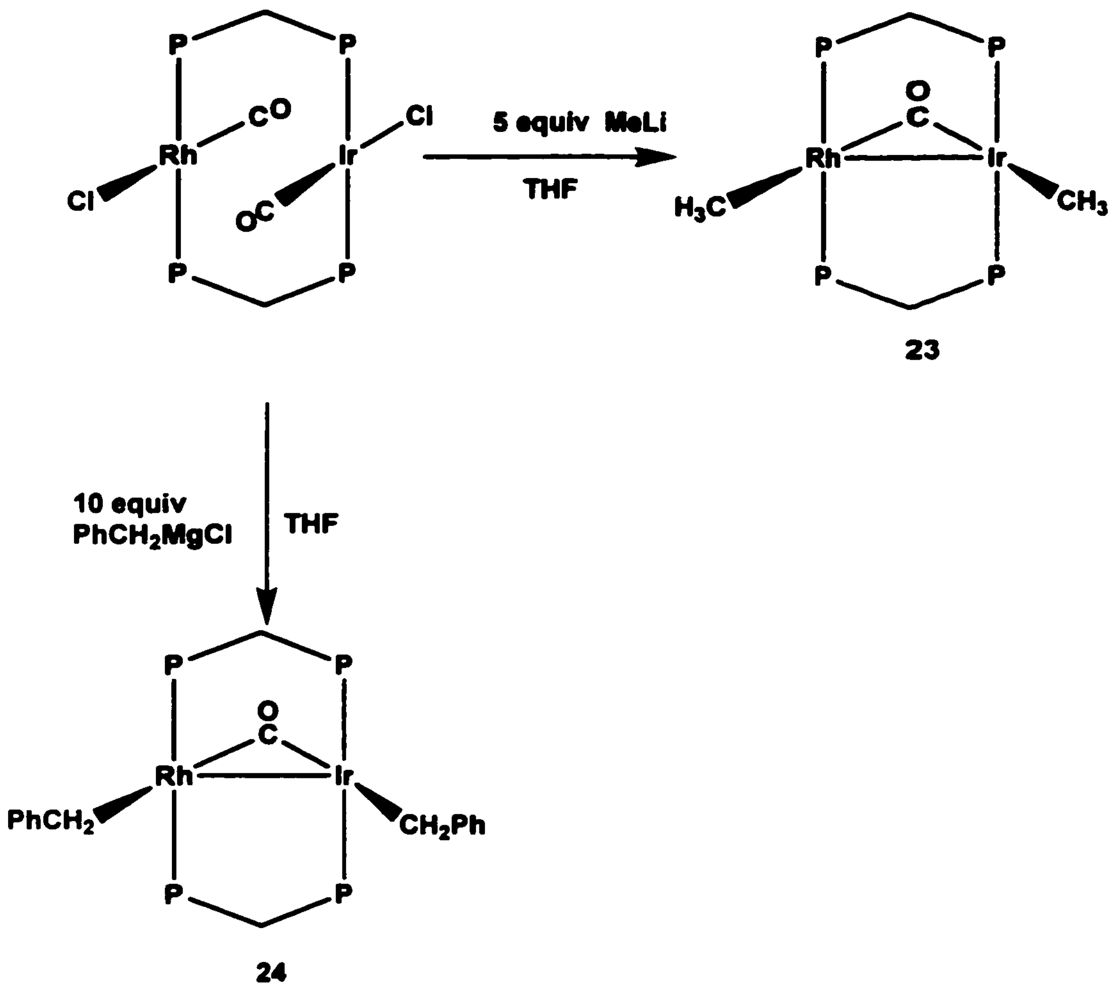
(b) Reaction of Compound 23 with sulfur dioxide. Approximately 0.3 mL of SO_2 gas was syringed into an NMR tube containing 30 mg (0.027 mmol) of **23** dissolved in 0.6 mL of THF-d_8 at -78 °C. The spectra showed

$[RhIr(CH_3)_2(\mu\text{-}SO_2)(CO)(dppm)_2]$ (**32**) as the only product present in solution. A mixture of **23** and **32** were obtained if less than 0.3 mL of SO_2 gas was used.

Results and Discussion

(a) Dimethyl and related compounds. The A-frame dimethyl monocarbonyl species $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**) is readily prepared from the reaction of $[RhIrCl_2(CO)_2(dppm)_2]$ with excess MeLi at -78 °C, as outlined in Scheme 3.1. Although this product can also be synthesized using methyl magnesium chloride, this route proved to be more troublesome, giving a number of unidentified impurities. Also, the use of methanol or degassed water to destroy the excess Grignard reagent led to further decomposition since these reagents rapidly attack the targeted product. The infrared spectrum of **23** shows a single carbonyl stretch at 1715 cm^{-1}, which is attributed to a symmetrically bridging carbonyl group. Additional support for the bridging mode of the CO group comes from the solution $^{13}C\{^1H\}$ NMR spectrum which displays a doublet of multiplets at δ 230.8 with a coupling to Rh of 29.3 Hz. The low-field shift of this resonance, as well as the magnitude of the coupling constant are typical of bridging carbonyls in these systems. The ^1H NMR spectrum shows, in addition to the dppm phenyl and methylene resonances, a triplet at δ 0.22 and a triplet of doublets at δ -0.35 ($^2J_{RhH}$ = 2 Hz) each integrating as three protons. These resonances are assigned to the methyl groups bound to Ir and Rh, respectively. The spectroscopic data are in agreement with a dimethyl A-frame complex having μ-CO at the bridgehead position, reminiscent of that of the analogous dirhodium dimethyl species $[Rh_2Me_2(\mu\text{-}CO)(dppm)_2]$,[6] and the related dihalide complexes $[Rh_2Br_2(\mu\text{-}CO)(dppm)_2]$[7a,b] and $[Rh_2Cl_2(\mu\text{-}CO)(dppm)_2]$.[7a,c] The closely related dibenzyl A-frame complex $[RhIr(CH_2Ph)_2\text{-}(\mu\text{-}CO)(dppm)_2]$ (**24**) is prepared in a similar manner, by treatment of

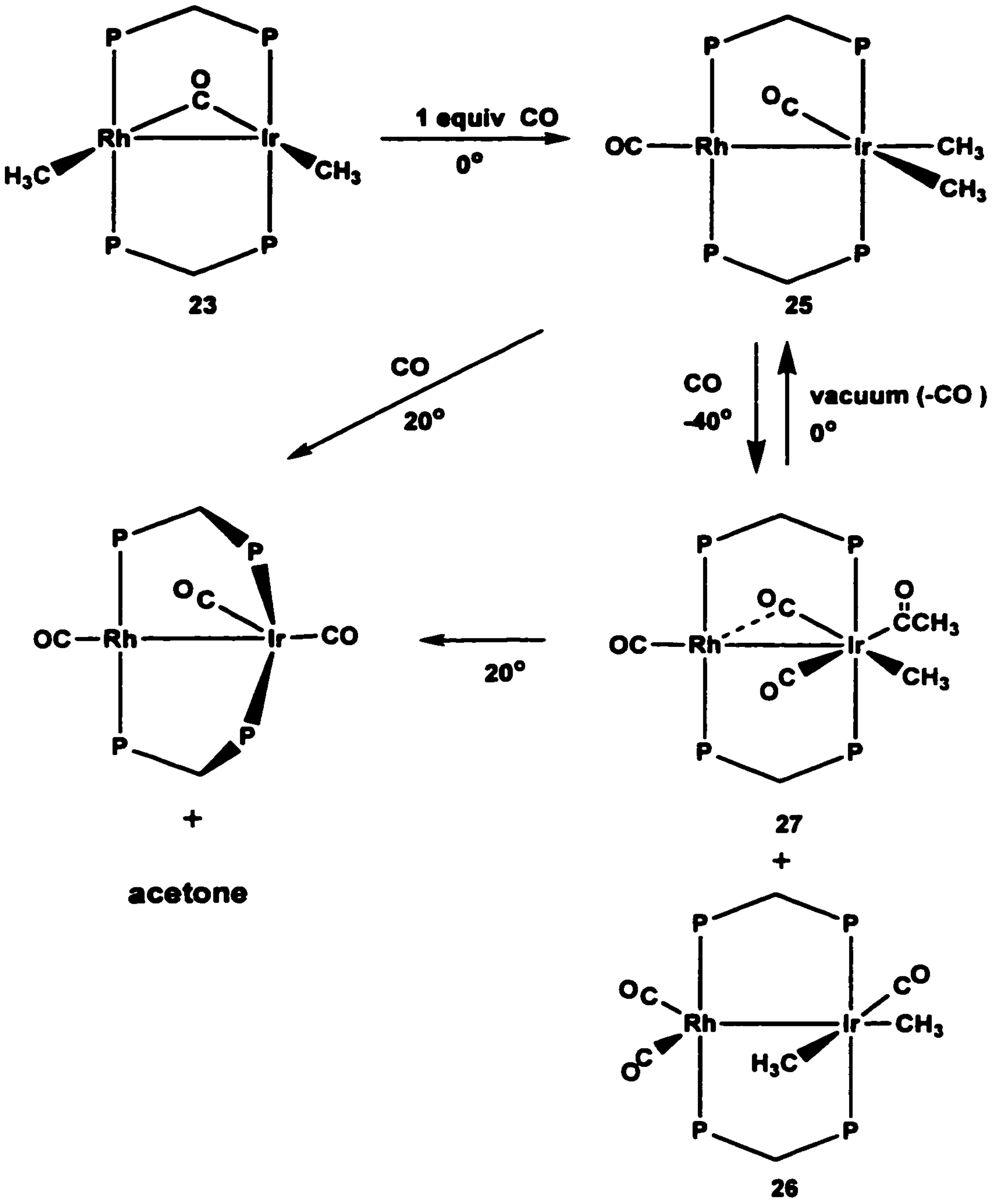
Scheme 3.1


5 equiv MeLi
THF
23
10 equiv PhCH₂MgCl
THF
24
Rh
Ir
P
CO
Cl
H₃C
CH₃
PhCH₂
CH₂Ph

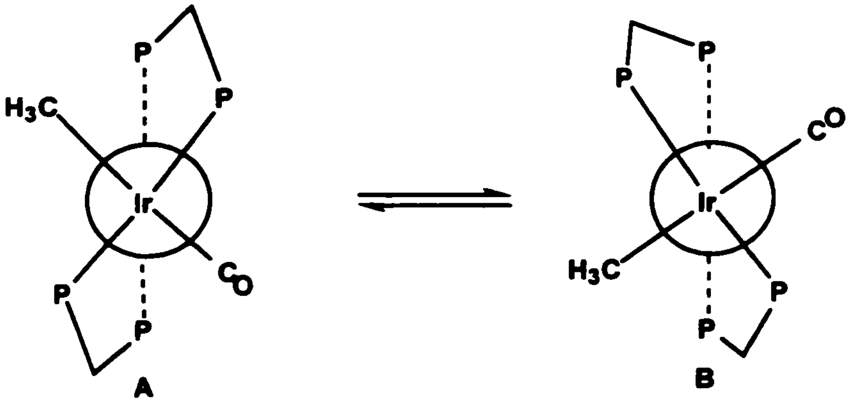
[$RhIrCl_2(CO)_2(dppm)_2$] with benzyl magnesium chloride. The ^1H NMR spectrum of **24** displays a triplet of doublets at δ 1.82 ($^2J_{RhH}$ = 1.5 Hz) and a triplet at δ 2.57, each integrating as two protons, assigned to the Rh- and Ir-bound methylene protons of the benzyl groups. Both the IR and $^{13}C\{^1H\}$ NMR spectra of **24** are similar to those of **23**, again indicative of a bridging carbonyl. Compounds **23** and **24** are air-sensitive, decomposing within a few minutes upon exposure to air. The chemistry of **24** was not pursued due to problems associated with the solvent signals in the ^1H NMR spectrum (see Experimental Section).

Previous studies on the carbonylation of the closely related dirhodium dimethyl species[6] has revealed that the product distribution depended on the CO pressure applied; at lower pressures (50-700 torr) both acetone and butanedione were produced, while at higher pressures (~1500 torr) butanedione was the major organic product in addition to the only metal-containing species [$Rh_2(CO)_3(dppm)_2$]. In these reactions the results obtained were variable, being influenced by the extent of sample agitation and concentration. It was of interest to compare the above results with those of the of the RhIr analogue. Reaction of **23** with one equiv of CO gives the dicarbonyl species [$RhIr(CH_3)_2(CO)_2(dppm)_2$] (**25**), as shown in Scheme 3.2, in which both methyl groups are now in mutually cis positions on Ir. In the ^1H NMR spectrum the methyl resonances of **25** appear at δ -0.24 and -1.39, as triplets, and the inequivalence of the methyl groups suggests that they are located trans and cis to the Rh-Ir bond axis. The $^{13}C\{^1H\}$ NMR data show the carbonyl resonances at δ 185.7 and 182.6 with the latter displaying coupling to Rh ($^1J_{RhC}$ = 67.8 Hz), indicative of a terminally bound CO on this metal; the low-field chemical shift of the Ir-bound carbonyl suggests that it is engaged in a weak semibridging interaction with the adjacent Rh center, although no resolvable coupling to this

Scheme 3.2



metal was observed. The similarities of the spectral parameters for **25** with those of the hydrido-methyl (**11**) and methyl-cyano (**10**) complexes, described earlier (see Chapter 2) strongly suggest that the three species have analogous structures. Compound **25** is shown to be fluxional in solution. The room temperature $^{31}P\{^1H\}$ NMR spectrum is characteristic of an AA'BB'X spin system (X = Rh) and transforms to a complex pattern of an ABCDX spin system (see Fig. 3.1) when the sample is cooled to -80 °C. At -40 °C, the four resonances coalesce pairwise giving broad unresolved peaks. However, the $^{13}C\{^1H\}$ NMR signals for both carbonyl groups remain invariant between 20 °C and -80 °C, indicating that no carbonyl exchange appears to be involved. We suggest that the fluxional process involves a twisting of the IrP_2 unit relative to the RhP_2 unit about the Rh-Ir bond as shown below. In either extreme (**A** or **B**) the phosphorus nuclei on Rh are in inequivalent environments, being either adjacent to CH_3 or CO. At -80 °C the exchange is slow enough that the different environments can be detected on the NMR time scale. At higher temperatures only an average environment is observed.



It is perhaps noteworthy that the methyl groups on Ir do not interchange as their ^{13}C resonances remain invariant between 20 °C and -80 °C. A similar fluxional process has been observed for the related hydrido-alkynyl species

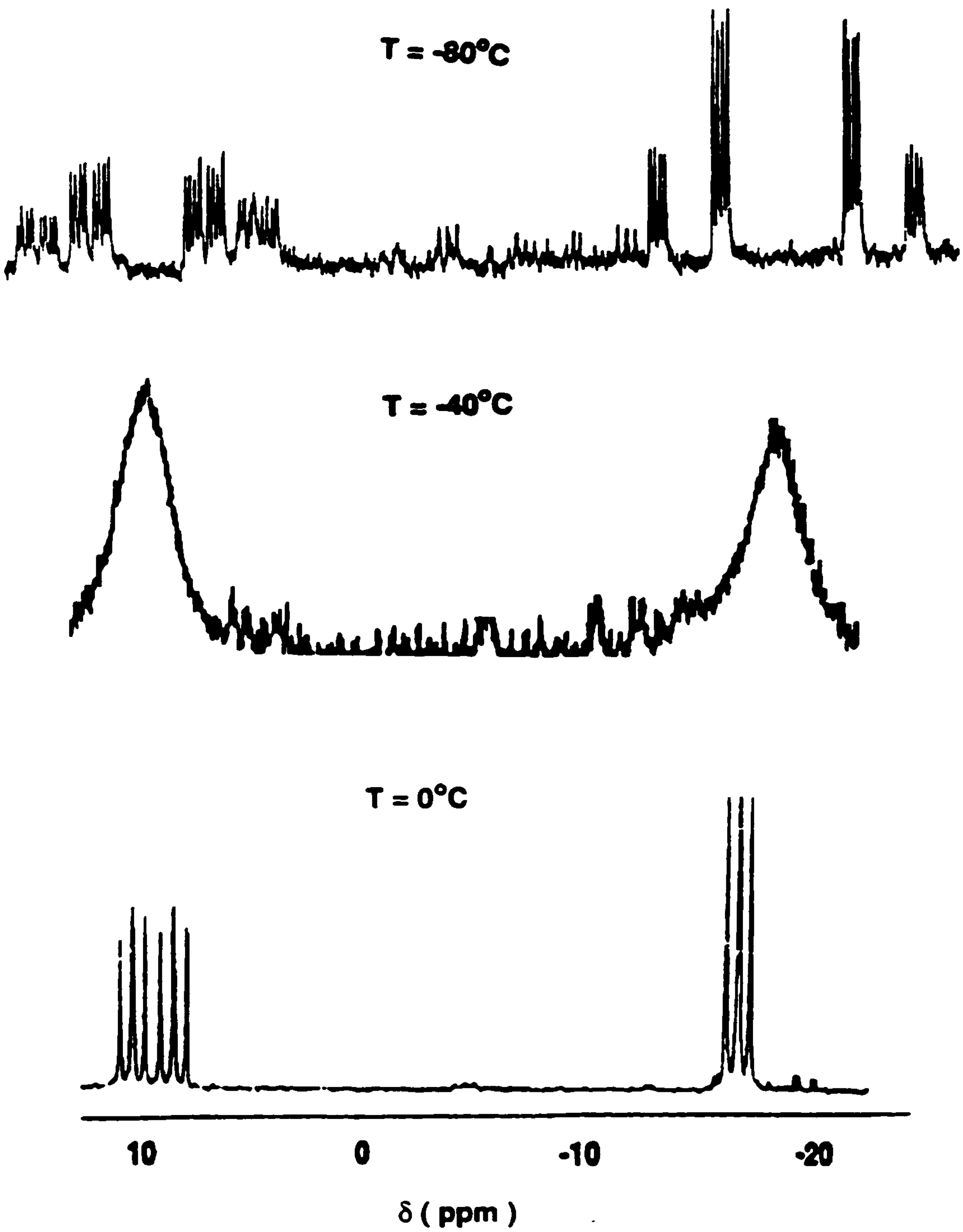
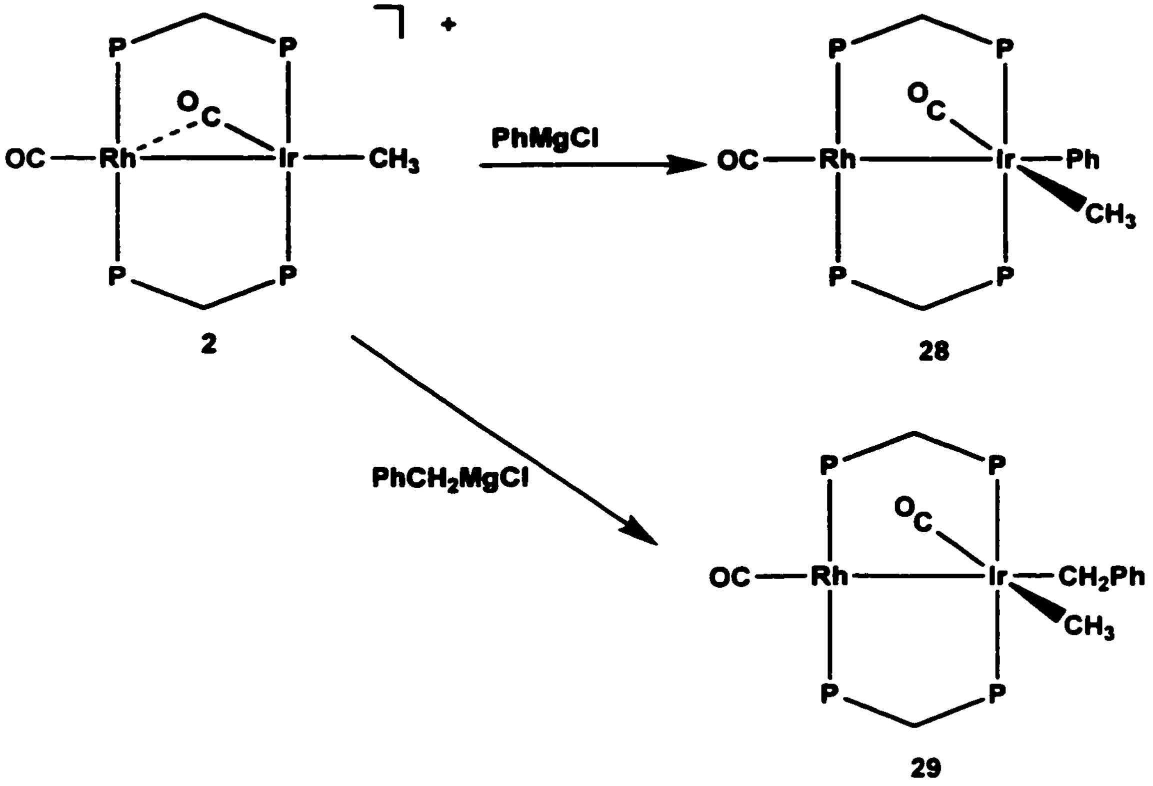


Figure 3.1. Variable-temperature $^{31}P\{^{1}H\}$ NMR spectra showing the fluxional behaviour of compound **25**.

$[RhIr(H)(CO)_2(\mu\text{-}C_2Ph)(dppm)_2]$.[8] Compound **25** is stable in solution at room temperature for a few hours, after which it converts to an unidentified species. Under excess CO at ambient temperature, the known tricarbonyl, $[RhIr(CO)_3(dppm)_2]$ and acetone are produced, along with other metal-containing unidentified products. If ^{13}CO gas is employed, an additional doublet peak ($^2J_{CC}$ = 9 Hz) appears, flanking the acetone resonance at δ 2.07 in the ^1H NMR spectrum, due to coupling of the methyl protons with the acetone carbonyl carbon. Acetone formation was also observed for the carbonylation of a related RhRu system,[9] although in this case the reaction took several days to complete. In an attempt to identify possible intermediates leading to the formation of acetone in order to determine the functions of the metals in the coupling of a methyl and acyl group, the reaction was repeated at -80 °C. As was the case with the dirhodium analogue, variable results are obtained; several species are present in solution making their characterization difficult. However, at -40 °C the major species present in solution is the dimethyl tricarbonyl complex $[RhIr(CH_3)_2(CO)_3(dppm)_2]$ (**26**) in addition to one other minor species proposed to be an acetyl tricarbonyl complex $[RhIr(COCH_3)(CH_3)(CO)_3(dppm)_2]$ (**27**), a plausible structure for which is shown in Scheme 3.2. The ^{13}C NMR spectrum for **26** is consistent with the presence of two carbonyls on Rh and one on Ir, while the ^1H NMR spectrum, like that of **25**, indicates the presence of two methyl groups bound to Ir. Removal of the CO atmosphere over the solution and warming the sample to 0 °C, regenerates **25**, together with trace amounts of the tricarbonyl product $[RhIr(CO)_3(dppm)_2]$. The structure proposed for **26**, with two carbonyl groups bound to Rh, closely resembles those of two previously characterized low-temperature intermediates described earlier; these species, $[RhIr(CH_3)(CO)_3(^tBuNC)(dppm)_2][CF_3SO_3]$[5] and $[RhIr(CH_3)(CO)_3(SO_2)(dppm)_2][CF_3SO_3]$,[4] are also labile, losing one carbonyl upon warming. The ^{1}H NMR spectrum for **27** displays broad peaks at δ 2.78 and 2.60 due to the dppm methylene protons. Unfortunately, due to the overlap of several peaks and the broadness of the resonances, the methyl and acetyl protons cannot be identified with certainty. However, resonances at δ 279.2 (broad), 221.4 (doublet of multiplets, $^{1}J_{RhC}$ = 17.4 Hz), 209.8 (doublet of triplets, $^{1}J_{RhC}$ = 72.5 Hz), and 185 (triplet) observed in the $^{13}C\{^{1}H\}$ NMR spectrum are consistent with those expected for the formulation given. More importantly, the absence of Rh coupling in the low-field acetyl carbonyl resonance suggests that this group is bound to Ir. The $^{13}C\{^{1}H\}$ NMR spectrum, at -40 °C, of the isotopomers $[RhIr(^{13}CH_3)(CH_3)(CO)_2(dppm)_2]$ and $[RhIr(CH_3)(^{13}CH_3)(CO)_2(dppm)_2]$[11] under CO atmosphere displays three triplet resonances at δ -7.7, -9.0, and -14.5, typical of Ir-bound methyl groups,[12] in addition to a sharp singlet at δ -1.0, consistent with that expected for an acetyl ligand. The peaks at δ -14.5 and -1.0 are assigned to the methyl and acetyl groups of species **27** on the basis of their lower intensities (it is the minor product in solution) while the other two peaks are assigned to methyl groups of compound **26**. Notwithstanding the uncertainty in the ^{1}H NMR data for the acetyl methyl species, the $^{13}C\{^{1}H\}$ NMR data permit us to tentatively propose its structure as diagrammed in Scheme 3.2. Although mechanistic evidence is lacking, it is suggested that reductive elimination of acetone occurs from Ir since it appears unlikely that migration of both the acetyl and methyl groups to Rh precedes the reductive elimination step. This view is reinforced by the absence of intermediates between the mixtures of **26** and **27**, and the final tricarbonyl species $[RhIr(CO)_3(dppm)_2]$. Migration of a methyl group from one metal to another (as in the conversion of **23** to **25**) preceeding the reductive elimination of acetone has been observed in related dimethyl cobalt species.[1a] In addition, migratory CO insertion, though not frequently encountered at the Ir center in the mixed RhIr systems,[10] has been observed in related diiridium complexes.[10] The preferential reductive elimination of acetone over ethane from either **25** or **26** is consistent with previous observations.[13-15] Unlike the related dirhodium complex $[Rh_2(CH_3)_2(\mu\text{-}CO)(dppm)_2]$[6] in which 2,3 butanedione was identified in the reaction mixture in addition to acetone, we find no evidence of this product in our RhIr system. In the absence of detailed mechanistic data, it is not certain whether the reductive elimination of acetone proceeds via an inter- or intramolecular process, although the latter appears more likely on the basis of a similar finding for the dirhodium system.[6]

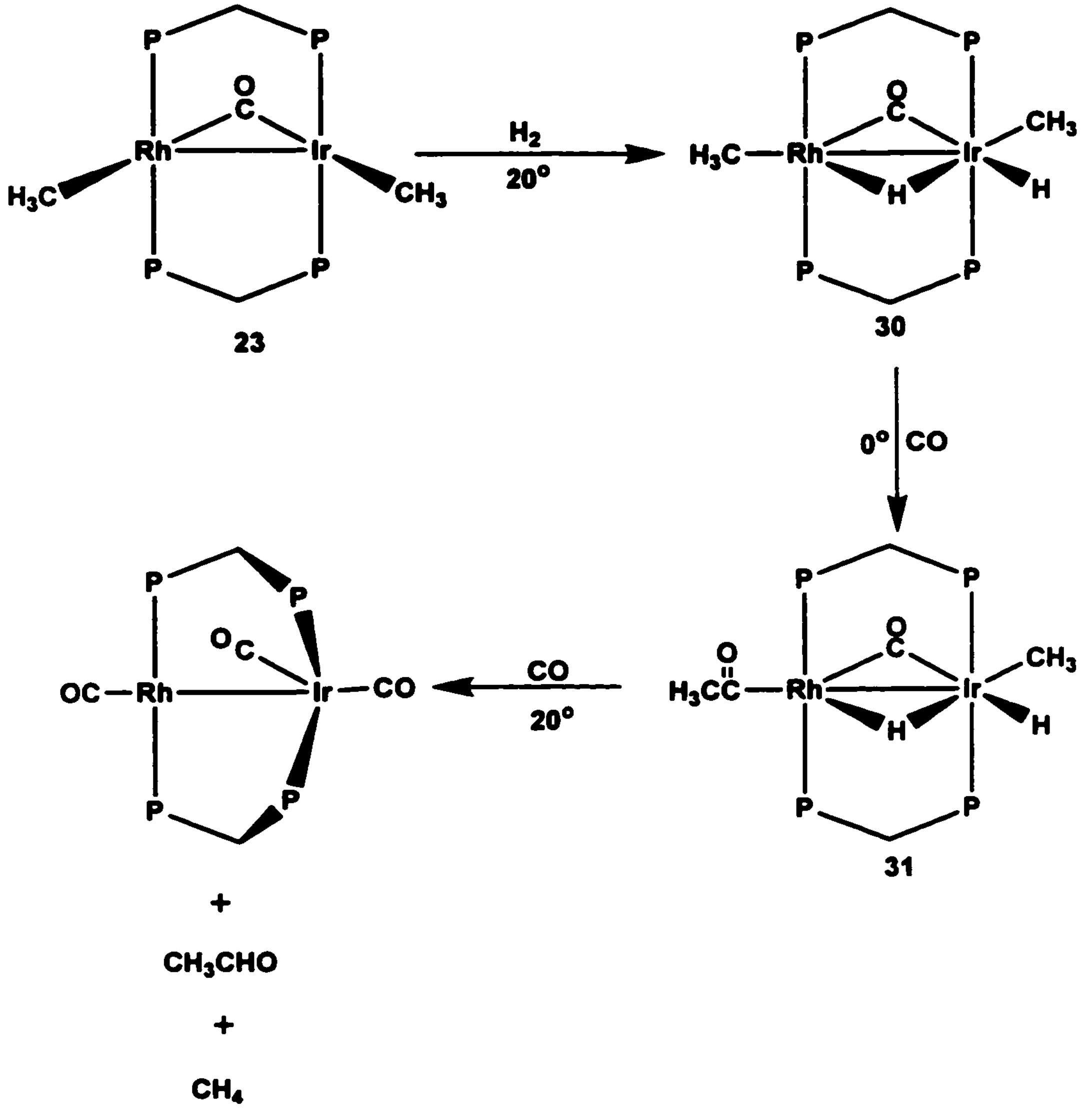
The mixed phenyl, methyl and benzyl, methyl analogues of **25**, namely $[RhIr(CH_3)(Ph)(CO)_2(dppm)_2]$ (**28**) and $[RhIr(CH_3)(CH_2Ph)(CO)_2(dppm)_2]$ (**29**), are readily prepared from the reaction of $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with the appropriate phenyl lithium or phenyl/benzyl magnesium chloride. The reaction to produce **29** also gives varying amounts of $[RhIr(CO)_3(dppm)_2]$, apparently from partial decomposition accompanied by scavenging of CO. The reaction with phenyl Grignard also gives a second species the identity of which is presently unknown (see Experimental Section). On the basis of spectral similarities, compound **28** is assumed to be structurally analogous to **25**, and to the related methyl-hydrido (**11**) and methyl-cyano (**10**) species discussed in Chapter 2. As with **28**, the benzyl-methyl species **29**, displays spectral parameters which closely resemble those of **25**. The proposed formulations for **28** and **29** are consistent with attack of the added substrate at an open coordination site on Ir, opposite the Rh-Ir bond, based on the solution structure of **2′**. Unfortunately, the carbonylation of these mixed phenyl, methyl and benzyl, methyl complexes was not pursued since they could not be obtained free from other products.

Scheme 3.3


P
P
OC
OC
Rh
Ir
CH3
+
P
P
2
PhMgCl
P
P
OC
OC
Rh
Ir
Ph
CH3
P
P
28
PhCH2MgCl
P
P
OC
OC
Rh
Ir
CH2Ph
CH3
P
P
29

One of the objectives of this thesis was to prepare cis hydrido-alkyl complexes that would allow the investigation of the possible roles of each metal in subsequent reductive elimination of the alkane fragment. Unfortunately, these species have proven to be quite elusive, frequently having transient existence owing to facile loss of alkane. Amongst the Ir and Rh complexes, mutually cis methyl and hydride groups are more commonly observed at Ir centers,[16a,17] and less so at Rh.[13c,18] It was also of interest to synthesize stable cis hydrido-acyl complexes, with the intent of modeling such intermediates in the olefin hydroformylation process.[19] In the previous chapter, the meta-stable hydrido-methyl species $[RhIr(H)(CH_3)(CO)_2(\mu\text{-}H)(dppm)_2][CF_3SO_3]$(**14**,**15**) were observed in solution at 0 °C or -20 °C following the treatment of $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**1**) and $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with dihydrogen. Like its RhOs counterpart,[9] **14** eliminated methane at ambient temperature, apparently from the less labile third-row metal. The related dirhodium species $[Rh_2(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ was also reported to react with hydrogen, giving a tetrahydride complex accompanied by methane loss,[20] although no hydrido-methyl intermediates were observed. The increased Ir-H and Ir-CH_3 bond strengths in the mixed RhIr system (**23**) suggested that the isolation (or at least detection) of a hydrido-methyl complex might be possible with the RhIr combination of metals. The reaction of **23** with dihydrogen at room temperature results in oxidative addition, affording the targeted cis dihydrido-dimethyl species $[RhIr(CH_3)_2(H)(CO)(\mu\text{-}H)(dppm)_2]$ (**30**), the ^1H NMR spectrum of which displays peaks at *ca* δ -10.6 (doublet of multiplets, $^1J_{RhH}$ = 14.0 Hz) and δ -13.3 (triplet), assigned to bridging and terminal hydride ligands, respectively. We propose that the hydrides are mutually cis as evidenced by absence of H-H coupling and on the basis of well-documented precedents.[8,21,22] The ^1H NMR spectra with selective

Scheme 3.4



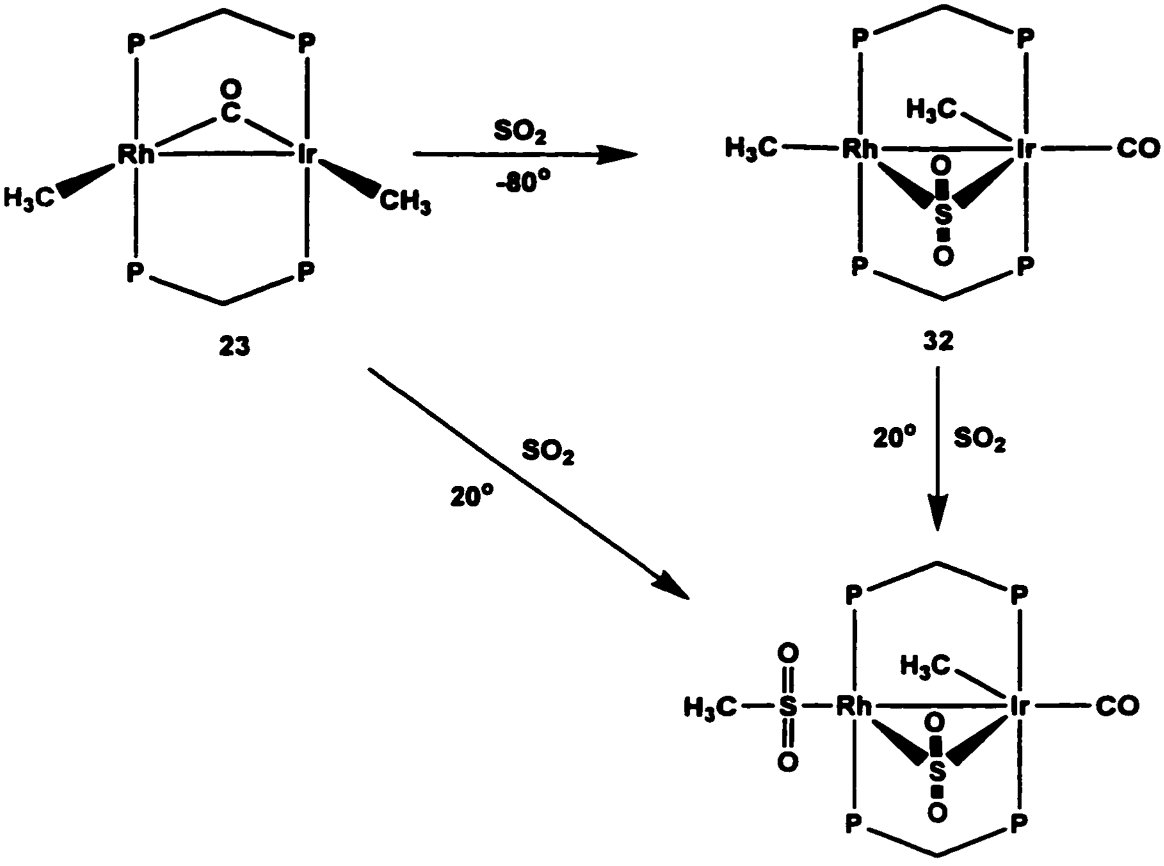
P
P
O
C
Rh
Ir
H_3C
CH_3
23
H_2
20°
H_3C
CH_3
H
H
30
0°
CO
O
H_3CC
31
CO
20°
OC
CO
+
CH_3CHO
+
CH_4

^{31}P decoupling also reveal that the methyl groups are bound, one to each metal. The Ir-bound carbonyl group interacts with Rh in a semi-bridging manner, as shown by its low-field chemical shift (δ 231.1) and coupling to this metal (19.8 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. In support of the above, the IR spectrum of **30** carried out immediately on a freshly prepared solution displays a band at 1816 cm^{-1}. Attack by dihydrogen is assumed to occur in the pocket of the A-frame yielding the hydride-bridged product shown. Similar inside attack of H_2 has been reported for the reactions of the related A-frame compounds $[RhIr(CO)_2(\mu-C_2Ph)(dppm)_2][CF_3SO_3]$,[8] $[RhIr(CO)_2(\mu-S)(dppm)_2]$[22] and $[RhIr(CO)_2(\mu-Cl)(dppm)_2][BF_4]$.[22] Compound **30** is stable in solution under an atmosphere of dihydrogen or dinitrogen at room temperature for about one day, after which it decomposes. It also slowly decomposes either in the solid-state under N_2 or in vacuum, presumably from loss of methane. This compound, in which two sets of mutually cis hydride and methyl groups are present, represents, to our knowledge, the first example of its kind in a binuclear system. It is suggested that the octahedral geometry at Ir and the strong Ir-CH_3 and Ir-H bonds probably contribute to its unusual stability.[23,24]

Compound **30** reacts with CO at 0 °C to give the acetyl-methyl species $[RhIr(COCH_3)(CH_3)(H)(CO)(\mu-H)(dppm)_2]$ (**31**), the result of migratory insertion. At temperatures below 0 °C, very little of **31** is present, with the starting material being predominant. The ^1H NMR spectrum shows, in addition to resonances for the hydride and methyl ligands, the acetyl protons, at δ 0.97, as a singlet; this resonance appears as a doublet if ^{13}CO is used together with ^{13}CO-enriched starting material. The acyl CO appears in the $^{13}C\{^1H\}$ NMR spectrum as a multiplet at δ 277.2 (with a 29.0 Hz coupling to Rh), and the semi-bridging carbonyl ligand appears as a multiplet at δ 227.2 (with a coupling of 24.4 Hz to Rh). The IR spectrum of a freshly prepared sample of **31** exhibits bands at 1742 and 1626 cm^{-1}, assigned to the bridging and acetyl CO groups, respectively. When an atmosphere of ^{13}CO gas is placed over a sample of unlabelled compound **30**, and the $^{13}C\{^1H\}$ NMR spectrum is taken immediately prior to scrambling of the carbonyls, the ^{13}CO group is found to occupy only the bridging position. The lack of incorporation into the acyl position suggests that migratory insertion precedes CO coordination. Upon warming to room temperature under an atmosphere of CO, **31** transforms into the known tricarbonyl species $[RhIr(CO)_3(dppm)_2]$, with concomitant formation of methane and acetaldehyde, identified by their proton peaks at δ 0.21 (singlet, CH_4), 2.17 (doublet, CH_3CHO) and 9.97 (quartet, CH_3CHO) in the ^{1}H NMR spectrum. The ratio of acetaldehyde to methane protons released could not be confirmed by NMR spectroscopy due to the greater volatility of methane, being present in the gas phase above the solution mixture. Since the acetyl group in **31** is bound to Rh with the CH_3 group on Ir, and in the absence of any observable intermediates between compound **31** and the organic products, it is suggested that acetaldehyde elimination occurs from Rh while methane loss occurs from Ir. The above reaction is reminiscent of the formation of acetaldehyde from the reaction of the related $[RhRe(COCH_3)(CO)_4(dppm)_2][CF_3SO_3]$ with $Li(HBEt_3)$,[12] and represents one of the few examples of directly observed acetaldehyde reductive elimination from a well-characterized hydrido-acyl species.[16] Unfortunately, compound **31** decomposes upon work-up.

The presence of methyl groups on each of the different metal centers of **23** suggested that insertion of SO_2 into one metal-alkyl bond might be preferred over the other. Compound **23** reacts with SO_2 within minutes at room temperature to give the alkylsulfonate adduct $[RhIr(SO_2CH_3)(CH_3)(CO)(\mu\text{-}SO_2)(dppm)_2]$ (**33**) as shown in Scheme 3.5. Although two equiv of SO_2 have

Scheme 3.5



23

32

33

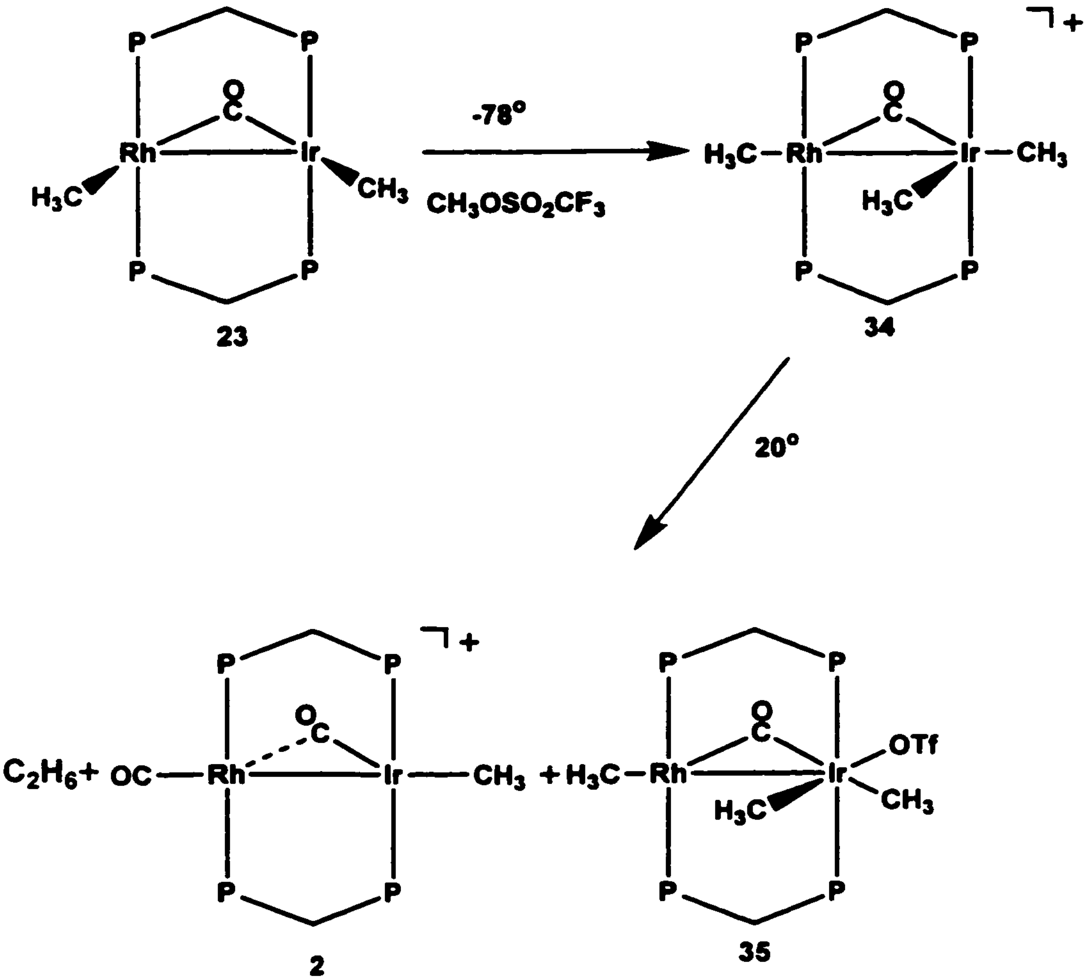
reacted only a single insertion has apparently occurred at the Rh-CH_3 bond, with the additional SO_2 molecule bridging the Rh-Ir bond. The protons of the alkylsulfonate group for compound **33** appear as a singlet at δ 1.51 while those of the Ir-bound methyl group resonate as a triplet at δ 0.60. The carbonyl group in **33** occupies a terminal position on Ir as shown by its triplet signal at δ 177.8 in the $^{13}C\{^1H\}$ NMR spectrum. The IR spectrum displays absorption bands at 1130, 1090, and 1024 cm^{-1} attributable to ν_{SO} stretches in addition to a band at 1982 cm^{-1} due to the terminal carbonyl group. The close similarities of the S-O bands for **33** to those of the monomethyl species $[RhIr(SO_2CH_3)(CO)_2(\mu\text{-}SO_2)(dppm)_2][CF_3SO_3]$ (**9**),[5] suggest analogous bonding modes for the SO_2 ligands. The reluctance of SO_2 to insert into the Ir-CH_3 bond in **33** is in contrast to a similar reaction involving the mononuclear complex $[Cp^*Ir(CH_3)(PMe_3)(OTf)]$ for which insertion into the Ir-CH_3 bond was observed.[25] If the reaction is carried out at -78 °C and one equiv of SO_2 is used, an intermediate species $[RhIr(CH_3)_2(\mu\text{-}SO_2)(CO)(dppm)_2]$ (**32**) is obtained, in which the SO_2 ligand is proposed to bridge both metals. This parallels the results of SO_2 addition to the alkynyl species, $[RhIr(CO)_2(\mu\text{-}C_2Ph)(dppm)_2][CF_3SO_3]$,[8] and is consistent with the known tendency of SO_2 to bridge two late metals.[26] The carbonyl group in **32** is terminal as shown by its triplet signal (δ 171.3) in the $^{13}C\{^1H\}$ NMR spectrum. Although the exact geometry at Ir in compounds **32** and **33** is unknown, we favor the structures diagrammed in Scheme 3.5 in which the CO group in each case is pointing away from the Rh center on the basis of their high-field chemical shifts (δ 177.8 (**33**), 171.3 (**32**)). For comparison, the Ir-bound CO group in **25** which is shown to be angled toward the Rh center, displays a low-field signal *ca* δ 185.7. A similar chemical shift trend for terminal carbonyl groups pointing towards an adjacent metal or away from it has been observed for related Rh/Ir systems.[8] The ^1H NMR spectrum of **32** at

-80 °C displays peaks consistent with a methyl group on each metal, indicating that SO_2 insertion into these metal-alkyl bonds has not occurred. At temperatures above -80 °C, several intermediates were observed but were not characterized owing to their low concentration and the complexity of the spectra. Compound **32** rapidly converts to other unidentified species upon warming to ambient temperature so its structure is based on NMR spectroscopy. Upon warming to room temperature under excess SO_2 reagent, **32** converts cleanly to **33**. However, prolonging the reaction beyond a few minutes transforms **33** to several unidentified species, presumably from further reaction with dissolved SO_2 gas.

(b) Trimethyl Complexes.

The trimethyl species $[RhIr(CH_3)_3(CO)(dppm)_2][CF_3SO_3]$ (**34**) is readily prepared by the reaction of **23** with methyl triflate at -78 °C. In the ^1H NMR spectrum of **34** the three methyl groups are observed as broad resonances at δ 0.98, 0.15 and 0.13. Selective decoupling experiments establish that the high-field resonance corresponds to the methyl group on Rh while the former two are assigned to methyl groups on Ir. The use of labelled $^{13}CH_3OSO_2CF_3$ in the preparation of **34** confirms the site of electrophilic attack at Ir. The $^{13}C\{^1H\}$ NMR spectrum shows triplets at δ -11.5 and -18.3 for the Ir-bound methyls, and a doublet of triplets at δ 7.4 with coupling of 22.4 Hz to Rh. Although the labelled methyl group scrambles to a small extent with all non-enriched ones, the triplet signal at δ -11.5 is ten times more intense than the others, so is assigned to the added electrophile. This spectrum also indicates the presence of a bridging carbonyl group at δ 211.5, with coupling of 36.8 Hz to Rh. When a sample of **34** is slowly warmed to 0 °C, it transforms to a new trimethyl species identified as $[RhIr(CH_3)_3(CF_3SO_3)(CO)(dppm)_2]$ (**35**), which is

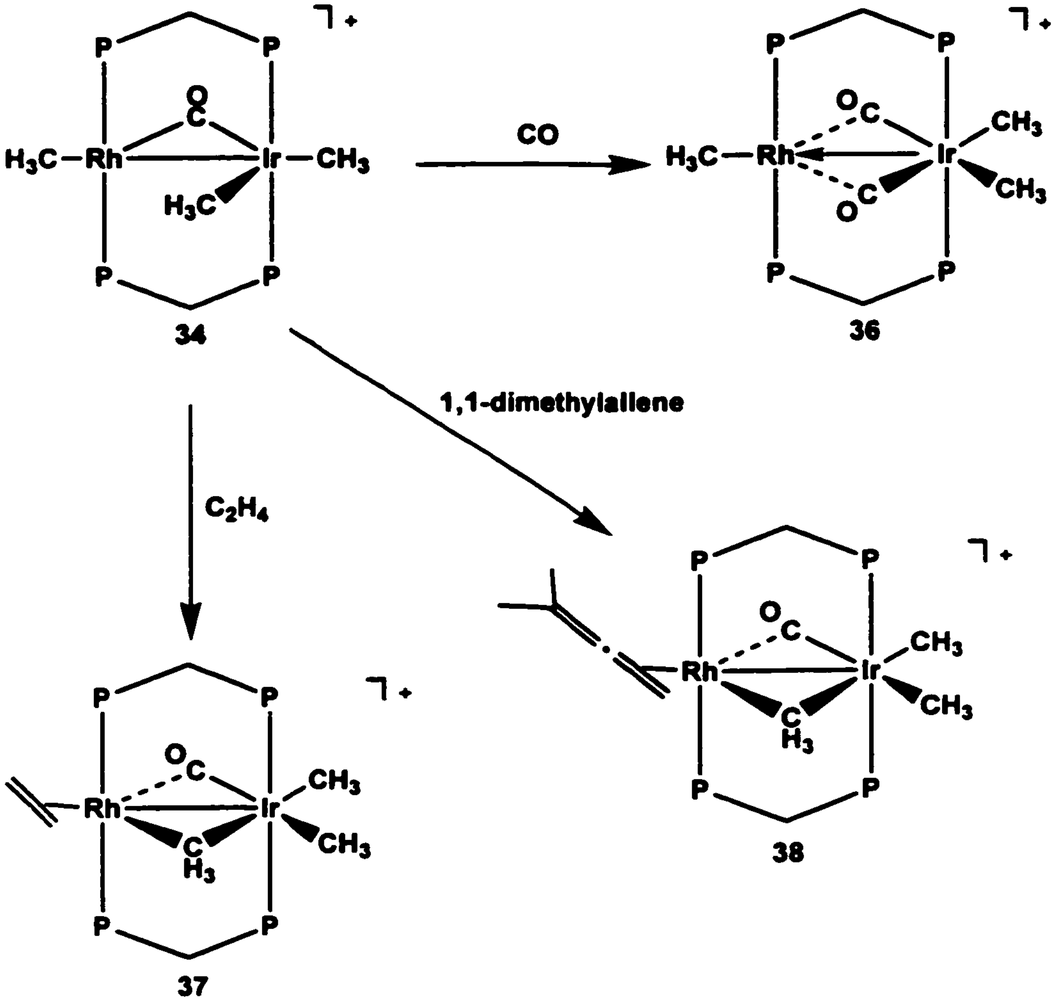
Scheme 3.6



proposed to have the triflate group covalently bonded to the Ir center. The $^{31}P\{^1H\}$ NMR spectrum (δ 28.1(Rh), 4.7(Ir)) of **35** is dramatically different from that of **34** (δ 26.1, 22.9), with a more significant shift in the ^{31}P resonance at Ir, consistent with coordination of the triflate ion to this metal. In addition, the $^{31}P\{^1H\}$ and ^1H NMR spectra showed the presence of the previously characterized monomethyl species $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) together with several minor unidentified products. In addition, ethane was identified as a singlet at δ 0.82 in the ^1H NMR spectrum. Ethane evolution was also reported for the trimethyl dipalladium species *fac*-$[Pd_2Me_3(I)(tmeda)]$[27] upon warming the sample above -20 °C. As with its precusor **34** two methyl groups are shown to be bound to Ir, and one to Rh while the carbonyl group bridges both metals. The methyl region in the $^{13}C\{^1H\}$ NMR spectrum (when **34** has been prepared from **23** using labelled methyl triflate) displays peaks at δ -16.5 (triplet), -28.4 (triplet) and -0.63 (doublet of triplets, $^1J_{RhC}$ = 27.9 Hz), with the peak at δ -16.5 being the most intense (peaks were present in an approximate integral ratio of 8:1:1). The ^{19}F NMR of the reaction mixture displays a sharp peak at δ -74.9 attributed to unreacted methyl triflate and a broad peak centered at δ -79.5. This latter peak could result from exchange of the Ir-bound triflate ions due to the presence of **35** and the monomethyl species **2** in solution. The solid state IR spectrum of the product mixture, shows a stretch at 1376 cm^{-1}, assigned to the coordinated triflate of **35**, in addition to other stretches due to the ionic triflate group of compound **2**. This value is almost identical to the value of *ca.* 1377 cm^{-1} observed for the olefin complex $[RhIr(CH_3)(CO)(\mu\text{-}C_2F_4)(\mu\text{-}CO)(dppm)_2(CF_3SO_3)]$ (**18**), which was also proposed to have a covalently bound triflate group.[5] This spectrum also displays a weak band at 1830 cm^{-1}, attributed to the bridging carbonyl of **35**. The evidence from NMR and IR spectral results support the suggested formulation of **35**, as diagrammed in Scheme 3.6, in which the triflate group is coordinated to Ir. However, the exact geometry at this metal is unknown.

Although compound **35** has proven to be remarkably inert to most added substrates (ethylene, allenes, phosphines and ^{t}BuNC), it is readily attacked by CO at room temperature to give the dicarbonyl species $[RhIr(CH_3)_3(CO)_2(dppm)_2][CF_3SO_3]$ (**36**). This product is also the sole product when **34** is treated with CO gas at -78 °C and the reaction mixture allowed to warm to ambient conditions. It was anticipated that this reaction would result in migratory insertion into one of the metal-alkyl bonds to give an acyl species as was seen for the dihydrido-dimethyl species; instead simple CO coordination occurs. The spectral characterization of **36** is straightforward. Its ^{13}C NMR spectrum shows one peak at δ 214.8 with a Rh-C coupling of 20.3 Hz, indicating that both carbonyl groups are semi-bridged. The ^1H NMR spectrum displays peaks at δ -0.13 (triplet) and 0.82 (triplet of doublets), integrating as 6:3, and assigned to two equivalent methyl groups on Ir and one on Rh, respectively. Consistent with an effective mirror plane in the molecule, only one signal at δ 3.33, integrating as four protons, is observed for the four equivalent dppm methylene protons. These data suggest the formulation of **36** as shown in Scheme 3.7. This structure bears a close resemblance to that of the related olefin adduct $[RhIr(CH_3)(CO)_2(C_2H_4)(dppm)_2][CF_3SO_3]$,[10a] except that the ethylene group is now replaced by two methyl groups. Like the latter species, a dative bond from Ir to Rh is invoked to satisfy the electron count at Rh, giving a 16e Rh(I) and 18e Ir(III) center. Also, the Ir portion of the molecule bears a striking resemblance to that of the mononuclear Ir species $[(\eta^1\text{-Ind})Ir(CH_3)_2(CO)_2(PMe_3)]$ (Ind = Indenyl) reported by Bergman and co-workers[28] in which the alkyl and CO groups are mutually trans to each other. Compound **36** resists thermal degradation up to 50 °C in methylene chloride. However, at 70 °C in THF-d_8 it

Scheme 3.7



decomposes with no discernable metal-containing species observed in solution. A singlet at δ 2.07 observed in the ^{1}H NMR spectrum after the sample is cooled to ambient conditions is attributed to acetone formation. The stability of **36** toward reductive elimination of acetone or ethane at room temperature is noteworthy in view of the presence of CO and methyl groups in the required cis arrangement; although its reluctance to eliminate ethane is in accord with theoretical predictions.[29] It may be that the semi-bridging nature of the carbonyls in **36** inhibits migratory insertion.

Reaction of **34** with ethylene at 0 °C results in the formation of the ethylene adduct $[RhIr(CH_3)_2(CO)(C_2H_4)(\mu\text{-}CH_3)(dppm)_2][CF_3SO_3]$ (**37**) in which one terminal methyl group has apparently moved to a bridging site. The ethylene protons appear as broad peaks at δ 2.59 and 2.22 in the ^{1}H NMR spectrum and selective ^{31}P decoupling experiments establish that the ethylene moiety is bound to Rh. The spectrum also displays, in addition to two terminal methyl groups on Ir, a resonance for the bridging methyl group, at δ 0.28, as a doublet of multiplets ($^2J_{RhH}$ = 3 Hz). This peak appears to couple more strongly to the ^{31}P nuclei on Ir as demonstrated by the fact that ^{31}P selective decoupling at the Rh-bound ^{31}P nuclei leaves this signal unaffected while irradiating the Ir-bound ^{31}P nuclei simplifies it to a doublet. The carbonyl group has moved from a symmetrical position in **34** to a semi-bridging one in **37** as evidenced by an up-field chemical shift (δ 211.5 vs. 203.2) and lower Rh-C coupling constant (36.8 Hz vs. 20.2 Hz). The ethylene ligand is coordinated to Rh, in contrast to the behaviour shown by the related monomethyl complex $[RhIr(CH_3)(CO)_2(C_2H_4)(dppm)_2][CF_3SO_3]$[5,10] for which ethylene attack apparently occurs at Ir. We attribute the site of attack in the present case to the greater steric crowding about the 5-coordinate Ir in **34**, whereas in the case of the monomethyl complex **2**, both metals are 4 coordinate with steric factors favoring attack at Ir in this case (see previous discussion on this in Chapter 2).

The reaction of **34** with 1,1-dimethylallene gives another methyl-bridged product $[RhIr(CH_3)_2(\mu\text{-}CH_3)(CO)(\eta^2\text{-}H_2C{=}C{=}CMe_2)(dppm)_2][CF_3SO_3]$ (**38**), having a structure analogous to that of **37** as suggested by the similarities in their spectral parameters. The acquisition of natural abundance $^{13}C\{^1H\}$ NMR data enabled us to establish the bridging mode of the one of the methyl groups in the $^{13}C\{^1H\}$ NMR spectrum. Whereas the Ir-bound methyl groups appear as a triplet (δ -9.9) and a broad peak (δ -20.7), the bridging methyl group resonates as a doublet of multiplets at δ 21.3, having a 11 Hz coupling to Rh. The magnitude of this coupling to Rh is smaller than is normally observed for a terminally bound methyl group (*ca.* 20-30 Hz),[9,13] and is close to the value of 9.5 Hz reported for the methyl-bridged dirhodium species $[Rh(\mu\text{-}CH_3)(COD)]_2$;[30] this together with the downfield chemical shift (Ir-bound methyl groups generally resonate upfield between 5 and -30 ppm), argues for a symmetrically-bridged methyl group. The possibility that the bridging methyl group may be interacting in an agostic fashion with the Rh center, by utilizing a bonding C-H electron pair of the methyl substituent was considered but appears unlikely for two reasons. First, the relatively low-field chemical shift of the protons of this group (δ 0.28 and 0.16 for **37** and **38**, respectively) is not consistent with that expected for an agostic methyl group, for which high-field values (*ca.* -1 to -10 ppm) are more common.[31,32] Although a symmetrically-bridged methyl group in the ^1H NMR spectra may resonate as high field as -6.5 ppm,[33c] they generally tend to resonate downfield from that of TMS. In the latter context, there is at least one report[33a] of a symmetrically-bridged methyl group resonating at extremely low-field (*ca.* δ 3.34). Second, the methyl resonance in the $^{13}C\{^1H\}$ NMR spectrum for agostic methyls are often observed to higher fields (up to -59 ppm) whereas symmetrically-bridged methyl groups usually resonate at lower fields.[33]

To further discriminate between a symmetrical or agostic μ-CH_3 group in **38**, the partially deuterated and ^{13}C-labelled methyl groups were obtained by using ^{13}C- or ^{2}H-labelled methyl triflate in preparing the starting material **34**. The observed $^{1}J_{CH}$ value (121.4 Hz) for the μ-CH_3 group of **38** in the ^{1}H NMR spectrum is lower than *ca.* 130.9 Hz observed for one of the corresponding terminal CH_3 groups. Significantly, this value lies outside the range normally reported for agostic methyls (60-100 Hz)[32e] and for terminal methyls (130-140 Hz).[32f,g] Also, there was no discernible difference in the chemical shift for the μ-CH_2D compared to that of μ-CH_3 (**38**), again, in accord with a symmetrically-bridged methyl group.

Unlike **36** which is stable in solution for an extended period of time, compounds **37** and **38** have limited lifetimes in solution with the former being unstable to isolation; the olefin ligands dissociate with time, frustrating attempts to grow crystals for X-ray analysis. This finding, which parallels the results for several ethylene complexes of the mixed-metal RhIr combination in our group,[8,10] reflects the greater lability at the Rh center over Ir for which there is literature precedent.[13d]

Conclusions

The reactions of the dimethyl A-frame compound $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**) with a number of unsaturated substrates and π-acids have been investigated in attempts to induce migratory insertion processes leading to C-C bond formation and to establish the reductive elimination (of alkanes, ketones and aldehydes) pathways in its carbonylation and hydrogenolysis. The evidence presented, although not unambigous, seems to reflect two contrasting scenarios; reductive eliminations of acetone and methane appear to occur at the less labile Ir center while acetaldehyde formation appears to occur at Rh. The migratory insertion steps seem to occur at the same metals as the reductive eliminations.

A series of related dimethyl, and mixed methyl/aryl and methyl/benzyl complexes, $[RhIr(CH_3)(R)(CO)_2(dppm)_2]$ (R = CH_3, Ph, CH_2Ph), have also been synthesized in which, the anionic ligands are bound to Ir. This gives 16e/18e d^9/d^7 Rh(0)/Ir(+2) configurations in which the third-row Ir stabilizes the high oxidation state at this metal.[34]

Our goal of effecting SO_2 insertion into metal-alkyl bonds was also realized as shown by the formation of the alkyl sulfonate species $[RhIr(SO_2CH_3)(CH_3)(\mu\text{-}SO_2)(CO)(dppm)_2]$ (**33**) from the reaction of **23** with SO_2. As was the case with the monomethyl dicarbonyl species, insertion was shown to occur at the Rh-CH_3 bond. We had anticipated that this might also occur at the Ir to yield a bis methyl sulfonate complex but this was not realized under the reaction conditions.

Perhaps one of the most significant findings of this study is the synthesis of several cationic trimethyl complexes, the first of their kind involving dppm-bridged complexes of group 9 metals. Reaction of $[RhIr(CH_3)_3(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**34**), observed only at -80 °C, with ethylene and dimethylallene yielded the first examples of methyl-bridged complexes of the RhIr framework. Bridging methyls, although usually regarded as transient intermediates, have long been associated with facile methyl migrations between two metal centers,[35] and so the detection of **37** in solution and the isolation of **38** provides experimental confirmation for their intermediacy in methyl group transfer reactions and could potentially model how these transformations occur on metal surfaces.

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Chapter 4

Alkyne Additions to Mono-, Di- and Trimethyl Complexes

Introduction

The alkyne molecule can bind to transition metal centers in a variety of ways.[1] In monometallic centers it can bind to the single metal in an η^2-fashion in which the alkyne can function as either a 2- or 4-electron donor.[2] When two or more metals are involved the alkyne is also capable of bridging two or more metals.[1a,c,e] In bimetallic systems which are the subject of this thesis the bridging alkyne molecule can orient itself either parallel or perpendicular to the metal-metal axis; in these binding modes the neutral alkyne can be viewed as functioning as either a 2- or a 4-electron donor to the pair of metals, respectively.[3] In addition to the interesting structural aspects of alkyne complexes, they are also endowed with a rich chemistry,[2-7] which includes alkyne condensation with other substrates,[2] migratory insertions involving metal-hydride[1c,6] and metal-heteroatom bonds,[7] and C-C bond formations with carbonyl,[1c] alkyl[3] and other alkyne fragments.[5] A previous study[3a] in our group had investigated the reactivity of the methyl species $[RhIr(CH_3)(CO)_3(dppm)_2]$-$[CF_3SO_3]$ (**1**) with a number of alkynes. One of these reactions in which dimethyl acetylenedicarboxylate (DMAD) inserted into the Ir-CH_3 bond to give a vinylic product, $[RhIr(CO)_3(RC{=}(CH_3)R)(dppm)_2][CF_3SO_3]$ (R = CO_2CH_3), warranted further investigation. We were interested in pursuing this chemistry further to gain information about intermediates in these transformations, in order to assess the functions of the different metals. As described in the previous chapters, the chemistry of alkyl complexes of the RhIr combination of metals has been extended to include the mono-, di- and trimethyl species,

$[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**), $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**) and $[RhIr(CH_3)_3(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**34**). It was of obvious interest to investigate the chemistry of these species with alkynes in order to probe their potential for C-C bond formation. The results of these studies are reported herein.

Experimental Section

General Comments. Experimental conditions were as described in Chapter 2. Hexafluorobut-2-yne was purchased from PCR Inc., while dimethyl acetylenedicarboxylate (DMAD), 3-phenylpropyne, $Li[HBEt_3]$ and $NaBH_4$ were purchased from Aldrich, and acetylene was obtained from Matheson. ^{13}C-labelled acetylene was purchased from Cambridge Isotope Laboratories Inc., and ^{13}CO (99%) was supplied by Isotec Inc. All NMR data are for isotopically non-enriched nuclei unless otherwise stated. The compounds $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**),[8] $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**),[9] $[RhIr(CH_3)_2(CO)_2(dppm)_2]$[9] (**25**) and $[RhIr(CH_3)_3(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**34**)[9] were prepared as previously described. Spectroscopic parameters for the new compounds are found in Table 4.1.

Preparation of Compounds.

(a) Low-Temperature Reaction of Compound 2 with 3-phenylpropyne. 30 mg (0.023 mmol) of compound **2** was dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube at -78 °C and 3-phenylpropyne (2.9 µL, 0.023 mmol) was added by syringe. The NMR spectra (^{31}P, ^{1}H) at this temperature, indicated the presence of $[RhIr(H)(CH_3)(CO)_2(C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**39**) and $[RhIr(CH_3)(CO)_2(\mu\text{-}HC{\equiv}CCH_2Ph)(dppm)_2][CF_3SO_3]$ (**40**). Upon warming the solution to 0 °C, compound **40** disappeared to be replaced by a new species, identified as

Table 4.1 Spectroscopic Parameters for the compounds^{a}

Compounds	IR,^{b,c}cm^{-1}	NMR^{d}		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{1H\})$
[RhIr(H)(CH$_3$)(CO)$_2$(μ-η^1:η^2-CCR)(dppm)$_2$][CF$_3$SO$_3$] (R = CH$_2$Ph) (**39**)^{f}	-	25.9(dm,$^1J_{RhP}$=104.8Hz) -12.1(m)	4.16(m,2H), 3.75(m,2H) 2.22(s,2H), 0.18(t,3H) -9.10(t,1H)	192.4(dt,$^1J_{RhC}$=80.9Hz,1C) 192.7(m,1C)
[RhIr(CH$_3$)(CO)$_2$(μ-HCCR)(dppm)$_2$][CF$_3$SO$_3$] (R = CH$_2$Ph) (**40**)^{f}	-	16.8(dm,$^1J_{RhP}$=123.9Hz) -3.1(m)	6.06(dt,$^2J_{RhH}$=2.9Hz), 3.88(m,2H), 3.20(m,2H), 2.98(s,2H), 0.10(t,3H)	199.2(dt,$^1J_{RhC}$=56.1Hz,1C) 180.2(t,1C)
[RhIr(CH$_3$)(CO)$_2$(μCCHR)-(dppm)$_2$][CF$_3$SO$_3$] (R = CH$_2$Ph) (**41**)^{f}	-	24.2(dm,$^1J_{RhP}$=121.3Hz) -0.1(m)	5.60(t,1H), 4.18(m,2H) 3.06(d,$^3J_{HH}$=5.0Hz,2H) 3.04(m,2H), 0.19(t,3H)	195.3(dt,$^1J_{RhC}$=62.1Hz,1C) 184.0(t,1C)
[RhIr(CO)$_2$(μ-η^1:η^2-CCR)-(dppm)$_2$][CF$_3$SO$_3$] (R = CH$_2$Ph) (**42**)	1975(sb)^{c}	20.8(dm,$^1J_{RhP}$=112.2Hz) 6.3(m)	4.20(m,2H), 3.62(m,2H) 2.58(s,2H)	185.3(dt,$^1J_{RhC}$=79.4Hz,1C) 184.1(t,1C)
[RhIr(CO)$_2$(CCR)$_2$(μ-H)-(dppm)$_2$][CF$_3$SO$_3$] (R = CH$_2$Ph) (**43**)	2196(w)^{e}, 2090(w)^{e} 1963(s), 1922(s)	25.0(dm,$^1J_{RhP}$=110.4Hz) -21.8(m)	4.06(m,2H), 3.90(m,2H) 3.48(s,2H), 2.22(s,2H) -8.54(dm,$^1J_{RhH}$=14.0Hz)	191.6(dt,$^1J_{RhC}$=80.9Hz,1C) 163.6(t,1C)
[RhIr(CO)$_2$(μ-C=CH(R))-(CCR)$_2$(μ-H)(dppm)$_2$] (R = CH$_2$Ph) (**44**)	2091(w)^{c,e}, 2010(m)^{c} 1927(sb)^{c}, 1745(m)^{c,g}	27.8(dm,$^1J_{RhP}$=184.9Hz) - 7.8(m)	4.06(m,2H), 3.70(s,2H) 2.83(m,2H), 2.05(d,$^2J_{HH}$= 6.1Hz,2H), -7.98 (dm, $^1J_{RhH}$=12.8Hz, $^2J_{P(Rh)H}$= 6.0Hz,$^2J_{P(Ir)H}$=10.0Hz,1H)	207.2(dt,$^1J_{RhC}$=59.3Hz,1C) 172.0(m,1C)

Table 4.1 (contd)

		NMR[d]		
Compounds	IR[b,c]	$\delta(^{31}P\{^{1}H\})$	$\delta(^{1}H)$	$\delta(^{13}C\{1H\})$
$[RhIr(CHO)(CO)(CCR)_2(\mu\text{-}H)(dppm)_2]$ ($R = CH_2Ph$) **(45)**	2092(w)[c,e], 2033(w)[c,e] 1959(m)[c], 1580(w)[c,f]	27.9(dm, $^{1}J_{RhP}$=109.7Hz) -16.9(m)	14.34(dt, $^{3}J_{HH}$=5.0Hz) 5.08(m,2H), 3.42(m,2H) 2.94(s,2H), 2.20(s,2H) -11.73(dm, $^{1}J_{RhH}$=21.1Hz, $^{2}J_{P(Ir)H} \approx {}^{2}J_{P(Rh)H}$=14.0Hz, 1H)	251.4(s,1C), 195.4(dt, $^{1}J_{RhC}$=79.5Hz,1C) 116.6 (t, 1C), 106.2 (b, 1C) 90.8 (dm, $^{1}J_{RhC}$=7.3Hz, 1C) 58.8 (d, $^{1}J_{RhC}$=9.0Hz, 1C)
$[RhIr(CH_3)(CO)_2(\mu\text{-}RCCR)(dppm)_2][CF_3SO_3]$ ($R = CO_2Me$) **(46)**[k]	-	13.0(dm, $^{1}J_{RhP}$=107.9Hz) 11.9(m)	4.04(m,2H), 3.26(m,2H) 2.68(s,3H), 2.23(s,3H) 1.38(td,3H)	197.3(dt, $^{1}J_{RhC}$=50.4Hz, 1C), 187.5(t,1C), 4.3(dt, $^{1}J_{RhC}$=22.0Hz,1C)
$[RhIr(CH_3)(CO)_2(\mu\text{-}RCCR)(dppm)_2][CF_3SO_3]$ ($R = CO_2Me$) **(47)**	2030(ss)[c], 1955(m)[c] 1688(sb)[c,h]	17.9(dm, $^{1}J_{RhP}$=115.8Hz) -9.3(m)	3.79(m,2H), 3.24(m,2H) 2.68(s,3H), 2.62(s,3H) 1.08(t,3H)	194.4(dt, $^{1}J_{RhC}$=54.8Hz, 1C), 181.8(bs,1C)
$[RhIr(CH_3)(CO)_3(\mu\text{-}RCCR)(dppm)_2][CF_3SO_3]$ ($R = CO_2Me$) **(48)**	2036(s), 2004(m) 1724(m), 1690(b)[h] 1630(w)[g]	17.7(dm, $^{1}J_{RhP}$=144.9Hz) -8.6(m)	4.62(m,2H), 3.42(s,3H) 2.95(m,2H), 1.70(s,3H) -0.75(t,3H)	216.5(dm, $^{1}J_{RhC}$=18.6Hz, 1C), 189.9(dt, $^{1}J_{RhC}$= 54.8Hz,1C), 172.3(t,1C)
$[RhIr(CH_3)(CO)_3(\mu\text{-}RCCR)(dppm)_2][CF_3SO_3]$ ($R = CO_2Me$) **(49)**[j]	-	21.6(dm, $^{1}J_{RhP}$=98.1Hz) -23.9(m)	4.78(m,2H), 3.80(m,2H) 3.48(s,3H), 2.32(s,3H) -0.17(td,3H)	195.6(dm, $^{1}J_{RhC}$=46.0Hz, 1C), 184.(t,1C), 160.1 (t,1C)
$[RhIr(COCH_3)(CO)_2(\mu\text{-}RCCR)(dppm)_2][CF_3SO_3]$ ($R = CO_2Me$) **(50)**	-	10.9(dm, $^{1}J_{RhP}$=109.3Hz) -21.8(m)	4.84(m,2H), 3.65(m,2H) 3.55(s,3H), 2.40(s,3H) 0.92(s,3H)	237.6(dm, $^{1}J_{RhC}$=25.5Hz, 1C), 193.1(dm, $^{1}J_{RhC}$= 49.3Hz,1C),184.5(t,1C)

Table 4.1 (contd)

Compounds	IR^{b,c}	NMR^{d}		
		$\delta(^{31}P\{^{1}H\})$	$\delta(^{1}H)$	$\delta(^{13}C\{^{1}H\})$
[RhIr(CH$_3$)$_2$(μ-CO)(η^2-RCCR)(dppm)$_2$] (R = CO$_2$Me) **(51)**^{k}	-	32.6(dm,$^1J_{RhP}$=158.1Hz) -9.3(m)	3.88(m,2H), 3.60(m,2H) 3.56(s,3H), 2.60(s,3H) 1.84(t,3H), -1.80(td,3H)	218.8(dm,$^1J_{RhC}$=32.5Hz,1C)
[RhIr(CH$_3$)$_2$(μ-CO)(η^2-RCCR)(dppm)$_2$] (R = CF$_3$) **(52)**^{k}	-	30.4(dm,$^1J_{RhP}$=154.0Hz) -5.8(m)	3.88(m,2H), 3.52(m,2H) 1.73(t,3H), -0.61(td,3H)	218.1(dm,$^1J_{RhC}$=34.4Hz,1C)
[RhIr(CH$_3$)$_2$(CO)(μ-RCCR)-(dppm)$_2$] (R = CO$_2$Me) **(53)**	1950(bs), 1696(m)^h 1630(w)^g	21.8(dm,$^1J_{RhP}$=158.1Hz) -19.8(m)	4.62(m,2H), 3.89(s,3H) 3.22(s,3H), 2.88(m,2H) 0.63(t,3H), -0.90(t,3H)	196.7(dt,$^1J_{RhC}$=62.3Hz,1C)
[RhIr(CH$_3$)$_2$(CO)(μ-η^1:η^2-CCH)(μ-H)(dppm)$_2$] **(54)**	2029(s)^e, 2004(s)	8.0(dm,$^1J_{RhP}$=127.8Hz) -10.4(m)	5.58(m,1H), 4.50(m,2H) 3.47(m,2H), 0.32(td,3H) -0.60(t,3H), -13.28(dm, $^1J_{RhH}$=12.1Hz, 1H)	174.2(t,1C), 138.1(ddm, $^1J_{RhC\alpha}$=23.8Hz,$^1J_{CC}$=55.4Hz, $^2J_{P(Rh)C\alpha}$=11.1Hz,1C), 116.1(dm, $^2J_{RhC\beta}$=3.7Hz, $^2J_{P(Ir)C}$= 8.0Hz 1C)
[RhIr(CH$_3$)$_3$(CO)(μ-C$_2$H$_2$)-(dppm)$_2$][CF$_3$SO$_3$] **(55)**	2008(m), 1811(w)^g	17.8(dm,$^1J_{RhP}$=125.9Hz) -14.4(m)	8.08(dt,$^2J_{RhH}$=2.0Hz, 1H), 6.28 (t,1H), 4.18 (m,2H), 3.30(m,2H), 0.88(td,3H), 0.69(t,3H), -0.49(t,3H)	194.6(dm,$^1J_{RhC}$=6.4Hz,1C) 130.4(ddm,$^1J_{RhC}$=26.2Hz, $^1J_{CC}$=70.4Hz,1C), 94.6(dm, $^1J_{CC}$=70.4Hz,1C)

Table 4.1 (contd)

[a] IR abbreviations: ss = strong sharp, sb = strong broad, ms = medium sharp, m = medium, w = weak, sh = shoulder. NMR abbreviations: t = triplet, d = doublet, dt = doublet of triplets, dd = doublet of doublets, tt = triplet of triplets, ddt = doublet of doublets of triplets, ddm = doublet of doublets of multiplets, dm = doublet of multiplets, td = triplet of doublets, bs = broad singlet, m = multiplet, q = quartet, s = singlet. [b] Nujol mull except as indicated. Values quoted are ν(CO) except as indicated. [c] CH_2Cl_2 cast. [d] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4 while ^1H and $^{13}C\{^1H\}$ are referenced vs TMS. Chemical shifts for the phenyl hydrogens are not given in the ^1H NMR data.

[e] ν(C≡C). [f] ν(CO) for CHO group. [g] ν(C=C). [h] ν(CO). [i] 0°C. [j] -40°C. [k] -60°C.

[RhIr(CH_3)$(CO)_2$(μ-C=C(H)CH_2Ph)$(dppm)_2$][CF_3SO_3] (**41**), together with **39** and trace amounts of the final product [RhIr$(CO)_2$(C_2CH_2Ph)$(dppm)_2$][CF_3SO_3] (**42**). At ambient temperature, compound **42** is the predominant species in solution.

(b) [RhIr$(CO)_2$(C_2CH_2Ph)$(dppm)_2$][CF_3SO_3] (42) To a solution of [RhIr(CH_3)$(CO)_2$$(dppm)_2$][$CF_3SO_3$] (**2**) (50 mg, 0.039 mmol) in 10 mL of dichloromethane at 0 °C was added 1 equiv of 3-phenylpropyne (4.8 µL, 0.039 mmol). The mixture was stirred for 2 h under a slow stream of dinitrogen gas during which time the color changed from light orange to burgundy red. The resulting solution was allowed to warm to room temperature, stirred for a further 0.5 h and concentrated to *ca*. 3 mL. Addition of 10 mL of ether resulted in the precipitation of red, powdery solid which was washed twice with 5 mL portions of ether, dried briefly under a nitrogen stream and then *in vacuo* overnight (42 mg, 78%). Anal. Calcd for $IrRhSP_4F_3O_5C_{62}H_{51}$: C, 53.71; H, 3.68. Found : C, 53.55; H, 3.61.

(c) [RhIr$(CO)_2$$(C_2CH_2Ph)_2$($\mu$-H)$(dppm)_2$][$CF_3SO_3$] (43) The procedure for preparing compound **43** was the same as described for **42** except that an excess (*ca*. 4 equiv) was used instead of 1 equiv of 3-phenylpropyne, and the reaction was conducted at room temperature for 3 h. The color of the solution turned from light orange to burgundy and then finally dark orange-red. The dull orange product was obtained in 66% isolated yield. Anal. Calcd for $IrRhSP_4F_3O_5C_{71}H_{59}$ C, 56.75; H, 3.93. Found : C, 56.45; H, 4.39.

(d) [RhIr$(CO)_2$(μ-C=C(H)CH_2Ph)(C≡CH_2Ph)(μ-H)$(dppm)_2$] (44). Compound 43 (30 mg, 0.020 mmol) was dissolved in 0.6 mL of THF-d_8 in an NMR tube at ambient temperature. To this was added $NaBH_4$ (1.5 mg, 0.040 mmol) causing the orange color of the solution to turn dark brown. The NMR data were collected immediately since compound **44** transformed to several unidentified products after 8 h and was unstable to isolation.

(e) $[RhIr(CHO)(CO)(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CCH_2Ph)(C{\equiv}CCH_2Ph)(\mu\text{-}H)(dppm)_2]$ (45)

The procedure used to prepare compound **45** was the same as described for **44** except that $Li[HBEt_3]$ (10 equiv, 200 µL in 1 M THF solution) and CD_2Cl_2 were used instead of sodium borohydride ($NaBH_4$) and THF-d_8, respectively. The NMR analysis carried out immediately showed quantitative conversion to compound **45**. Attempts to isolate this product led to decomposition.

(f) Low-Temperature Reaction of $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ with DMAD. 30 mg (0.023 mmol) of $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) was dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube equipped with a rubber septum cap at -78 °C. To this was added 1 equiv of DMAD (2.9 µL, 0.023 mmol). The NMR analysis on this solution showed $[RhIr(CH_3)(CO)_2(\mu\text{-}CH_3O_2CC{\equiv}C\text{-}CO_2CH_3)(dppm)_2][CF_3SO_3]$ (**46**) as the main product. Upon warming to -40 °C, new peaks due to $[RhIr(CH_3)(CO)_2(\mu\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(dppm)_2][CF_3SO_3]$ (**47**), an isomer of **46**, appeared in the $^{31}P\{^1H\}$ NMR spectrum. Complete conversion from **46** to **47** took 10 h in the NMR tube. Compound **47** could be more conveniently prepared by adding 1 equiv of DMAD (5.8 mL, 0.047 mmol) to a dichloromethane solution (3 mL) of **2** (60 mg, 0.047 mmol) followed by stirring for 3 h. Precipitation of a yellow-orange flocculent solid resulted upon addition of 10 mL of pentane (50 mg, 75%). Anal. Calcd for $IrRhSP_4F_3O_9C_{60}H_{53}$: C, 50.48; H, 3.72. Found : C, 50.59; H, 4.00.

(g) $[RhIr(CH_3)(CO)_3(\mu\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(dppm)_2][CF_3SO_3]$ (48) 40 mg (0.028 mmol) of compound **47** was placed in a flask and dissolved in 3 mL of CH_2Cl_2. A static atmosphere of CO was placed over the solution causing an immediate change in color from orange to yellow. The solution was stirred for 5 min and 10 mL of pentane was added. The bright yellow solid was washed twice with 5 mL aliquots of pentane and dried first under N_2, then *in vacuo*

(28 mg, 69%). Anal. Calcd for $IrRhSP_4F_3O_{10}C_{61}H_{53}$: C, 50.33; H, 3.67. Found : C, 49.99, H, 3.55.

(h) Reactions of Compound 46 with CO. Compound **46** was prepared as described above (f) at -78 °C. After the solution was allowed to stand at this temperature for 0.5 h, a static atmosphere of CO was placed over the sample. The NMR analysis carried out immediately at -60 °C indicated the presence of $[RhIr(CH_3)(CO)_3(\mu\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(dppm)_2][CF_3SO_3]$ (**49**) as the major product in addition to peaks due to two minor products, the previously characterized vinyl species, $[RhIr(CO)_3(CH_3O_2CC{=}C(CH_3)CO_2CH_3)(dppm)_2]$-$[CF_3SO_3]$,[3a] and the acetyl species $[RhIr(COCH_3)(CO)_2(\mu\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)$-$(dppm)_2][CF_3SO_3]$ (**50**). Upon standing for 6 h in solution in the NMR tube at ambient temperature, the peaks due to the latter two species increased in intensity while those due to **46** decreased.

(i) Reaction of $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (23) with DMAD. 30 mg (0.027 mmol) of compound **23** was dissolved in 0.5 mL of THF-d_8 in an NMR tube at -78 °C. 1 equiv of DMAD (3.3 μL, 0.027 mmol) was added by syringe causing the deep red color of the solution to turn dark orange. The NMR spectra showed $[RhIr(CH_3)_2(\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(\mu\text{-}CO)(dppm)_2]$ (**51**) as the only product in solution. Upon warming to 0 °C and allowing the solution to stand for 2 h at this temperature, **51** completely disappeared to be replaced by $[RhIr(CH_3)_2(CO)(\mu\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(dppm)_2]$ (**53**), together with two unidentified products. Compound **53** can be prepared independently by addition of 1 equiv of DMAD to a solution of $[RhIr(CH_3)_2(CO)_2(dppm)_2]$ (**25**) (30 mg, 0.026 mmol), followed by stirring for 0.5 h (22 mg, 67%). Anal. Calcd for $IrRhP_4O_5C_{59}H_{56}$: C, 56.02; H, 4.43. Found : C, 55.84.; H, 3.91.

(j) Reaction of $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ with HFB. The procedure is as described for preparing **51** except that a static atmosphere of hexafluoro-2-

butyne (HFB) gas was placed over a sample of [RhIr$(CH_3)_2$(μ-CO)(dppm)$_2$] (**23**). The NMR spectra carried out at -60 °C showed [RhIr$(CH_3)_2$(η^2-$CF_3C{\equiv}CCF_3$)(μ-CO)(dppm)$_2$] (**52**) as the only product in solution. Compound **52** transformed to several unidentified products at temperatures above -40 °C so its identification was made on the basis of NMR spectroscopy. ^{19}F NMR (-60 °C) : -50.4 (b, 3F)., -52.6 (b, 3F).

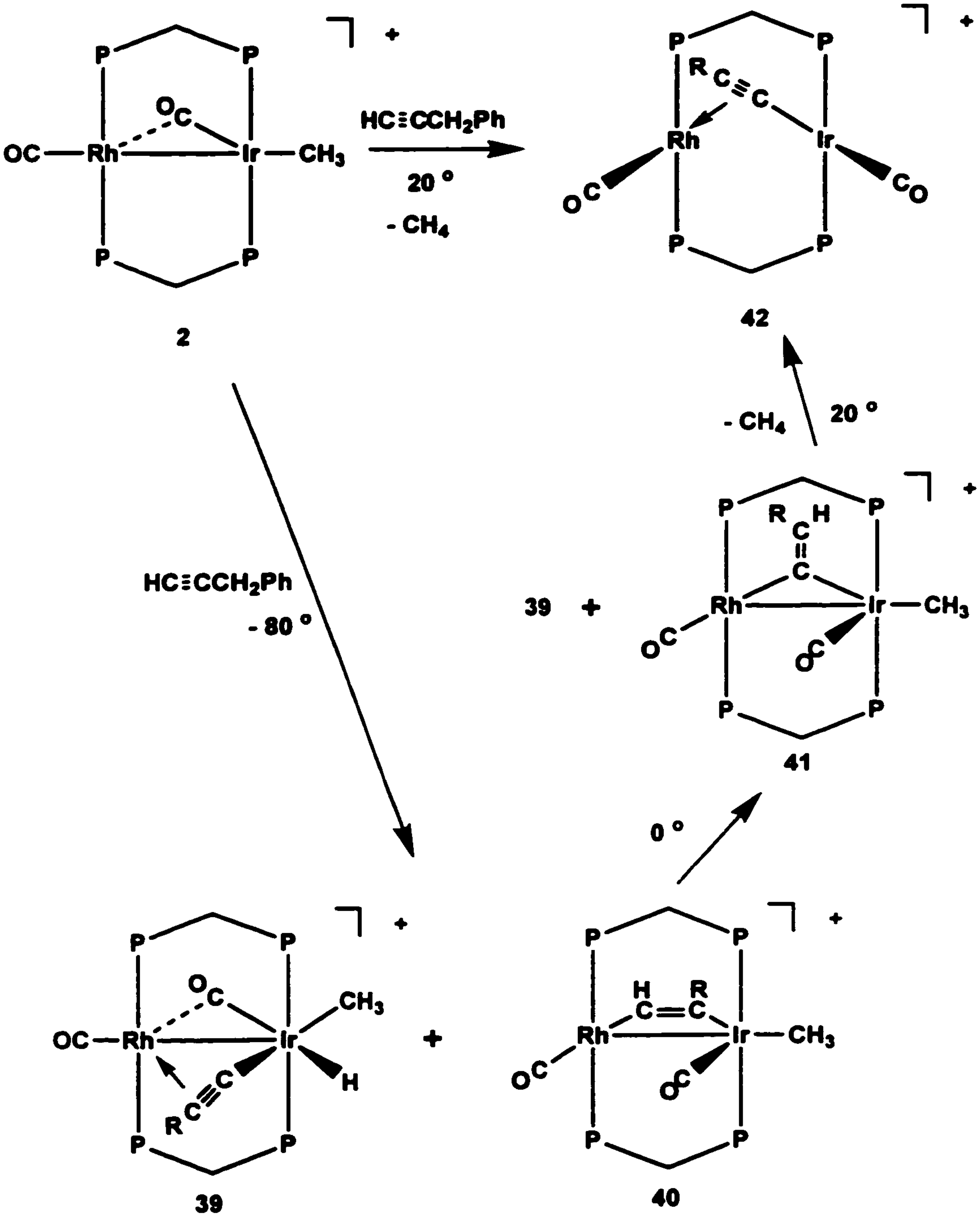
(k) **[RhIr$(CH_3)_2$(CO)(μ-η^1:η^2-C≡CH)(μ-H)(dppm)$_2$] (54).** 40 mg (0.036 mmol) of [RhIr$(CH_3)_2$(μ-CO)(dppm)$_2$] (**23**) was dissolved in 0.6 mL of THF-d_8 in an NMR tube at -78 °C. Approx. 0.4 mL of acetylene gas was added via a gas-tight syringe causing an immediate color change from red to brown. The solution was left to stand at this temperature for 1 h, and then slowly taken to room temperature over a 15 min period. The NMR showed the presence of **54** as the only product in solution. The solution was transferred to a 3-neck 10 mL flask and precipitation was induced by addition of pentane. Recrystallization from THF/pentane afforded a light orange-brown flocculent solid (15 mg, 37%). Anal. Calcd for $IrRhP_4OC_{55}H_{52}$: C, 57.51; H, 4.53. Found : C, 57.57; H, 4.12.

(l) **[RhIr$(CH_3)_3$(CO)(μ-HC≡CH)(dppm)$_2$][CF_3SO_3] (55).** [RhIr$(CH_3)_3$(μ-CO)(dppm)$_2$][CF_3SO_3] (**34**) was prepared *in situ* at -78 °C as previously described in Chapter 3 of this thesis. Excess acetylene gas was bubbled briefly through the solution at -78 °C. The NMR spectra taken at -40 °C and at room temperature showed compound **55** as the only product in solution. The solution was transferred to a flask and precipitated with ether. Recrystallization from CH_2Cl_2/ether gave a dark brown solid (24 mg, 80%). Anal. Calcd for $IrRhSP_4O4C_{57}H_{53}$: C, 52.13; H, 4.04. Found: C, 52.33.; H, 4.08.

Results and Discussion

In this chapter, we extend the investigation into the reactions of the dicarbonyl monomethyl species, $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with alkynes, in the hope of establishing the roles of the adjacent metals in alkyne activation. Reaction of **2** with one equiv of 3-phenylpropyne at ambient temperature gave the A-frame acetylide complex $[RhIr(CO)_2(\mu\text{-}C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**42**) accompanied by methane loss. Compound **42** has very similar spectral characteristics (*vide supra*), to the phenyl acetylide derivative, which has been prepared and characterized in our group,[10a] so is assumed to be structurally analogous. The only distinguishing feature in the spectroscopy of these two compounds is in the ^1H NMR spectrum for **42** which displays an additional singlet at δ 2.58 for the benzyl methylene protons. In order to further probe the formation of **42** from the monomethyl complex and learn more about possible intermediates leading to its formation, the reaction was repeated and monitored at -80 °C. The NMR data of the sample indicate the presence of two species; the acetylide hydride $[RhIr(H)(CH_3)(CO)_2(\mu\text{-}C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**39**) and the alkyne-bridged species $[RhIr(CH_3)(CO)_2(\mu\text{-}HC_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**40**), formed in an approximate ratio of 1.6:1. It is proposed that compound **39** has the alkynyl moiety bridging the metals in an $\mu\text{-}\eta^1\text{:}\eta^2$ fashion, as has been commonly observed in binuclear complexes.[1c,1d,3a,10] The ^1H NMR spectrum of **39** exhibits triplet resonances at δ 0.18 and -9.10, assigned to the methyl and hydride groups, both terminally bound to Ir. The formulation for **39**, in which the Ir-bound CO displays a weak semi-bridging interaction with Rh, as depicted in Scheme 4.1, is based on the chemical shift for the Ir-bound carbonyl which appears at δ 192.7 as a multiplet, at a lower field than normally associated with a purely terminal CO on Ir. Examples of this type of semi-bridging CO have been observed earlier in this thesis for $[RhIr(CH_3)(CO)_2$-

Scheme 4.1



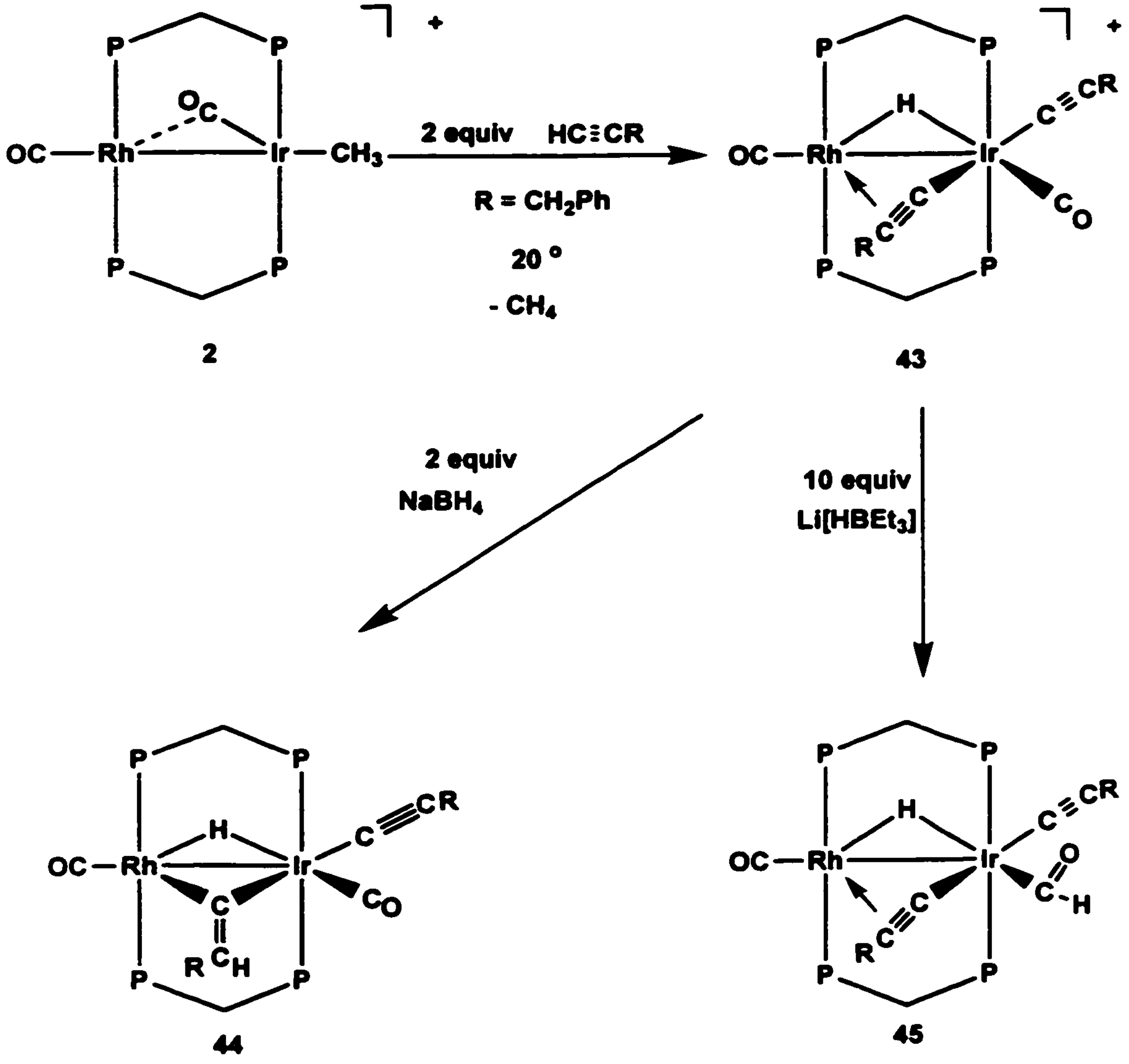
$(dppm)_2][CF_3SO_3]$ (**2**) (δ 184.9, $^1J_{RhC}$ = 7 Hz) and for a series of compounds $[RhIr(CH_3)(R)(CO)_2(dppm)_2]$ (R = H, CN, CH_3, CH_2Ph, Ph) in which these peaks appear at low-field (δ 184.3-190.4 ppm) compared to the resonances for the corresponding Rh-bound carbonyls (δ 182.0-183.8 ppm). With the Ir-bound carbonyl and acetylide groups occupying bridging sites, the methyl and hydride groups on Ir are, by necessity, assumed to be in mutually cis disposition.

The ^1H NMR spectrum of **40** displays the methyl group at δ 0.10 (triplet), a singlet at δ 2.98 due to the benzyl methylene and a doublet of triplets at δ 6.06 ($^2J_{RhH}$ = 3.0 Hz) due to the alkyne hydrogen, in the intensity ratio 3:2:1. The results from selective ^{31}P decoupling experiments and the observation of Rh coupling to the alkyne hydrogen leads to the assignment, as shown, in which the unsubstituted end of the alkyne is adjacent to Rh rather than to Ir. Compounds **39** and **40** persist in solution upon warming to -40 °C, with no discernible change in their intensity ratio after 1 h. However, upon warming the sample to 0 °C, compound **40** transforms into the vinylidene complex $[RhIr(CH_3)(CO)_2(\mu\text{-}C_2(H)CH_2Ph)(dppm)_2][CF_3SO_3]$ (**41**) while compound **39** remains, and traces of the final product **42** also begin to appear. The formation of **41** coincides with the disappearance of **40**, indicating that the vinylidene product originates from the alkyne-bridged and not from the alkynyl hydride species. The vinylidene hydrogen of **41** appears as a triplet of doublets in the ^1H NMR spectrum at δ 5.60 while the benzyl methylene protons appear as a doublet ($^3J_{HH}$ = 5.0 Hz) at δ 3.06. The coupling of these two groups was confirmed by selective $^1H\{^1H\}$ experiments. The additional doublet splitting in the former resonance is ascribed to Rh-H coupling (*ca.* 2 Hz), since selective irradiation of the peak at δ 3.06 led to the collapse of the triplet of doublets at δ 5.60 to a doublet. Although it is often difficult, on the basis of ^1H NMR to distinguish between a vinylidene and an alkyne-bridged complex, the coupling observed between the methylene protons of the benzyl group and the vinylidene hydrogen serves to identify the vinylidene moiety as such. The geometry at the β-carbon of the vinylidene is not certain; however, the structure suggested in Scheme 4.1 is based on having the bulky benzyl group oriented toward the less sterically encumbered Rh center. Finally at room temperature, the acetylide species **42** is the major product in solution together with trace amounts of **41** and two other unidentified species which are presumed to be the precursors to **42**, present in low concentrations; these two unidentified species ultimately disappear along with **41**. Compound **39** is rapidly consumed at room temperature accompanied by formation of **42** and methane. On the other hand, compound **41** is only slowly depleted (half-life of 0.5 h) at this temperature. It is not certain how this vinylidene species transforms to the final product **42**; however, we assume that rearrangement to a species resembling **39** occurs, which eliminates methane. Reversible interconversion of a vinylidene and an acetylide group in an analogous diiridium complex has been observed.[3h]

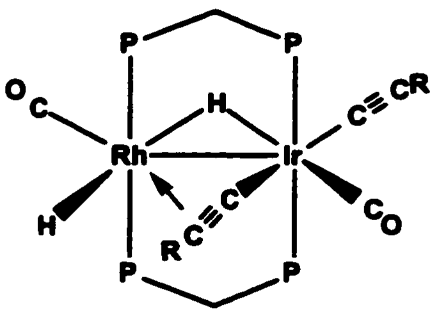
In the presence of a 2-fold excess of alkyne, the bisacetylide species $[RhIr(CO)_2(C_2CH_2Ph)_2(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**43**) is obtained in the reaction with compound **2**. This product is also structurally analogous to the crystallographically characterized bis(phenylacetylide) derivative;[3a] again, the two differ spectroscopically only in the presence of two singlet resonances at δ 3.48 and 2.22 in the ^1H NMR spectrum of **43**, attributed to the benzyl methylene protons.

In an attempt to convert the bis acetylide species **43** into a vinylidene-bridged product, it was reacted with $NaBH_4$. This reaction did produce the targeted vinylidene species $[RhIr(CO)_2(\mu\text{-}C{=}C(H)CH_2Ph)(C_2CH_2Ph)(\mu\text{-}H)\text{-}(dppm)_2]$ (**44**), the $^{13}C\{^1H\}$ NMR spectrum of which displays peaks consistent

Scheme 4.2


2 equiv HC≡CR
R = CH2Ph
20 °
- CH4
2
43
2 equiv
NaBH4
10 equiv
Li[HBEt3]
44
45

with one carbonyl on each metal. Unfortunately, the vinylidene proton could not be identified in the ^{1}H NMR spectrum, presumably being masked by those due to phenyl protons. The methylene protons of the vinylidenic benzyl substituent appear as a doublet at δ 2.05 with a 6.0 Hz coupling, presumably to the vinylidene proton. This large coupling between these protons discounts the possibility of a bridging alkyne as the resulting four-bond would be much smaller if not unobserved. Unfortunately, an attempt to identify the the vinylidene C_α and C_β atoms through overnight $^{13}C\{^1H\}$ NMR data acquisition was unsuccessful owing to the decomposition of the sample into two unidentified species. The IR spectrum of **44** exhibits bands at 2010, 1927, 2091 and 1745 cm^{-1}, of which the latter two weaker stretches are assigned to the acetylide and vinylidene groups, respectively. For steric reasons, the vinylidenic hydrogen is assumed to be positioned adjacent the carbonyl group on Ir as depicted in Scheme 4.2; the alternate arrangement, which places the benzyl group adjacent to this CO, would be less sterically favored. In order to probe the source of the hydrogen atom at the vinylidene, the reaction was repeated using $NaBD_4$. The ^{1}H NMR spectrum for **44-D** showed a bridging hydride signal at δ -7.98, which is identical with that observed for **44-H** (*vide supra*), suggesting that the hydride ligand in **43** has retained its bridging site and by the same token, that the vinylidenic hydrogen is derived from the added reagent. Further work aimed at identifying the vinylidene deuterium using ^{2}H NMR analysis is continuing. Formation of **44** could arise either from nucleophilic attack of the hydride directly at the bridging acetylide group or at the coordinatively unsaturated Rh in **43** to yield an (unobserved) dihydrido-bisacetylide (shown below).



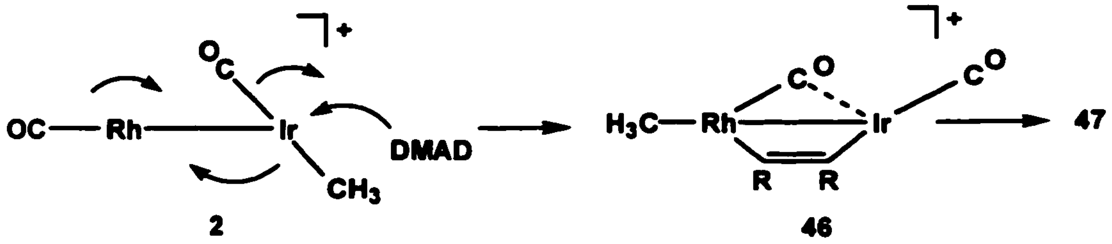
Transfer of this metal-bound hydride to the bridging acetylide ligand should be facile owing to the mutual proximity of the acetylide β-carbon and the hydride. Direct attack at the acetylide would be favored by its π interaction to the Rh which should enhance its electrophilicity, making it susceptible to hydride attack. However, there are few precedents for this mechanism due to the fact that the metal centers generally tend to be more electrophilic compared to the acetylide function.[11] Furthermore, all documented cases of similar processes within our group[3a,10,12,13] and others[14] clearly demonstrate initial formation of an acetylide-hydride species which subsequently transforms to a vinylidene adduct via hydride migration to the acetylide. Compound **44** is unstable and transforms in solution to several uncharacterized products within 12 h; attempts to isolate it as a solid also led to decomposition. The reaction of **43** with MeLi was also attempted, but the complex nature of the NMR spectra and overlapping signals of other unidentified species precluded a satisfactorily characterization of the presumed methylvinylidene species.

Compound **43** also reacts with excess Li[HBEt$_3$], but in this case the product is the unusual formyl species, [RhIr(CHO)(CO)(C$_2$CH$_2$Ph)$_2$(μ-H)-(dppm)$_2$] (**45**), an apparent result of direct hydride attack at the coordinated carbonyl group on Ir. The formyl carbon appears as a singlet at δ 251.4 while the other carbonyl group appears as a doublet of triplets at δ 195.4 with Rh-C coupling of 79.5 Hz. The absence of coupling of the resonance at δ 251.4 to Rh indicates that the formyl group is Ir-bound. The formyl proton appears as a triplet of doublets ($^3J_{HH}$ = 5.0 Hz) at δ 14.34, and selective $^{31}P\{^1H\}$ decoupling experiments confirm that the triplet arises from a three-bond P-H coupling to the Ir-bound ^{31}P nuclei. The doublet coupling was established by selective $^1H\{^1H\}$ decoupling experiments as resulting from three-bond H-H coupling between the formyl proton and the bridging hydride (δ -11.73) consistent with a trans alignment of these groups, as diagrammed in Scheme 4.2. If the carbon atoms of the carbonyl groups are isotopically enriched, the formyl proton exhibits an additional doublet coupling with $^1J_{CH}$ of 144.0 Hz; this value is as expected for an sp^2 carbon center.[15] Further support for the formulation of **45** is derived from the IR spectrum which displays, in addition to bands at 2033 and 1959 cm^{-1} due to two terminal carbonyl groups, stretches at 1580 cm^{-1} and 2092 cm^{-1}, assigned to the formyl and acetylide groups, respectively. Consistent with the transformation of the Ir-bound CO group to a formyl, the $^{31}P\{^1H\}$ spectral parameters corresponding to the ^{31}P nuclei bound to Ir in **43** and **45** are different while there is no significant change at the Rh end (*vide supra*). It is suggested that hydride attack occurs directly at the carbonyl since attack of the hydride at Ir appears unlikely in view of the coordinative saturation at this center. Also the possibility of initial attack at Rh accompanied by migration to Ir can be ruled out since such migration would be inhibited by the presence of the bridging acetylide and hydride groups. Furthermore the 1,2 hydride migration onto a carbonyl group to afford a formyl complex is believed to be a thermodynamically uphill step[16] and has only been rarely observed[17,18] with highly oxophilic early transition metal systems in which the resulting formyl group is stabilized by coordination of the oxygen to an early metal. The factors which directly dictate preferential hydride attack at the Ir-bound carbonyl group over other potential sites such as the metal centers, the Rh-bound carbonyl group and the β-carbons of the acetylides in **43**, are not understood. However, it may be that the large trans influence of the bridging hydride in **43** plays a role by increasing the electrophilicity of the trans CO.

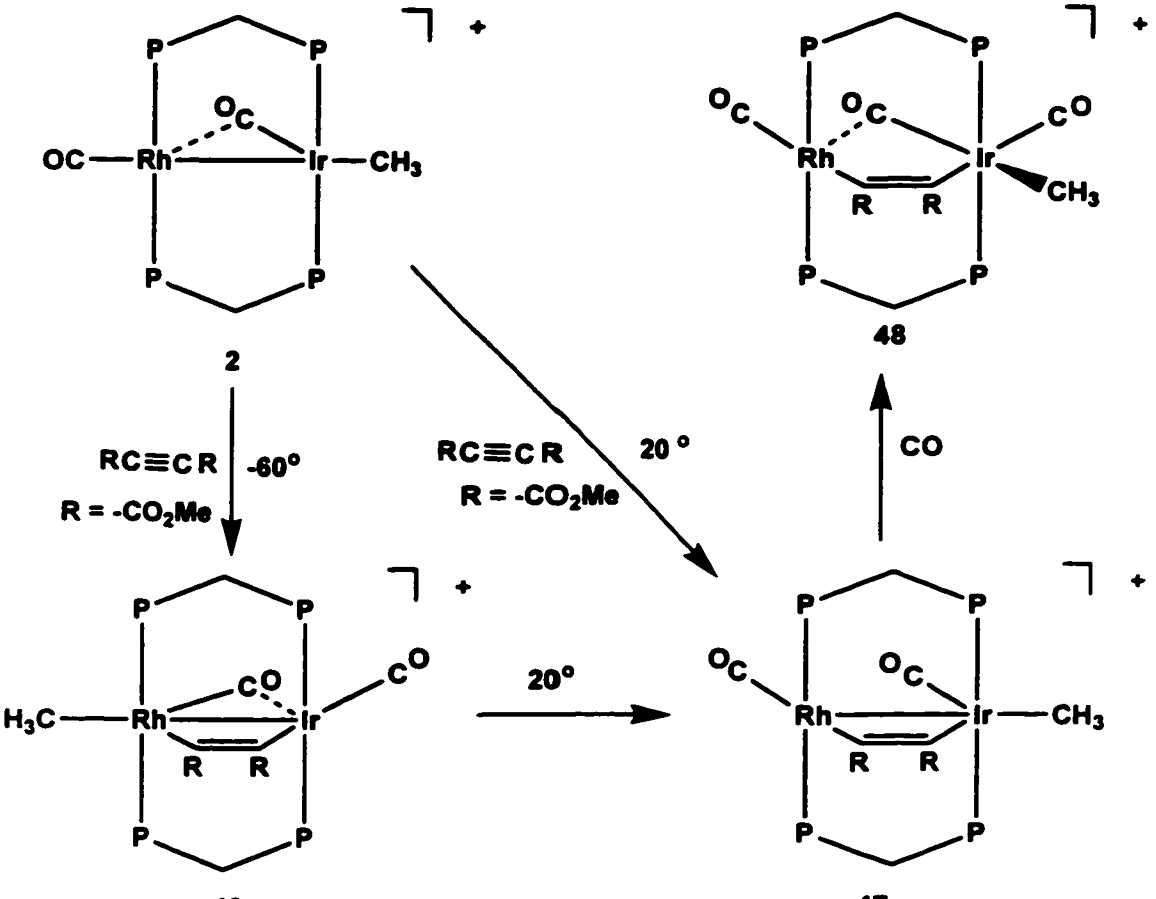
The vast majority of transition-metal formyls reported in the literature are mononuclear complexes.[16a,19] The formation of the neutral formyl species **45** from nucleophilic attack at a coordinated carbonyl functionality of a cationic precursor, although not without precedent in mononuclear complexes,[19] presents an interesting transformation occurring at a bimetallic system, particularly involving late metals. As noted earlier, most cases of binuclear formyls involve stabilization of this group through interaction with an oxophilic metal.[17,18] Catalyst-bound formyls have been implicated during the reduction of carbon monoxide to hydrocarbons in the Fischer-Tropsch synthesis.[20,21] In addition, the formyl group can be subsequently functionalized[21d,22] to give alcohols and carboxylic acids.

The difference in the outcomes of the reactivity of $NaBH_4$ and $Li(HBEt_3)$ with compound **43** is interesting, and no clear rationale is obvious to us. However, the reactivity differences may result from the different sizes of the reagents with direct approach of the bulky $HBEt_3^-$ ligand to the β-carbon or the Rh atom at either face being sterically inhibited owing to repusions with phenyl groups of the dppm and acetylide moieties. Attack at the less encumbered carbonyl group should be sterically favored. Conversely, the BH_4^- is smaller in size and steric considerations are not as important, resulting in the observed hydride attack at the metal.

The reactivity of the methyl species $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with the electrophilic alkyne DMAD was investigated in order to compare with that of its tricarbonyl analogue which had been shown[3a] to give the vinyl product $[RhIr(CO)_3(\mu\text{-}RC{=}C(CH_3)R)(dppm)_2]^+$ (R = CO_2Me), by insertion of the alkyne into the Ir-CH_3 bond. Compound **2** reacts with 1 equiv of DMAD at room temperature to yield the alkyne-bridged product $[RhIr(CH_3)(CO)_2(\mu\text{-}RC{=}CR)(dppm)_2]^+$ (R = CO_2Me) (**47**), in which the methyl group has remained bound to Ir as shown by its coupling to the Ir-bound phosphorus in the ^1H NMR spectra. The $^{13}C\{^1H\}$ NMR spectrum also exhibits peaks at δ 194.4 ($^1J_{RhC}$ = 54.7 Hz) and 181.8, assigned to Rh- and Ir-bound carbonyl groups, respectively. It is presumed that the alkyne bridges both metals in a parallel fashion as has been observed previously.[13b,23,24] A perpendicular bridging arrangement of the alkyne appears less likely on the basis of the ^1H NMR spectrum which shows two separate resonances for the DMAD methyl groups (*vide supra*), which are in different environments by virtue of their proximity either to Rh or Ir; a perpendicular alignment should display only one methyl signal. When the reaction of **2** with DMAD is carried out at -60 °C, a new alkyne-bridged species **46** appears in which the methyl group is bound to Rh as revealed by its ^1H and $^{13}C\{^1H\}$ NMR spectra (*vide supra*). Upon warming to room temperature, **46** slowly transforms to **47** by transfer of the methyl group to Ir. The formation of **46** from **2** is envisioned as occurring by DMAD attack at Ir, as diagrammed below (recalling the solution structure of **2** discussed in Chapter 2), followed by a merry-go-round migration of ligands to bring the DMAD group to its favored bridging position. How compound **46** transforms to the thermodynamic product **47** is less clear.



Scheme 4.3



2

46

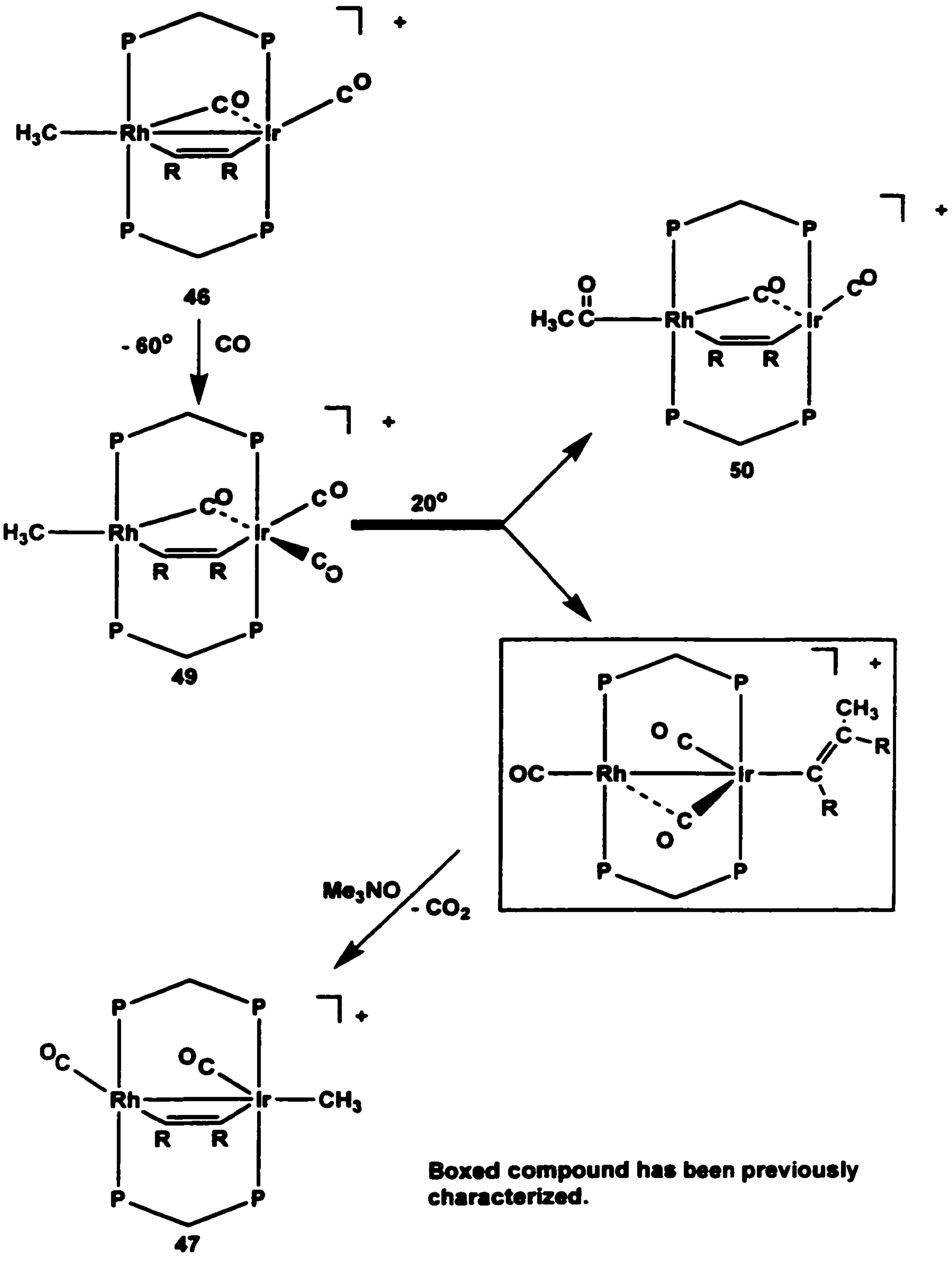
47

48

In an attempt to induce methyl group migratory insertion to give the previously characterized vinyllic product [RhIr(CO)$_3$(RC=C(CH$_3$)R)(dppm)$_2$]$^+$ (R = CO$_2$Me),[3a] compound **47** was treated with CO at room temperature. The reaction proceeded instantly as evidenced by the change in the color of the sample from orange to light yellow, and NMR analysis of this sample showed the quantitative formation of the tricarbonyl species [RhIr(CH$_3$)(CO)$_3$(μ-RC=CR)-(dppm)$_2$]$^+$ (R = CO$_2$Me) (**48**), in which the methyl group remains terminal on Ir (as shown in Sheme 4.3). The $^{13}C\{^1H\}$ NMR spectrum of **48** indicates the presence of a semi-bridged carbonyl group, at δ 216.5 ($^1J_{RhC}$ = 18.6 Hz), in addition to one carbonyl on each metal. The structural formulation for **48** in which the methyl group is proposed to be positioned adjacent the bridging alkyne is based on the absence of trans coupling between the two CO groups on Ir. A similar cis orientation between the alkyne and methyl groups has been established crystallographically for the related diiridium species [Ir$_2$(CH$_3$)-(CO)$_2$(μ-DMAD)(dppm)$_2$]$^+$, which was obtained by a similar sequence of steps.[12] As has been observed for several of our systems,[25] the Ir(III) center is octahedral whereas the Rh(I) center is square planar; both are the preferred geometries. Surprisingly, no migratory insertion of the alkyl and alkyne groups in **48** is observed in spite of its identical stoichiometry with that of the alkyne-inserted product [RhIr(CO)$_3$(RC=C(CH$_3$)R)(dppm)$_2$]$^+$ (R = CO$_2$Me).

In order to further probe the factors leading to the formation of the alkyne-inserted product in the previous study, and anticipating that coupling of the methyl and alkyne groups might occur more readily at the more labile Rh center, CO was added to intermediate **46** in which the methyl group is bound to Rh. Addition of CO to **46** at -60 °C generates the tricarbonyl species [RhIr(CH$_3$)(CO)$_3$(μ-RC=CR)(dppm)$_2$][CF$_3$SO$_3$] (R = CO$_2$Me) (**49**), in which the methyl group is still bound to Rh as shown by its triplet of doublet resonance at

Scheme 4.4



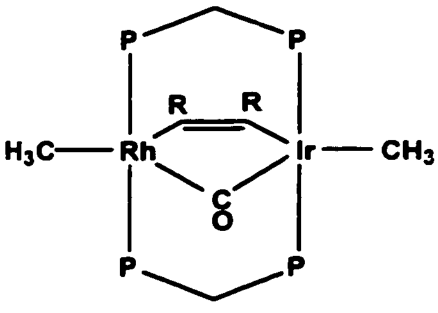
Boxed compound has been previously characterized.

δ -0.17 in the ^{1}H NMR spectrum. The $^{13}C\{^1H\}$ NMR spectrum displays carbonyl resonances at δ 195.6 ($^1J_{RhC}$ = 46.0 Hz), 184.8 and 160.1, and the magnitude of the Rh-C coupling of the low-field resonance, which is lower than expected (*ca.* 55-80 Hz) for a purely terminal Rh-bound carbonyls, suggests that it may be involved in a weak semi-bridging interaction with the adjacent Ir center.

Upon warming to ambient conditions, compound **49** disappears, to be replaced by two species; one is the targeted vinyl species $[RhIr(CO)_3(\mu\text{-}RC{=}C\text{-}(CH_3)R)(dppm)_2][CF_3SO_3]$ (R = CO_2Me)[3a] while the other is formulated as an acyl species, $[RhIr(COCH_3)(CO)_2(\mu\text{-}RC{=}CR)(dppm)_2][CF_3SO_3]$(R = CO_2Me) (**50**). The ^{1}H NMR spectrum for **50** shows the acetyl protons as a singlet at δ 0.92, which appears as a doublet ($^2J_{CH}$ = 5.5 Hz) if the CO groups in the starting material and added CO are isotopically (^{13}CO) labelled. The acetyl CO group displays a characteristic low-field resonance at δ 237.6 with a coupling to Rh of 25.5 Hz in the $^{13}C\{^1H\}$ NMR spectrum, and the carbonyl ligand resonances are observed at δ 193.1 ($^1J_{RhC}$ of 49.3 Hz) and δ 184.5; the lower-field resonance is attributed to a terminal CO group on Rh which is weakly bound to Ir while the high-field resonance is assigned to a terminal carbonyl on Ir. As was the case with **46**, compound **50** is proposed to have a structure in which the Rh center is the more coordinatively saturated site.

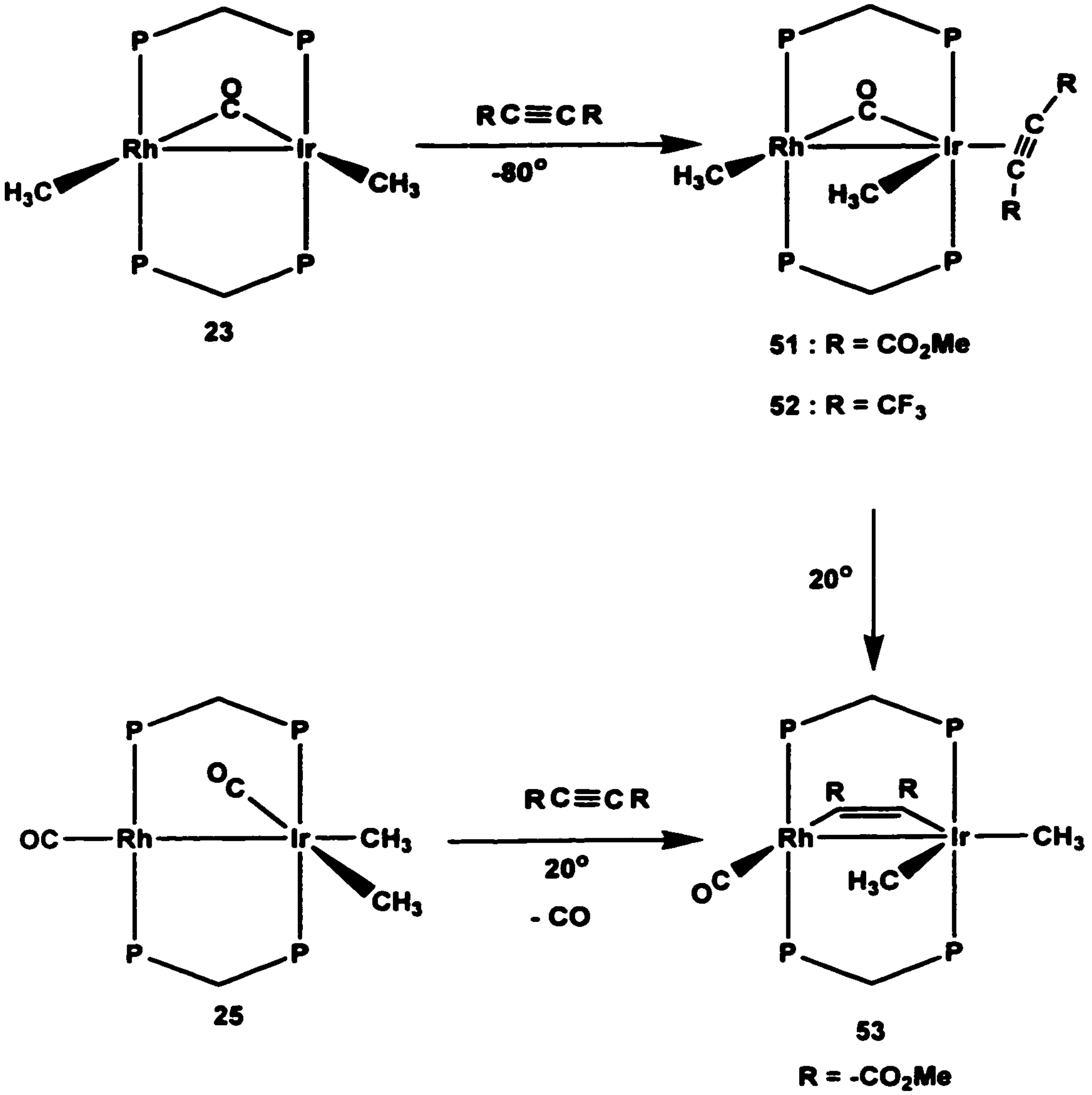
The targeted vinyl compound is exactly that previously obtained in the reaction of $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**1**) with DMAD. Its generation from **49** but not from **47** is in accord with the greater lability at Rh[26] and the expected lower tendency of Ir to undergo migratory insertion.[27] Preliminary results of the reaction of the tricarbonyl species $[RhIr(CH_3)(CO)_3(dppm)_2]^+$ (**1**) with DMAD at low-temperature indicated the presence of trace amounts of **49** in the $^{31}P\{^1H\}$ NMR spectrum, reinforcing the view that in this case also, migratory insertion occurs at Rh. Although this is the anticipated site of migratory insertion, there are cases in this thesis and elsewhere[28] in which insertion appears to occur at the less labile, third-row metal. Attempts to obtain crystals of the alkyne-inserted species have failed, yielding only poor quality crystals. Removal of one carbonyl from the vinyl species using Me_3NO, yields mainly compound **47**, resulting from de-insertion of the methyl and alkyne groups, in addition to an incompletely characterized product formulated as a monocarbonyl alkyne-bridged species arising from further decarbonylation of **47**.

Having observed one example of alkyne insertion involving monomethyl complexes, we turned our attention to the dimethyl complexes described in Chapter 3. The dimethyl A-frame complex $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**) reacts with DMAD at -80 °C to give an η^2-alkyne adduct $[RhIr(CH_3)_2(\mu\text{-}CO)(\eta^2\text{-}RC_2R)(dppm)_2]$ (**51** : R = CO_2Me), having the structure proposed in Scheme 4.5, and resulting from attack of the alkyne at Ir on the outside of the A-frame. An alternate structure that also conforms to the spectral data is that shown below (**A**), in which the alkyne molecule bridges the metals; in particular, the bridging carbonyl resonance at δ 218.8 ($^1J_{RhC}$ = 34.4 Hz) observed for **51** in the $^{13}C\{^1H\}$ NMR spectrum, is consistent with both formulations. We rule out this DMAD-bridged structure for a number of reasons. In an analogous study, the A-frame



A

Scheme 4.5

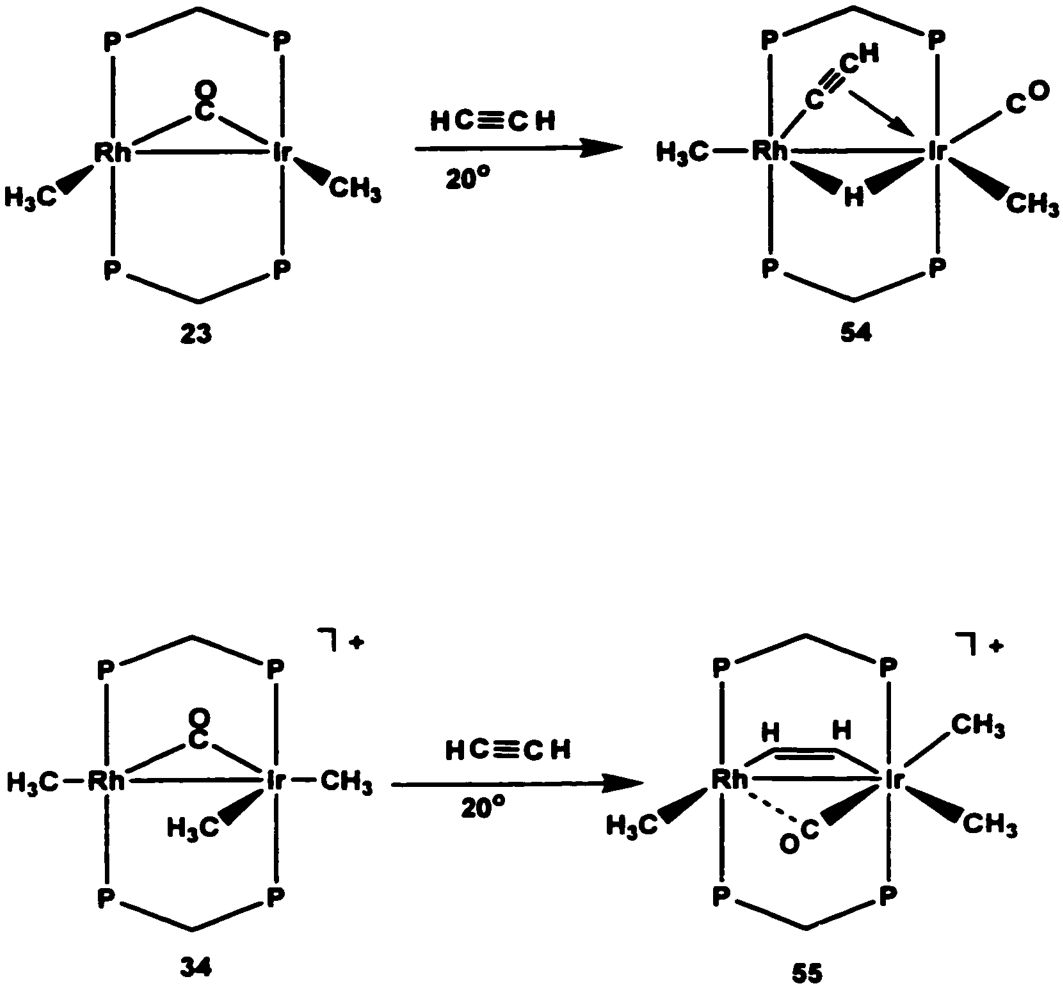

RC≡CR
-80°
20°
RC≡CR
20°
- CO
P
Rh
Ir
H_3C
CH_3
OC
23
51 : R = CO_2Me
52 : R = CF_3
25
53
R = $-CO_2Me$

species $[RhIr(\mu\text{-}CO)_2(C_2Ph)(dppm)_2]^+$ was shown[10a] to retain the alkynyl group in its bridging site with the added alkynes and olefins binding to Ir in an η^2 fashion. In addition, we would anticipate that the ^{31}P NMR parameters in structure **A** would differ from those of the precursor (**23**) for both the Rh- and Ir-bound phosphines. Instead the Rh-bound phosphines appear at almost the same chemical shift as in the precursor (δ 32.6 (**51**) *vs* 31.9 (**23**)) indicating little change at this metal whereas there is a dramatic shift in the ^{31}P resonances (δ -9.3 (**51**) *vs* 21.5 (**23**)) at the Ir-bound phosphorus nuclei indicating a substantial change at Ir. A similar trend in ^{31}P NMR spectral characteristics (significant change at the Ir end only) has been reported[4b] for the related A-frame $[RhIr(CO)_2(\mu\text{-}S)(\eta^2\text{-}C_4F_6)(dppm)_2]$ in which the alkyne was coordinated at Ir. Upon warming to 0 °C, **51** transforms to the alkyne-bridged monocarbonyl product $[RhIr(CH_3)_2(CO)(\mu\text{-}RC_2R)(dppm)_2]$ (**53**: R = CO_2Me), in addition to trace amounts of other uncharacterized species in solution. Alternatively, compound **53** can be more conveniently synthesized from the reaction of the dicarbonyl species $[RhIr(CH_3)_2(CO)_2(dppm)_2]$ (**25**) (see Chapter 3) with 1 equiv of DMAD at room temperature. The ^1H NMR spectrum for **53** shows that both methyl groups are now bound to Ir (triplets at δ 0.63 and -0.90), one of them having migrated from Rh to Ir, while the $^{13}C\{^1H\}$ NMR spectrum displays only one peak at δ 196.7 ($^1J_{RhC}$ = 62.3 Hz) attributed to a terminal carbonyl group on Rh. Based on the previous case of alkyne insertion into the Rh-CH_3 bond, it is suggested that the absence of migratory insertion in this case results from the absence of an isomer in which the bridging DMAD group is adjacent to a methyl group on the more labile Rh center.

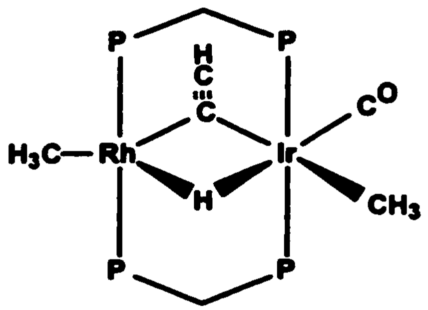
The reaction of **23** with hexafluorobutyne (HFB) at -60 °C also gives rise to the η^2-alkyne species $[RhIr(CH_3)_2(\mu\text{-}CO)(\eta^2\text{-}C_2(CF_3)_2)(dppm)_2]$ (**52**), assumed to have a structure like **51**, on the basis of closely comparable spectral parameters. The slight downfield shift of the Ir-bound ^{31}P nuclei (δ -5.8 *vs* -9.3) for **52** compared to **51**, is consistent with the greater π-acidity of the CF_3 groups[26] compared to the CO_2Me, resulting in greater deshielding at Ir. The ^{19}F NMR spectrum exhibits two broad peaks with no resolvable P-F coupling at δ -50.4 and -52.0 for the trifluoromethyl groups. Compound **52** is unstable at higher temperatures (> -40 °C) decomposing to several unidentified species. The intermediacy of terminal π-bound DMAD and HFB species, which has been postulated in the reaction of DPM-bridged complexes with alkynes, and seen in this study and in others,[4b,10,29] has demonstrated that neutral dimethyl η^2-alkyne complexes are accessible. It is interesting that most of the binuclear complexes containing η^2-DMAD and η^2-HFB groups, have been obtained from A-frame precursors, in which the bridgehead ligand does not readily move from bridging to terminal coordination modes,[4b,10,30] thereby inhibiting movement of the alkyne from its initial site of attack to its favored bridging coordination mode.

The reaction of **23** with acetylene proceeds differently from that described for DMAD and HFB. In the presence of excess substrate, three hydride products are produced which are difficult to characterize owing to the complexity of the spectra. Using approximately one equivalent instead, only one of these products is observed and is identified as $[RhIr(CH_3)_2(CO)(\mu\text{-}C_2H)(\mu\text{-}H)(dppm)_2]$ (**54**), shown in Scheme 4.6. The ^1H NMR spectrum for **54** indicates that the methyl groups have remained bound, one to each metal, the hydride signal appears as a multiplet at δ -13.28 ($^1J_{RhH}$ = 12.0 Hz), indicating that it bridges the metals while the acetylide proton resonates as a multiplet at δ 5.58. The carbonyl group has moved from a bridging site in **23** to a terminal position in **54** as revealed by the triplet at δ 174.2 in the $^{13}C\{^1H\}$ NMR spectrum. If the carbon atoms of the acetylene are ^{13}C-enriched, additional peaks appear at δ 138.1 (doublet of doublets of multiplets, $^1J_{CC}$ = 55.4 Hz, $^1J_{RhC_\alpha}$ = 23.8 Hz,

Scheme 4.6



$^2J_{RhC_\beta}$ = 3.7 Hz) and δ 116.1 (doublet of multiplets), assigned to the C_α and C_β atoms of the acetylide groups on the basis of similarities to chemical shifts for carbon nuclei reported for several related compounds in our group.[3a,10] Although the magnitude of the Rh-C_α is lower than that expected for a $^1J_{RhC_\alpha}$ (40-60 Hz),[2i-l] it is significantly larger than those commonly observed for a $^1J_{RhC_\alpha}$ ≈ $^1J_{RhC_\beta}$ (3-9 Hz)[10] in complexes in which the acetylide is σ bound to Ir and π bonded to Rh. Significantly, it is close to *ca.* 26.2 Hz observed for the trimethyl bridging acetylene complex **55** (described later), indicating the possibility of a partial rehybridization of the acetylide carbons towards sp^2 due to π interaction with the adjacent Ir center. Selective $^{13}C\{^{31}P\}$ NMR experiments reveal that whereas both C_α and C_β carbons of the acetylide couple equally with the Ir-bound ^{31}P nuclei ($^2J_{PC}$ = 8.0 Hz), only the C_α carbon shows coupling to the Rh-bound ^{31}P nuclei ($^2J_{PC}$ = 11.1 Hz). Both ^{13}C resonances give simple doublet of doublets upon broad-band decoupling of the ^{31}P nuclei, with the high-field resonance displaying a small coupling to Rh of 3.7 Hz. The above spectroscopic evidence supports the proposed formulation for **54**, as diagrammed in Scheme 4.6, in which the acetylide ligand is σ-bound to the less basic Rh center while π-bound to Ir. This is opposite of what is normally observed for acetylide adducts involving the these RhIr systems in which the acetylide group preferentially binds to the more basic Ir center.[3a,10] We have considered the possibility of an alternate formulation for **54** in which the acetylide ligand binds to both metals in a symmetrically-bridged fashion as diagrammed below (**B**). However, this formulation is less likely for a number of reasons.



B

First, we would have expected a much lower chemical shift for the C_α nucleus than was observed (*vide supra*). In addition, the results of the $^{31}P\{^{13}C\}$ experiments do not agree with such a formulation for which both Rh- and Ir-bound phosphines ought to show coupling to the C_β atom. We are also not aware of examples of symmetrically-bridged acetylide complexes of late transition metals, although such complexes of main-group metals[31] and organocopper clusters[32] are known. Reductive elimination of methane from **54** is not observed, in spite of the cis-hydride/methyl alignment. This finding is reminiscent of that demonstrated by the cis dihydrido-dimethyl species[9] (**30**) but is unlike that observed for the monomethyl hydrides (**11**, **14**, **15**, **39**) which have tended to be stable only at sub-ambient temperatures.[3a]

The cationic trimethyl species $[RhIr(CH_3)_3(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**34**) reacts with acetylene at -40 °C, yielding the alkyne-bridged species $[RhIr(CH_3)_3(\mu\text{-}CO)(\mu\text{-}C_2H_2)(dppm)_2][CF_3SO_3]$ (**55**). The acetylene protons appear as a doublet of triplets and a broad unresolved signal at δ 8.08 ($^2J_{RhH}$ = 2 Hz) and 6.28, respectively. Selective decoupling the Rh-bound ^{31}P resonance results in simplification of the resonance at 8.08 to a doublet, whereas irradiating the Ir-bound ^{31}P signal results in significant sharpening of the broad peak at 6.28, suggesting that the upfield signal corresponds to the hydrogen adjacent to Ir. This trend in chemical shifts in which the proton adjacent to Rh appears downfield of that which is adjacent to Ir, parallels a similar finding[3a] for the monomethyl acetylene-bridged species $[RhIr(CH_3)(CO)_3(\mu\text{-}C_2H_2)(dppm)_2]^+$ (δ 9.12 *vs* 7.63), providing further support for the formulation for **55** as diagrammed in Scheme 4.6. The $^{13}C\{^1H\}$ NMR spectrum, prepared with ^{13}C-enriched C_2H_2, displays peaks at δ 130.4 (doublet of doublets of multiplets, $^1J_{RhC}$ = 26.2 Hz, $^1J_{CC}$ = 70.4 Hz) and 94.6 (doublet of multiplets). The carbonyl group has moved from a symmetrical bridging site in **34** to a semi-bridging position in **55** as revealed by its weak coupling to Rh (δ 194.6, $^1J_{RhC}$ = 6.4 Hz). In spite of its formulation in which the carbonyl and the alkyne are each bordered by two methyl groups, and the two methyls are adjacent, **55** displays no apparent tendency to reductively eliminate ethane or undergo C-C bond-formion leading to acetyl or vinyl products. Compound **55** is surprisingly robust, showing no tendency to rearrange to a vinylidene product after several days in solution. Attempts at carbonylating this species in order to induce C-C coupling failed, with no reaction being observed. presumably due to the coordinative saturation at both metals. The reaction of **34** with DMAD at ambient temperature gave a number of unidentified products, and so was not pursued further.

Conclusions

The results of this study have demonstrated two site-specific processes in reactions involving the monomethyl complex **2** and the bisacetylide complex **43**. In the first, it was shown that the C-C bond forming processes leading to the formation of the vinyl complex $[RhIr(CO)_3(\mu\text{-}RC{=}C(CH_3)R)(dppm)_2][CF_3SO_3]$ ($R = CO_2Me$) and the acetyl species **50**, occurred only for species having the methyl group bound to Rh in the low-temperature intermediate. When the methyl group is bound to Ir simple CO coordination occurs. Site-specific reactions were also observed for the reaction of hydride sources with **43**. When $NaBH_4$ is used, yielding the vinylidene complex **44**, attack of the substrate presumably occurs at Rh followed by a 1,2 hydride migration onto a bridging acetylide ligand. In the second reaction using Super-Hydride ($Li(HBEt_3)$), and yielding the rare formyl complex **45**, hydride attack is assumed to occur directly at a coordinated carbonyl.

A number of η^2-alkyne complexes of neutral dimethyl complexes $[RhIr(CH_3)_2(\mu\text{-}CO)(\eta^2\text{-}C_2R_2)(dppm)_2]$ (**51** : R = CO_2CH_3; **52** : R = CF_3) have been observed at sub-ambient temperatures. Compound **51** was shown to rearrange, upon warming, to an alkyne-bridged species which results from facile migration of a methyl group from Rh to Ir. Such methyl migrations have become ubiquitous in these RhIr systems.

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Chapter 5

Oxidative-Addition Reactions of Silanes

Introduction

The chemistry of transition-metal complexes containing metal-silicon bonds occupies a prime position in studies of metal-mediated catalytic processes such as olefin hydrosilation,[1] reduction of oxygen-containing functional groups[2] and silane oligomerization.[3] In addition, there are close analogies between Si-H and H-H bonds in silanes and dihydrogen,[4,5] as demonstrated by their analogous chemistry involving oxidative additions to low-valent metal centers and metal-catalyzed addition reactions of unsaturated organic substrates. In this chapter, we extend the studies on the reactions of the monomethyl species $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) and the related A-frame dimethyl species $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**) with dihydrogen, to reactions involving secondary silanes with the intent of comparing both chemistries. We are interested in the possibility of promoting Si-C bond formations mediated by adjacent metal centers since silyl groups are expected to behave much like the congeneric alkyl group[1a,e] in such important transformations as migratory insertions, C-heteroatom couplings and reductive elimination processes. The possibility of inducing dehydrogenative silane coupling leading to Si-Si bond formation[3d,f,h,k] was of additional interest. Furthermore, the target metal-alkyl-silyl complexes would offer the unique opportunity to directly compare the relative aptitudes of methyl and silyl groups to undergo migratory insertions.

Previous work involving the oxidative addition of silanes to the low-valent homobinuclear complexes $[M_2(CO)_3(dppm)_2]$ (M = Rh, Ir) carried out by

Eisenberg and co-workers[5b,d] and by members of our research group[5a] have demonstrated facile activation of two Si-H bonds, presumably at different metals, leading to silylene-bridged products. This present work is also aimed at extending this chemistry to the mixed-metal Rh/Ir system in the hope that the different combination of metals will reflect a different reactivity pattern.

Experimental Section

General Comments. General experimetal conditions were as described in Chapters 2 and 3. Diphenylsilane and diethylsilane were purchased from Petrarch Systems Inc., and were distilled and dried over CaH_2 prior to use, while dimethylsilane was supplied by Gelest Inc and was used as received. The compounds $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**),[6] $[RhIr(CO)_2(\mu\text{-}C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**42**),[7] $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**),[8] and $[RhIr(CO)_3(dppm)_2]$[5a] were prepared as previously described. Spectroscopic parameters for the new compounds are given in Table 5.1.

Preparation of Compounds.

(a) Low-temperature reaction of $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (2) with H_2SiPh_2. 30 mg (0.023 mmol) of **2** was dissolved in 0.5 mL of CD_2Cl_2 in an NMR tube at -78 °C. H_2SiPh_2 (4.3 μL, 0.023 mmol) was syringed into the sample, producing an immediate change in color of the solution from dark orange to light yellow. NMR analyses carried out at -60 °C indicated that $[RhIr(CH_3)(SiHPh_2)(CO)_2(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**56**) was the major product in solution. Upon warming to 0 °C, compound **56** was replaced by $[RhIr(CH_3)(CO)_2(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^2\text{-}SiHPh_2)(dppm)_2][CF_3SO_3]$ (**57**). Finally at room temperature, two new species $[RhIr(COCH_3)(CO)(H)(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2][CF_3SO_3]$ (**58**)

Table 5.1. Spectroscopic Parameters for the Compounds^a

Compounds	IR,^{b,c}cm^{-1}	NMR^d		
		δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C{^{1}H})
[RhIr(CH$_3$)(CO)$_2$(μ-H)(SiHPh$_2$)(dppm)$_2$][CF$_3$SO$_3$] **(56)**^{f}	-	28.1(dm,$^1J_{RhP}$=132.9Hz) -8.3(bm)	5.50(td,1H), 4.12(m,2H) 3.59(m,2H), 0.42(td,3H) -8.49(dm,$^1J_{RhH}$=13.2Hz,1H)	216.5(dm,$^1J_{RhC}$=29.2Hz, 1C), 173.8(bs,1C), 15.1 (d,$^1J_{RhC}$=27.1Hz,1C)
[RhIr(CH$_3$)(CO)$_2$(μ-H)(μ-η^1:η^2-SiHPh$_2$)(dppm)$_2$][CF$_3$SO$_3$] **(57)**^{g}	-	21.7(dm,$^1J_{RhP}$=99.5Hz) -14.9(m)	4.12(m,2H), 3.26(m,2H) 0.75(t,3H), -0.73(ddm, $^1J_{RhH}$=23.2Hz,$^2J_{HH}$=6.5Hz, $^2J_{PH}$=9.0Hz,1H), -9.22(dm, $^1J_{RhH}$=13.1Hz,1H)	192.9(dt,$^1J_{RhC}$=64.1Hz,1C) 178.0(bs,1C), -22.6(t, $^2J_{PC}$=6.0Hz,1C)
[RhIr(COCH$_3$)(CO)(μ-H)(H)(μ-SiPh$_2$)(dppm)$_2$][CF$_3$SO$_3$] **(58)**	1938(ss),^{c,e} 1602(s)^{c,e} 2020(m),^{c,e} 1980(ss)^{c,e}	25.0(dm,$^1J_{RhP}$=118.6Hz) 1.8(m)	4.28(m,2H), 3.49(m,2H) 1.24(s,3H) -8.86(t,1H), -14.98 (dm, $^1J_{RhH}$=21.0Hz, $^2J_{P(Ir)H}$=13.2Hz,$^2J_{P(Rh)H}$= 10.9Hz,1H)	279.8(d,$^1J_{CC}$=25.5Hz,1C) 193.7(dt,$^1J_{RhC}$=70.8Hz, 1C), 46.0(d,$^1J_{CC}$=25.5Hz, 1C)
[RhIr(CO)$_2$(μ-H)(μ-SiPh$_2$)(dppm)$_2$][CF$_3$SO$_3$] **(59)**	-	22.1(dm,$^1J_{RhP}$=113.4Hz) -6.9(m)	4.42(m,2H), 4.20(m,2H) 3.98(b,1H), -10.22(b,1H)	187.6 (dm, $^1J_{RhC}$=77.3Hz 1C), 176.8(t, 1C)

Table 5.1 (contd)

		NMR[d]		
Compounds	IR,[b,c] cm^{-1}	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(CO)_2(\mu\text{-}H)_2\text{-}(Si(OH)Me_2)(dppm)_2]\text{-}[CF_3SO_3]$ (**60**)	2040(m), 1981(ss)	22.5(dm, $^1J_{RhP}$=109.8Hz) -4.4(m)	4.58(m,2H), 4.30(m,2H), 3.80 (tsept, $^4J_{HH}$=3.1Hz, $^4J_{HH}$=4.0Hz, 1H), -0.12(d, $^4J_{HH}$=4.0Hz,6H), -9.72(dm, $^1J_{RhH}$=14.0Hz,1H), -10.64(dm, $^1J_{RhH}$=16.9Hz,1H)	186.9(dt, $^1J_{RhC}$=76.4Hz, 1C), 177.7(t,1C)
$[RhIr(CO)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SiPh_2C{\equiv}CCH_2Ph)(\mu\text{-}H)(H)\text{-}(CO)(dppm)_2][CF_3SO_3]$(**61**)	2061(m),[f] 1972(ss)	25.8(dm, $^1J_{RhP}$=108.0Hz) -10.8(m)	4.02(m,2H), 3.83(dm,2H), 2.47(s,2H), -9.64(dm, $^1J_{RhH}$ =15.0Hz, $^2J_{P(Rh)H}$=11.8Hz, $^2J_{P(Ir)H}$ =14.3Hz,1H), -10.45(t,1H)	191.9(dt, $^1J_{RhC}$=81.2Hz,1C), 167.1(t,1C), 93.4 (d, $^1J_{RhC}$= 5.4Hz,1C), 60.4 (d, $^1J_{RhC}$= 5.4Hz,1C), 15.4(s,1C)
$[RhIr(CO)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SiMe_2C{\equiv}CCH_2Ph)(\mu\text{-}H)(H)\text{-}(CO)(dppm)_2][CF_3SO_3]$(**62**)	2057(ms),[f] 1959(ss)	26.2(dm, $^1J_{RhP}$=107.6Hz) -10.6(m)	4.08(m,2H), 3.92(m,2H), 2.57 (s,2H), -0.08(s,3H) -0.10 (s,3H), -9.63(dm, $^1J_{RhH}$ =15.7Hz,1H), -10.42(t,1H)	192.8(dt, $^1J_{RhC}$=80.8Hz, 1C) 167.2(t,1C), 93.7(b,1C), 60.5 (d, $^1J_{RhC}$=6.0Hz,1C), 15.7 (s,1C), -1.3(s,1C), -1.5(s,1C)

Table 5.1 (contd)

Compounds	IR,[b,c] cm^{-1}	NMR[d]		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(CH_3)_2(CO)(H)$- $(SiHEt_2)(dppm)_2]$ (**63**)[h]	-	39.9(dm, $^1J_{RhP}$=142.5Hz) 8.0(m)	3.69(b,1H), 3.42(m,2H) 3.12(m,2H), 0.62(q,4H) 0.53(t,6H), 0.30(t,3H) -0.49(td,3H), -10.61(t,1H)	255.1(dm, $^1J_{RhC}$=28.1Hz, 1C)
$[RhIr(CH_3)_2(CO)(H)$- $(SiHMe_2)(dppm)_2]$ (**64**)	1960(m)	39.8(dm, $^1J_{RhP}$=142.3Hz) 9.2(m)	3.69(b,1H), 3.45(m,2H) 2.98(m,2H), 0.18(s,3H) 0.16(s,3H), 0.24(t,3H) -0.52(td,3H), -10.75(t,1H)	254.8(dm, $^1J_{RhC}$=32.7Hz, 1C)
$[RhIr(CH_3)_2(CO)(H)$- $(SiHPh_2)(dppm)_2]$ (**65**)[i]	-	25.5(dm, $^1J_{RhP}$=147.0Hz) 13.5(dm, $^1J_{RhP}$=162.0Hz) -11.1(m),-13.6(m)	4.56(m,1H), 4.45(m,1H) 4.19(m,1H), 4.04(dd,1H) 3.52(m,1H), -0.12(td,3H) -0.72(t,3H), -10.60(dd, $^2J_{PH}$ =45.0Hz, $^2J_{PH}$=13.0Hz,1H)	210.5(dm, $^1J_{RhC}$=33.1Hz, 1C)
$[RhIr(CH_3)(CO)(\mu\text{-}H)(H)$- $(SiMePh_2)(dppm)_2]$ (**66**)[g]	-	28.2(dm, $^1J_{RhP}$=113.8Hz) 0.97(m)	4.39(m,2H), 4.24(m,2H) 0.32(t,3H), -0.26(s,3H),-9.18 (dm, $^1J_{RhH}$=16.5Hz, $^2J_{P(Rh)H}$= 9.8Hz, $^2J_{P(Ir)H}$=12.1Hz,1H)	190.4(dt, $^1J_{RhC}$=68.4Hz, 1C)

Table 5.1 (contd)

		NMR^d		
Compounds	IR,^{b,c}cm^{-1}	δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C{^{1}H})
[RhIr(CO)$_2$(H)$_2$(μ-SiPh$_2$)-(dppm)$_2$] (**67**)	1887(ss) 1900(ss)	20.5(dm, $^1J_{RhP}$=112.0Hz) -13.2(m)	4.83(m,2H), 3.18(m,2H) -9.72(dm, $^1J_{RhH}$=13.9Hz, 1H), -11.83(m,1H)	198.7(dt, $^1J_{RhC}$=69.4Hz, 1C), 182.9(t,1C)
[RhIr(CO)$_4$(μ-SiPh$_2$)-(η^1-Ph$_2$PCH$_2$PPh$_2$)(μ-dppm)] (**68**)	-	P$_A$ 17.0(ddd, $^1J_{RhP}$=100.8), P$_B$ −11.3(dd), P$_C$ −11.2 (ddd, $^1J_{RhP}$=11.9Hz) P$_D$ -27.3 (dd) J(P$_A$P$_B$)=124.7Hz, J(P$_B$P$_D$)=5.0Hz, J(P$_C$P$_D$)= 40.0Hz, J(P$_A$P$_C$)=4.7Hz.	3.18 (m,1H), 3.15 (m,1H), 2.82 (m,1H), 3.30 (m,1H),	212.4(dm, $^1J_{RhC}$=5.6Hz,1C), 201.7(dm, $^1J_{RhC}$=71.8Hz, 1C), 201.6(dm, $^1J_{RhC}$= 73.6Hz, 1C), 185.3(b,1C)
[RhIr(CO)$_3$(μ-SiPh$_2$)-(dppm)$_2$] (**69**)	-	P$_A$ 37.8(ddd, $^1J_{RhP}$= 106.7Hz), 27.5 (ddd, $^1J_{RhP}$=97.8Hz), P$_C$ 1.5(dd) P$_D$ -5.3(dd) J(P$_A$P$_B$)= 30.2Hz, J(P$_A$P$_C$) =254.9Hz, J(P$_B$P$_D$) =155.6Hz, J(P$_C$P$_D$)=22.3Hz,	4.37(m,1H), 3.98(m,1H) 2.66(m, 1H), 2.32(m, 1H)	227.6(dm, $^1J_{RhC}$ = 40.7Hz, 1C), 201.3(dm, $^1J_{RhC}$= 70.0Hz, 1C), 186.0 (bs, 1C),

Table 5.1 (contd)

		NMR^d		
Compounds	IR^{b,c}	δ (^{31}P{1H})	δ (^{1}H)	δ (^{13}C{^{1}H})
[RhIr(CO)$_3$(H)(μ-SiPh$_2$)-(SiHPh$_2$)(η^1-Ph$_2$PCH$_2$PPh$_2$)-(μ-dppm)] **(70)**	2031(w)^c 1972(ss)^c, 1943(m)^c	P$_A$ 2.1(ddd, $^1J_{RhP}$=94.3Hz), P$_B$ -10.7(ddd), P$_C$ -3.6(dddd, $^1J_{RhP}$=5.1Hz) P$_D$ -29.6(dd) J(P$_A$P$_B$)=102.6Hz, J(P$_B$P$_C$)= 6.5Hz, J(P$_B$P$_D$)=8.3Hz, J(P$_C$P$_D$)= 35.6Hz, J(P$_A$P$_C$)=5.6Hz.	5.50(m,1H), 5.38(d, $^3J_{PH}$= 4.0Hz,1H), 3.78(m,1H), 3.30 (m,1H), 2.75(m,1H), -10.46 (dd, $^2J_{PH}$=12.3Hz, $^2J_{PH}$=8.0Hz 1H)	203.9(dddd, $^1J_{RhC}$=55.8Hz, $^2J_{PC}$=24.1Hz, $^3J_{PC}$=8.6Hz $^2J_{CC}$=22.3Hz,1C), 201.7 (dddd, $^1J_{RhC}$=55.3Hz, $^2J_{PC}$=22.3Hz, $^3J_{PC}$=9.4Hz 1C), 186.1(bs,1C)
[RhIr(CO)$_3$(H)(μ-SiMe$_2$)-(SiHMe$_2$)(η^1-Ph$_2$PCH$_2$PPh$_2$) (μ-dppm)] **(71)**	1999(m), 1977(m)	P$_A$ 6.6(ddd, $^1J_{RhP}$=100.3Hz), P$_B$ -9.9(ddd), P$_C$ 0.1(ddd) P$_D$ -26.7(dd) J(P$_A$P$_B$)= 111.3Hz, J(P$_B$P$_C$)= J(P$_A$P$_C$) =6.1Hz, J(P$_B$P$_D$) =3.0Hz, J(P$_C$P$_D$)=50.6Hz	4.84(m,1H), 4.40(m,1H) 4.20(dtt, $^3J_{HH}$=4Hz, $^3J_{PH}$= 7.9Hz,1H), 2.92(m, 2H), 0.84(m, $^4J_{PH}$=3.2Hz, 3H), 0.75(m, $^4J_{PH}$=3.2Hz, 3H), 0.24(d, $^3J_{HH}$=4.0Hz, 3H), 0.17(d, $^3J_{HH}$=4Hz, 3H) -11.18(dd, $^2J_{PbH}$=15Hz, $^2J_{PcH}$=14Hz,1H)	204.5(dddd, $^1J_{RhC}$=55.0Hz, $^2J_{CC}$=21.8Hz, $^2J_{PC}$= 19.1Hz, $^3J_{PC}$=6.3Hz 1C), 203.4 (dddd, $^1J_{RhC}$= 55.5Hz, $^2J_{PC}$=19.0Hz, $^3J_{PC}$=8.9Hz 1C), 187.4(bs,1C)

Table 5.1 (contd)

Compounds	IR^{b,c}	NMR^d		
		δ ($^{31}P\{1H\}$)	δ (^1H)	δ ($^{13}C\{^1H\}$)
$[RhIr(CO)_3(H)(\mu\text{-}SiPh_2)\text{-}(SiHPh_2)(\eta^1$ $Ph_2PCH_2PPh_2Me)\text{-}(\mu\text{-}dppm)][CF_3SO_3]$ **(72)**	2036(w)^c, 1980(ss)^c 1953(m)^c	P_A 1.4(ddd,$^1J_{RhP}$=95.4Hz), P_B -10.2(ddd), P_C -8.2 ddd) P_D 14.2(dd) J(P_AP_B)= 100.1Hz,J(P_BP_C)=16.6Hz, J(P_BP_D)=15.1Hz,J(P_CP_D)= 43.0Hz,J(P_AP_C)=6.0Hz	5.38(dd,$^2J_{RhH}$=2.0Hz,$^3J_{PH}$= 8.0Hz,1H), 5.47(m,1H), 3.98(m,1H), 3.78(m,1H), 3.44(m,1H), 1.96(d,$^2J_{PH}$= 13.0Hz,3H), -10.52(dd, $^2J_{PH}$ =19.1Hz,$^2J_{PH}$=14.2Hz,1H)	203.3(dddd,$^1J_{RhC}$=54.4Hz, $^2J_{CC}$=24.4Hz, $^2J_{PC}$=15.7Hz. $^3J_{PC}$=9.9Hz 1C),200.4(dddd, $^1J_{RhC}$=57.6Hz,$^2J_{PC}$=16.2Hz, $^3J_{PC}$=7.4Hz 1C), 184.6(bs,1C)
$[RhIr(CO)_3(H)(\mu\text{-}SiMe_2)\text{-}(SiHMe_2)(\eta^1\text{-}Ph_2PCH_2PPh_2Me)$ $(\mu\text{-}dppm)][CF_3SO_3]$ **(73)**	2033 (m), 1974 (bs)	P_A 5.3(ddd,$^1J_{RhP}$=98.7Hz), P_B –9.1(ddd), P_C –5.3(ddd) P_D 16.8(dd) J(P_AP_B)= 112.1Hz,J(P_BP_C)= J(P_AP_C) =7.0Hz,J(P_BP_D) =6.3Hz, J(P_CP_D)=35.7Hz,	4.95(m,1H), 4.32(m,1H) 4.25(dtt,$^3J_{HH}$=4.0Hz,1H), 3.79(m, 2H), 1.98(d,$^2J_{PH}$= 16.4Hz,3H), 0.84(m, $^4J_{PH}$=3.2Hz, 3H), 0.73(m, $^4J_{PH}$=3.2Hz, 3H), 0.24 (d, $^3J_{HH}$=4.0Hz, 3H), 0.17 (d, $^3J_{HH}$=4.0Hz, 3H) –11.18 (dd, $^2J_{PbH}$=7.1Hz, $^2J_{PcH}$=9.0Hz, 1H)	203.4(dddd,$^1J_{RhC}$=58.4Hz, $^2J_{CC}$=23.9Hz, $^2J_{PC}$= 17.5Hz, $^3J_{PC}$=6.2Hz 1C),202.2(dddd, $^1J_{RhC}$= 58.1Hz, $^2J_{PC}$=17.4Hz, $^3J_{PC}$=10.3Hz 1C), 186.6(bs,1C)

Table 5.1 (contd)

[a] IR abbreviations: ss = strong sharp, sb = strong broad, ms = medium sharp, m = medium, w = weak, sh = shoulder. NMR abbreviations: t = triplet, d = doublet, dt = doublet of triplets, dd = doublet of doublets, tt = triplet of triplets, ddt = doublet of doublets of triplets, ddm = doublet of doublets of multiplets, dm = doublet of multiplets, td = triplet of doublets, bs = broad singlet, m = multiplet, q = quartet, s = singlet. [b] Nujol mull except as indicated. Values quoted are ν(CO) except as indicated. [c] CH_2Cl_2 cast. [d] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4 while ^1H and $^{13}C\{^1H\}$ are referenced vs TMS. Chemical shifts for the phenyl hydrogens are not given in the ^1H NMR data. [e] ν(CO) values are for a mixture of compounds 7 and 8 [f] ν(C≡C). [g] -20 °C. [h] –40 °C. [i] –60 °C.

[j] –80 °C

and [RhIr(CO)$_2$(μ-H)(μ-SiPh$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**59**) were identified in solution. The presence of methane was identified in the ^{1}H NMR spectrum.

(b) [RhIr(CO)$_2$(SiMe$_2$(OH))(μ-H)$_2$(dppm)$_2$][CF$_3$SO$_3$] (60). 40 mg (0.031 mmol) of compound **2** was dissolved in 2 mL of THF. Dimethylsilane was slowly passed (0.20 mLs^{-1}) through the solution for *ca.* 1 min, causing a lightening of the deep orange color of the solution. Addition of 10 mL of ether precipitated a yellow solid, which was washed twice with 5 mL portions of ether and dried *in vacuo*. Anal. Calcd for IrRhSP$_4$SiF$_3$O$_6$C$_{55}$H$_{53}$: C, 49.03; H, 3.93. Found : C, 48.71; H, 3.83.

(c-d) [RhIr(CO)$_2$(H)(μ-H)(μ-η^1:η^2-SiR$_2$C$_2$CH$_2$Ph)(dppm)$_2$][CF$_3$SO$_3$] (R = Ph, (61); R = Me, 62) To a solution of [RhIr(CO)$_2$(μ-C$_2$CH$_2$Ph)(dppm)$_2$][CF$_3$SO$_3$] (**42**) (50 mg, 0.036 mmol in 10 mL of THF) was added H$_2$SiPh$_2$ (7 μL, 0.038 mmol) and the mixture was stirred for 3 h. Removal of the solvent and recrystallization from THF/pentane gave a yellow solid. Anal. Calcd for IrRhSP$_4$SiO$_5$F$_3$C$_{74}$H$_{63}$: C, 56.61; H, 4.27. Found: C, 56.37; H, 4.10. The preparation of the dimethylsilyl analogue **62** followed a similar procedure except that an atmosphere of dimethylsilane was placed over a solution of **42** and the product was isolated immediately to circumvent hydrolysis. (41 mg, 79%). Anal. Calcd for IrRhSP$_4$SiO$_5$F$_3$C$_{64}$H$_{59}$: C, 53.11; H, 4.08. Found : C, 53.16; H, 3.93.

(e) Reaction of [RhIr(CH$_3$)$_2$(μ-CO)(dppm)$_2$] (23) with H$_2$SiR$_2$. 30 mg (0.027 mmol) of **23** was dissolved in 0.6 mL of THF-d$_8$, in an NMR tube fitted with a septum cap, at -40 °C. Diethylsilane (3.5 μL, 0.027 mmol) was syringed into the sample and the mixture was then agitated briefly. The NMR analysis showed [RhIr(CH$_3$)$_2$(H)(SiHEt$_2$)(CO)(dppm)$_2$] (**63**) as the only species present in solution. Compound **63** decomposed to several unidentified compounds at temperatures above 0 °C, so its characterization was based on NMR spectroscopy. The preparation of [RhIr(CH$_3$)$_2$(H)(SiHMe$_2$)(CO)(dppm)$_2$] (**64**) was as described above except that an atmosphere of dimethylsilane gas was placed over the solution instead of diethylsilane. NMR analysis was performed at room temperature. The solution was then transferred to a flask and precipitated with 5 mL of pentane. Recrystallization from THF/pentane afforded an air-sensitive orange-yellow solid. (21 mg, 66%). A satisfactory elemental analysis could not be obtained due to the extreme air and moisture sensitivity of **64**.

(f) Low-temperature Reaction of Compound 23 with H_2SiPh_2. The procedure used in part (e) was duplicated except that the reaction was started at -80 °C and H_2SiPh_2 (5 µL, 0.027 mmol) was used. The NMR analysis carried out at -60 °C indicated the presence of $[RhIr(CH_3)_2(CO)(H)(SiHPh_2)(dppm)_2]$ (**65**) as the only species in solution. Upon warming the sample to 0 °C, a new compound $[RhIr(CH_3)(CO)(H)(SiMePh_2)(\mu\text{-}H)(dppm)_2]$ (**66**) was identified in solution. At this stage, CO gas was passed through the solution and the sample was allowed to warm to ambient conditions. NMR analysis carried out 1.5 h later showed quantitative conversion of **66** to the known $[RhIr(CO)_3(dppm)_2]$. Methane and $HSiMePh_2$ were also identified in the ^1H NMR spectrum.

(g) Reaction of $[RhIr(CO)_3(dppm)_2]$ with H_2SiPh_2. 30 mg (0.026 mmol) of $[RhIr(CO)_3(dppm)_2]$ was dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube at room temperature. Diphenylsilane (19 µL, 0.102 mmol) was added via a syringe. The spectra obtained on this solution within 15 min indicated the presence of the starting material and $[RhIr(CO)_2(H)_2(\mu\text{-}SiPh_2)(dppm)_2]$ (**67**) in a typical ratio of 7:2, respectively. Within 0.5 h, new peaks due to $[RhIr(CO)_3(H)(SiHPh_2)(\mu\text{-}SiPh_2)(dppm)_2]$ (**70**) appeared in the spectra in addition to those due to **67** and **2**. Compound **70** was the only product present in solution after 2 d in the NMR tube. Typical characterization of compound **67** required cooling the sample to *ca.* -40 °C after 13-15 min of reaction at room temperature or precipitating the product mixture using pentane. Compound **67** could not be obtained free from [RhIr(CO)$_3$(dppm)$_2$], so its characterization was based on NMR and IR spectroscopy.

(h) Reaction of Compound 67 with CO. A sample mixture containing **67** and [RhIr(CO)$_3$(dppm)$_2$] prepared as described in (g) above was redissolved in 0.5 mL of CD_2Cl_2 in an NMR tube and pressurized with CO (1.5 atm). The NMR analysis of the resulting mixture showed the presence of the tetracarbonyl species [RhIr(CO)$_3$(μ-CO)(μ-SiPh$_2$)(dppm)$_2$] (**68**) in addition to unreacted [RhIr(CO)$_3$(dppm)$_2$]. This reaction mixture was transferred to a 10 mL flask, the solvent was removed, and the deep orange residue was dried *in vacuo* for 1 h. The residue was redissolved in 0.5 mL of CD_2Cl_2, and the NMR analysis of this mixture indicated the formation of the tricarbonyl silylene species [RhIr(CO)$_2$(μ-CO)(μ-SiPh$_2$)(dppm)$_2$] (**69**). Addition of diphenylsilane to a solution containing **69** and [RhIr(CO)$_3$(dppm)$_2$] showed the presence of only compound **70** after 1 d in the NMR tube. Attempts to isolate **70** failed as only an intractable oil was obtained.

(i) [RhIr(CO)$_3$(H)(SiHMe$_2$)(μ-SiMe$_2$)(η^1-Ph$_2$PCH$_2$PPh$_2$)(dppm)] (71). A static atmosphere of dimethylsilane (H_2SiMe_2) was placed over a solution of [RhIr(CO)$_3$(dppm)$_2$] (40 mg, 0.035 mmol in 3 mL of CH_2Cl_2) and the reaction mixture was stirred for 1 h. Addition of 10 mL of pentane caused the precipitation of a dull orange powdery solid which was washed twice with 5 mL portions of pentane and dried under N_2 (44 mg, 88%). Anal. Calcd for $IrRhP_4Si_2O_3C_{57}H_{58}$: C, 53.96; H, 4.57. Found : C, 53.84; H, 4.24.

(j) [RhIr(CO)$_3$(H)(SiHPh$_2$)(μ-SiPh$_2$)(η^1-Ph$_2$PCH$_2$PMePh$_2$)(dppm)][CF$_3$SO$_3$] (72). The procedure used to prepare compound **70** was duplicated. One equiv of methyl triflate ($CH_3OSO_2CF_3$, 3 μL) was syringed into the solution at -78 °C after which the sample was gradually warmed to room temperature over a 15 min period. NMR analysis conducted at this stage showed the quantitative conversion of **70** to $[RhIr(CO)_3(H)(SiHPh_2)(\mu\text{-}SiPh_2)(\eta^1\text{-}Ph_2PCH_2PMePh_2)(dppm)][CF_3SO_3]$ **(72)**. The solution was then transferred to a 10 mL flask and the solvent removed. Recrystallization from THF/ether gave a dark orange solid. Anal. Calcd for $IrRhSP_4Si_2F_3O_6C_{79}H_{69}$: C, 56.42; H, 4.11. Found : C, 56.37; H, 4.08.

(k) $[RhIr(CO)_3(H)(SiHMe_2)(\mu\text{-}SiMe_2)(\eta^1\text{-}Ph_2PCH_2PMePh_2)(dppm)][CF_3SO_3]$ (73). 35 mg (0.027 mmol) of compound **71** was dissolved in 2 mL of CH_2Cl_2. Methyl triflate (3.2 µL, 0.027 mmol) was added causing an immediate change in the orange color of the solution to light yellow. A yellow-orange solid precipitated from the solution upon addition of 5 mL of pentane. The product was recrystallized from CH_2Cl_2/pentane and dried *in vacuo* (32 mg, 82%). Anal. Calcd for $IrRhSP_4Si_2F_3O_6C_{59}H_{61}$: C, 49.45; H, 4.26. Found : C, 49.47; H, 4.06.

X-ray Data Collection for compound 70. Orange crystals of compound **70** were obtained by slow diffusion of pentane into a concentrated benzene solution of the compound (compound **70** was prepared as previously described in (h)). Several suitable crystals were mounted and flame-sealed in glass capillaries under solvent vapor to minimize decomposition or deterioration due to solvent loss. Data were collected at -60 °C to a maximum $2\theta = 50°$ on a Siemens P4/RA diffractometer using graphite-monochromated Cu Kα radiation. Unit cell parameters were obtained from least-squares refinement of the setting angles of 43 reflections in the range $54.3° < 2\theta < 58.0°$. The diffraction symmetry and the systematic absences indicated the space group P1 or P $\bar{1}$, the latter being established by successful refinement of the structure. Absorption corrections were applied by semi-empirical method (Ψ

Table 5.2. Crystallographic Data for compound 70.

A. Crystal Data	
formula	$C_{86}H_{75}IrO_3P_4RhSi_2$
formula weight	1631.63
crystal dimensions (mm)	0.33 X 0.12 X 0.08
crystal system	triclinic
space group	$P\overline{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	13.3971 (6)
b (Å)	15.8618 (7)
c (Å)	20.9238 (12)
α (deg)	97.730 (4)
β (deg)	104.590 (4)
γ (deg)	113.895 (4)
V (Å^3)	3791.0 (3)
Z	2
ρ_{calcd} (g cm^{-3})	1.429
μ (mm^{-1})	6.587
B. Data Collection and Refinement Conditions	
diffractometer	Siemens P4/RA[b]
radiation (λ [Å])	graphite-monochromated Cu Kα (1.54178)

Table 5.2. CrystallographicData for 70 (continued).

temperature (°C)	–60
scan type	θ–2θ
data collection 2θ limit (deg)	115.0
total data collected	10485 ($0 \leq h \leq 14$, $-16 \leq k \leq 15$, $-22 \leq l \leq 22$)
independent reflections	9993
number of observations (*NO*)	8438 ($F_o^2 \geq 2\sigma(F_o^2)$)
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	semiempirical (ψ scans)
range of transmission factors	0.9509–0.4429
data/restraints/parameters	9993 [$F_o^2 \geq -3\sigma(F_o^2)$]/10[e]/877
goodness-of-fit (S)[f]	1.052 [$F_o^2 \geq -3\sigma(\mathrm{Or}^2)$]
final R indices[g]	
$F_o^2 > 2\sigma(F_o^2)$	**R_1 = 0.0531,** wR_2 = 0.1383
all data	R_1 = 0.0638, **wR_2 = 0.1470**

Table 5.2. Crystallographic Data for **70** (continued).

largest difference peak and hole	1.981 and –2.348 e Å^{-3}

[a] Obtained from least-squares refinement of 43 reflections with 54.3° $< 2\theta <$ 58.0°.

[b] Programs for diffractometer operation and data collection were those of the XSCANS system supplied by Siemens.

[c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[e] The Ir–H(1) distance was fixed at 1.65(1) Å, and distances within one of the solvent benzene molecules were given idealized values (d(C(131)–C(132)) = d(C(131)–C(136)) = d(C(132)–C(133)) = d(C(133)–C(134)) = d(C(134)–C(135)) = d(C(135)–C(136)) = 1.36(1) Å; d(C(131)°C(134)) = d(C(132)°C(135)) = d(C(133)°C(136)) = 2.72(1) Å).

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0872P)^2 + 12.4713P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

scans). Crystal parameters and details of data collection are given in Table 5.2.

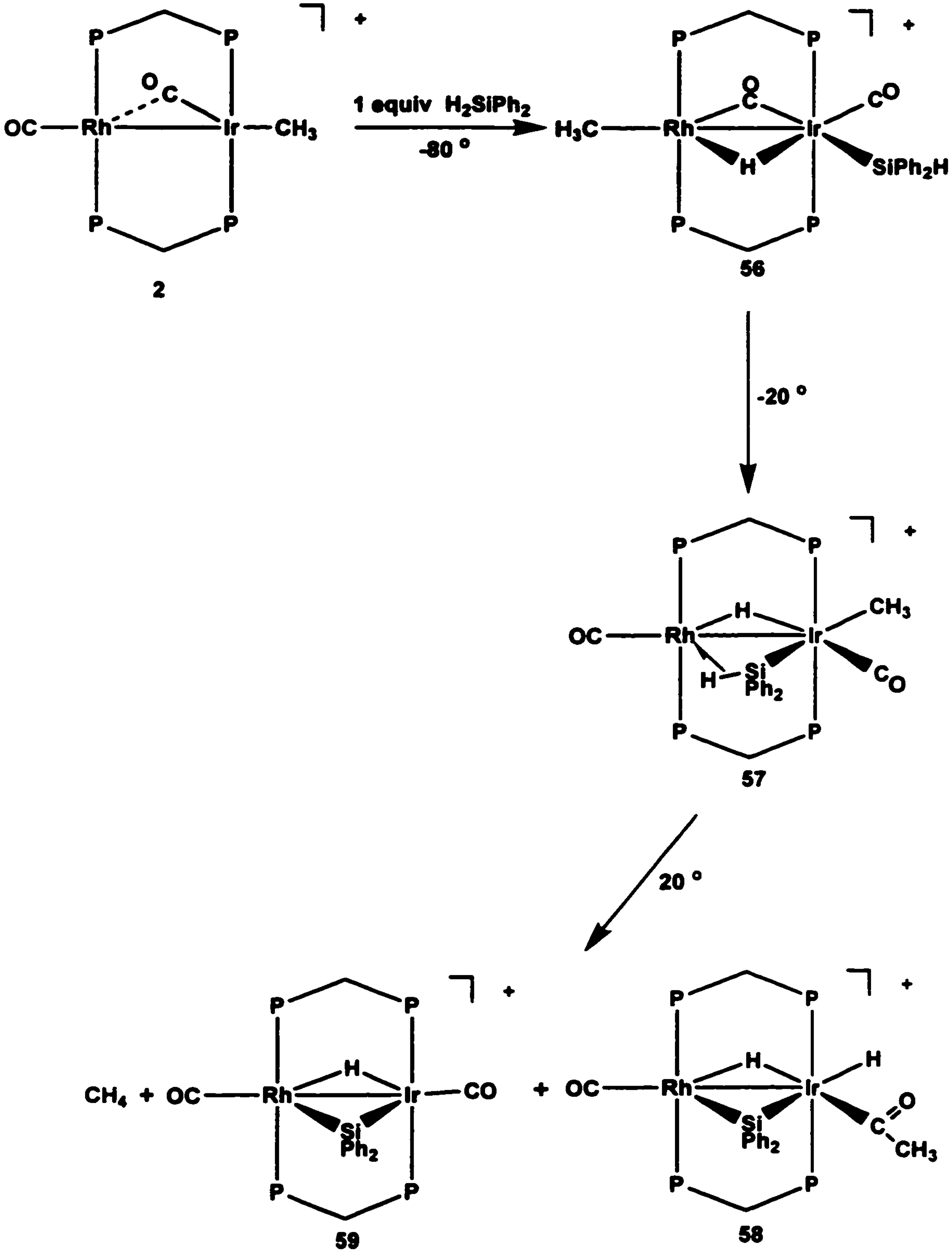
Structure Solution and Refinement. The structure was solved by direct methods using SHELXS-86 to locate the Ir, Rh, P and Si atoms. All other non-hydrogen atoms were located after a succession of least-squares cycles and difference Fourier syntheses. Refinement was completed using the program SHELXL-93. All hydrogen atoms were included as fixed contributions; their idealized positions were generated from the geometries of the attached carbon atoms and their thermal parameters set at 20% greater than the isotropic thermal parameters of those carbons. The hydride position was not located from a difference Fourier map, so was placed in the position (Ir-H(1) = 1.65 Å) in the vacant site opposite the carbonyl group on Ir as suggested by the spectroscopic data. The final model for the complex refined to values R_1 = 0.0531 (for $F_0^2 \geq 2\sigma(F_0^2)$) and wR_2 = 0.1470 (on all data). Details of the structure refinement are given in Table 5.2.

Results and Discussion

(a) Monomethyl and related compounds.

It will be recalled that in Chapter 2 the oxidative additions of dihydrogen, at low temperature, to the methyl tricarbonyl species $[RhIr(CH_3)(CO)_3(dppm)_2]$-$[CF_3SO_3]$ (**1**) and its dicarbonyl analogue (**2**) were described, yielding metastable methyl dihydrido species, accompanied by CO loss in the former case. At ambient temperature, these species reductively eliminated methane, accompanied by an uptake of one mole of dihydrogen to give a final trihydride species. Based on the analogies between dihydrogen and silanes we set out to react the dicarbonyl analogue $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with silanes, with the intention of comparing the chemistry of these reagents to that of H_2. Addition of Ph_2SiH_2 to a solution of **2** at -80 °C gave the methyl, silyl hydride complex $[RhIr(CH_3)(SiPh_2H)(CO)(\mu\text{-}CO)(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**56**), in which the methyl group has migrated to Rh from Ir as shown in Scheme 5.1. Compound **56** is structurally analogous to the oxidative addition product of **2** and H_2, therefore a similar reaction pathway for both products is suggested. The ^1H NMR spectrum for compound **56** shows the methyl protons resonating as a triplet of doublets at δ 0.42 in addition to a bridging hydride signal at δ -8.49 ($^1J_{RhH}$ = 13 Hz). The η^1-coordination mode of the silyl group on Ir was established by the ^1H NMR spectroscopy in which the triplets of doublets of the silyl hydrogen at δ 5.50 collapsed to a doublet upon irradiation of the Ir-bound ^{31}P nuclei; whereas irradiation of the Rh-bound ^{31}P nuclei resulted in no change in this signal. The doublet coupling (*ca.* 1 Hz) is shown to result from a three-bond coupling of the silyl hydrogen with the bridging hydride as confirmed by $^1H\{^1H\}$ NMR experiments. The $^{13}C\{^1H\}$ NMR spectrum exhibits resonances at δ 216.5 ($^1J_{RhC}$ = 31 Hz) and 173.8, the latter of which is assigned to a terminal carbonyl group on Ir while the low-field signal is consistent with a bridging carbonyl. If $^{13}CH_3$-enriched compound **2** is used, an additional doublet of triplets ($^1J_{RhC}$ = 28 Hz) appears in the $^{13}C\{^1H\}$ NMR spectrum at δ 15.1 due to the Rh-bound methyl group. Compound **56** is fluxional in solution. The $^{31}P\{^1H\}$ NMR spectra at these temperatures shown in Fig. 5.1 reveals that this fluxionality appears to be restricted to Ir as the Rh-bound phosphorus nuclei seem relatively unperturbed over the temperature range investigated. At -80 °C the Ir-bound dppm ^{31}P nuclei appear as two broad peaks at δ -7.1 and -9.6 while the Rh-bound phosphines exhibit the usual multiplet pattern. At -60 °C, the former peaks coalesce to a broad unresolved peak centered at δ -8.3 and finally at -40 °C, this resonance becomes resolved into a multiplet consistent with a BB' part of an AA'BB'X spin system. The signals due to the silyl hydrogen

Scheme 5.1



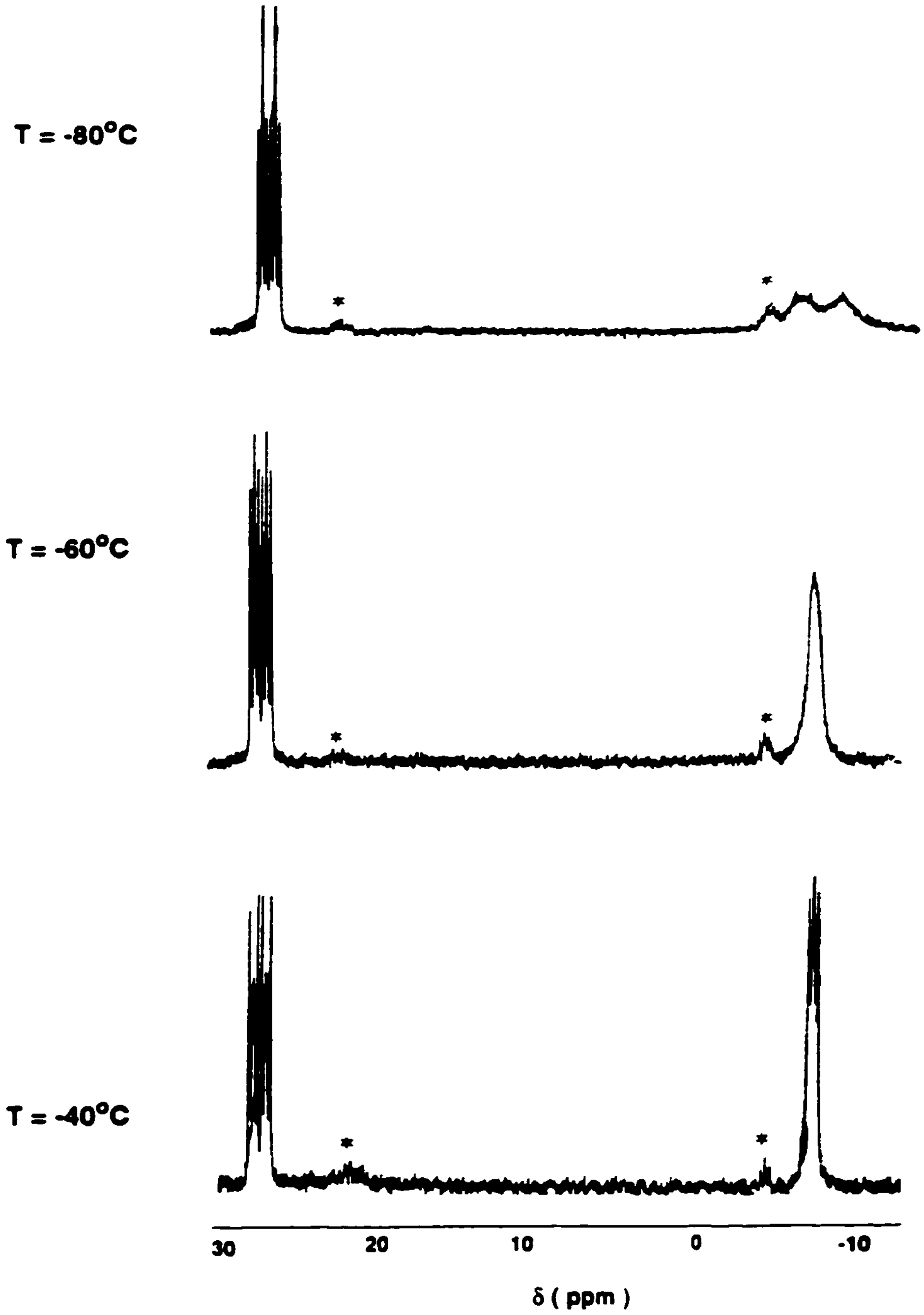


Figure 5.1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra showing the fluxional behaviour of compound **56**. * denotes impurity.

and the bridging hydride ligand remain unaffected between the temperature range -80 °C and -40 °C, suggesting that these groups do not participate in the fluxional process. The origin of this fluxional process is not clearly understood. However, it might be due to an asymmetry in the environments of the silyl phenyls which renders both dppm ^{31}P nuclei on Ir inequivalent in the ground state geometry. The dppm methylene protons exhibit a temperature-dependent spectrum; displaying a multiplet for the four protons at δ 4.10 at -80 °C which became two AB multiplets at δ 4.21 and 3.58 at -60 °C.

Upon warming to -40 °C, a new species $[RhIr(CH_3)(CO)_2(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^2\text{-}SiPh_2H)(dppm)_2][CF_3SO_3]$ (**57**), appears together with **56**, and by -20 °C, compound **57** is the major product observed in solution. This species has the methyl group bound to Ir, as evidenced by its proton signal at δ 0.75 (triplet), showing no Rh coupling. The signal for this ligand in the $^{13}C\{^1H\}$ NMR spectrum appears as a triplet at δ -22.6 ($^1J_{PC}$ = 6.0 Hz,) also showing no Rh coupling. The high-field shift of this signal has become a signature for an Ir-bound methyl substituent in this system; Rh-bound methyl groups tend to resonate at lower fields (*vide supra*) and to show coupling to Rh of between 20 and 30 Hz. The silicon-hydrogen bond is believed to be bound to Rh in an agostic interaction as shown by its ^{1}H NMR signal which appears as a doublet of doublets of multiplets at δ -0.73 ($^1J_{RhH}$ = 24 Hz, $^2J_{HH}$ = 7 Hz, $^2J_{PH}$ = 9 Hz); this signal integrates in a ratio of 1:1 with that of the hydride. The additional coupling shown by this hydrogen to the Ir-bound ^{31}P nuclei, as established by selective $^1H\{^{31}P\}$ decoupling experiments, indicates that the silyl group is bound to Ir. In addition, the hydridic character for this hydrogen is demonstrated by its relative high-field character. By comparison, the chemical shift for the silyl hydrogen in **56** is δ 5.50, so the observed chemical shift is intermediate between those expected for a terminal Si-H group and a classical hydride ligand (*vide supra*). Similar high-field signals for M-H-Si protons have been reported for $[Ir_2(CO)_2(\mu\text{-}\eta^1:\eta^2\text{-}SiPh_2H)(H)(dppm)_2]$[5a] and for the complexes, $[Cp_2Ti(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}HSiPhH)TiCp_2]$[5c] and $[Mn_2(CO)_6(\mu\text{-}\eta^3\text{-}H_2SiPh_2)(dppm)_2]$.[5f] Furthermore, the low P(Rh)-H coupling constant (*ca.* 8 Hz) compared to typical values for terminal hydrides on Rh (*ca.* 20-30 Hz)[5a,9] argues in support of a three-center Rh-H-Si interaction as formulated above and is consistent with the inherently weaker Rh-H interaction in compound **57**. Although several metal complexes with such three-centered, two electron M-H-Si interactions have been reported,[5,10] including recent examples involving the related homobinuclear Rh_2 and Ir_2 complexes,[5a,e] compound **57** is the first example to our knowledge of such agostic interaction for the mixed Rh/Ir combination. Compound **57** appears to be static in solution at -20 °C, displaying no exchange between the silyl hydrogen and bridging hydride, in contrast to reports[5e] of such exhanges for the related $[(dippe)(Rh)]_2(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}SiPh_2H)]$ (dippe = bis (diisopropyl-phosphino)ethane). In the absence of characterized intermediates relating **56** and **57** it is not clear how this rearrangement occurs, although CO loss and subsequent recoordination may be involved.

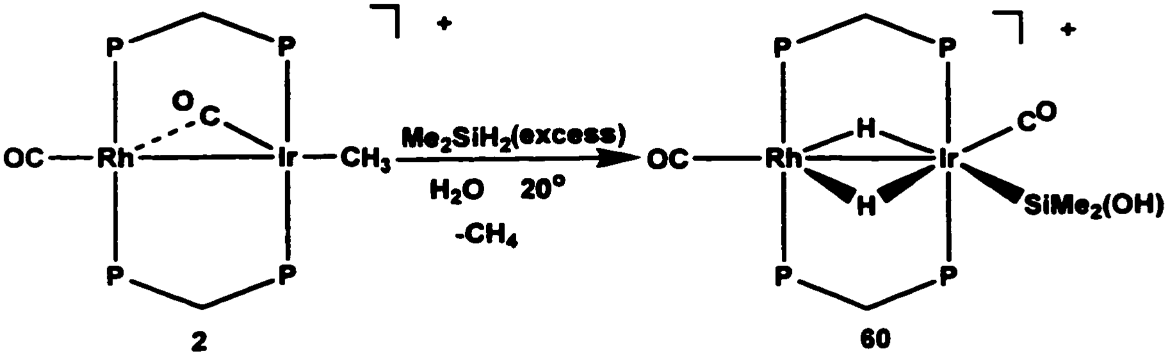
If the sample is allowed to warm to room temperature, two new species appear in an approximate ratio of 1:1, accompanying the disappearance of **57**. One of them, the silylene-bridged acetyl dihydride complex $[RhIr(COCH_3)(H)\text{-}(CO)(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2][CF_3SO_3]$ (**58**), is the result of oxidative addition of the second Si-H bond concomitant with migration of the methyl group onto carbonyl ligand. Although migratory insertion should be favored at the more labile Rh, there is no evidence to suggest that this is occurring. The other product, identified as a monohydride $[RhIr(CO)_2(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2][CF_3SO_3]$ (**59**), results from reductive elimination of methane, which was identified by its singlet peak at δ 2.03 in the ^1H NMR spectrum of the reaction mixture. The

$^{13}C\{^1H\}$ NMR spectrum of the crude product mixture also shows $^{13}CH_4$ as a singlet at δ -4.3, which disappears upon work-up as the gas is lost. The acetyl carbonyl group appears as a singlet at δ 279.8 in the $^{13}C\{^1H\}$ NMR spectrum, and the methyl group gives rise to a singlet at δ 46.0, which indicates that this group is no longer directly bound to either metal center. In addition, these signals appear as doublets in the doubly-enriched ($^{13}CH_3$/^{13}CO) compounds, showing a mutual coupling of 26 Hz. The other carbonyl group is shown to be Rh-bound (δ 193.7; $^1J_{RhC}$ = 70.8 Hz). The acetyl protons appear in the ^1H NMR spectrum as a singlet at δ 1.24, and the absence of Rh coupling to the acetyl carbonyl group is in accord with its position on Ir. The ^1H NMR spectrum for **58** also displays signals at -8.86 (triplet) and -14.98 (doublet of multiplets, $^1J_{RhH}$ = 21.0 Hz) assigned to terminal (Ir) and bridging hydride ligands, respectively. The $^{13}C\{^1H\}$ NMR spectrum for compound **59** shows a doublet of multiplets at δ 187.6 with a Rh coupling of 77.3 Hz and a triplet at 176.8, assigned to terminal carbonyls on Rh and Ir, respectively. The ^1H NMR spectrum for compound **59** displays broad multiplets at δ 4.42 and 4.40 for the dppm methylenes and a broad signal with unresolved P-H coupling at δ -10.22 for the hydride group which integrates as 1:4 with those of the dppm methylenes. Cooling the sample to -40 °C does not result in simplification of the hydride resonance; however, broadband $^1H\{^{31}P\}$ decoupling gives a doublet ($^1J_{RhH}$ = 15 Hz). Both compounds **58** and **59** react further upon standing in solution. In the case of **59** this appears to result from hydrolysis by adventitious water yielding the known trihydride $[RhIr(CO)_2(H)(\mu\text{-}H)_2(dppm)_2][CF_3SO_3]$.[5a] Hydrolysis or alcoholysis of metal silyl complexes has been shown to occur readily with Ir(III)[9a] and other systems,[9b,c] and this reaction is believed to be thermodynamically driven by the high oxophilicity[2] of the silicon atom. In the case of **58** decomposition yields acetaldehyde, as identified by its ^1H NMR spectrum (δ 2.17 (doublet) and δ 9.78 (quartet)). However, the metal-containing product has not yet been identified.

The transformation of **57** to the equimolar mix of the acetyl species **58** and the monohydride compound **59**, illustrates competitive acylation and reductive elimination (of methane) processes, presumably at Ir; thus providing a well-defined example of both processes occurring at the same metal. Intuitively, we would anticipate exclusive C-H bond formation (giving methane) in view of its more favorable energetics[11] over C-C bond formation (giving the acetyl species).

The reaction of **2** with dimethylsilane at low temperature results in the formation of several hydride products which were difficult to characterize. However, at room temperature a single hydrolysis product is obtained and identified as $[RhIr(CO)_2(SiMe_2(OH))(\mu\text{-}H)_2(dppm)_2][CF_3SO_3]$ (**60**), presumably formed by hydrolysis of an unobserved hydride species analogous to **59** by adventitious moisture present in the reagent. The silyl methyl groups exhibit a doublet resonance ($^4J_{HH}$ = 4 Hz) at δ -0.12 suggesting that these groups are chemically equivalent. The doublet coupling is shown by homonuclear $^1H\{^1H\}$ decoupling experiments to be due to four-bond coupling to the hydroxyl proton. The hydroxyl proton for **60** appears as a well-defined multiplet at δ 3.80 integrating in a ratio of 1:4:6 with the dppm methylene and silyl methyl protons. Homonuclear ($^1H\{^1H\}$) decoupling experiments establish that this peak is actually a doublet of doublets of septets, with the doublet of doublets coupling arising from a four-bond coupling (of *ca.* 3 Hz each) to the two hydride groups while the septet is due to coupling to the silyl methyl protons. In order to provide further support for the formulation of **60**, the hydrido tricarbonyl complex $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2][CF_3SO_3]$[5a] was treated with $HSiMe_2(OEt)$. Although the

Scheme 5.2



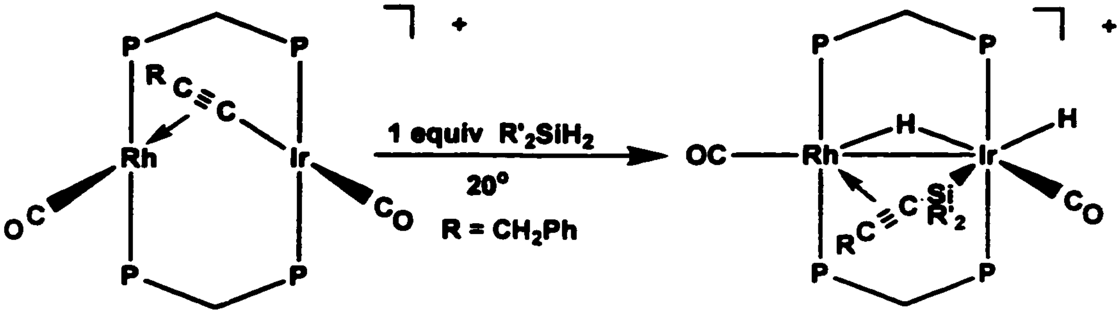
2

60

reaction proved to be very slow, after 2 days the ^{31}P NMR spectrum showed the presence of trace amounts of a species tentatively proposed as $[RhIr(CO)_2(\mu\text{-}H)_2(SiMe_2(OEt))(dppm)_2][CF_3SO_3]$ on the basis of spectral similarities (^1H and $^{31}P\{^1H\}$) with those of **60**.

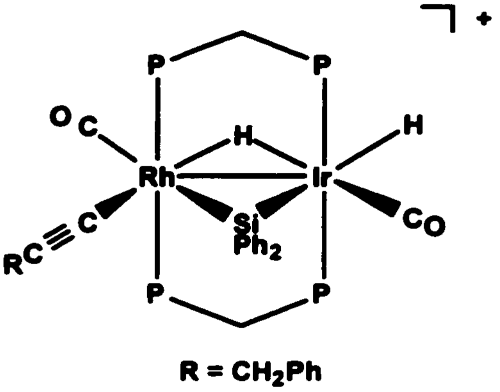
The reaction of silanes with the related alkynyl-bridged A-frame species $[RhIr(CO)_2(\mu\text{-}C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**42**), in which the methyl group of **2** is replaced by the alkynyl ligand was also investigated. We were interested in the possibility of migration of a silyl group to the alkynyl fragment giving a silylvinylidene species, analogous to the known migration of hydrides,[12a,d] and hydrocarbyl fragments.[12e,f] At room temperature the NMR spectra of the reaction mixture shows the initial presence of several species which were not characterized. However, allowing the sample to stir for 3 h results in the formation of the dihydride complex $[RhIr(CO)_2(H)(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^2\text{-}SiPh_2C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**61**), as depicted in Scheme 5.3. Compound **61** is the apparent result of oxidative addition of both silane Si-H bonds accompanied by a 1,2 alkynyl migration onto the silyl group. In addition, the alkynyl triple bond is shown to bind to the Rh center in a π fashion as evidenced by the appearance of doublet peaks at δ 93.4 ($^1J_{RhC}$ = 5.4 Hz) and 60.4 ($^1J_{RhC}$ = 6.0 Hz) in the $^{13}C\{^1H\}$ NMR spectrum, assigned to the C_β and C_α carbons, respectively. Similar Rh-C couplings of *ca.* 5 Hz have been observed[12a] for the phenylacetylide-bridged A-frame, $[RhIr(CO)_2(\mu\text{-}C_2Ph)(dppm)_2][CF_3SO_3]$, in which the alkyne group was shown to interact with the Rh center in a π fashion. The $^{13}C\{^1H\}$ NMR spectrum also indicates the presence of two terminal carbonyl groups (δ 191.9, $^1J_{RhC}$ = 81.2 Hz; 167.1), one on each metal, while the ^1H NMR spectrum shows that one of the hydride ligands is terminally bound to Ir (δ -10.45 ppm) with the other bridging both metals (δ -9.64, $^1J_{RhH}$ = 15 Hz). An alternative formulation for compound **61**, diagrammed below as **A**, assumes that the acetylide binds

Scheme 5.3



42

61 : R' = Ph
62 : R' = Me



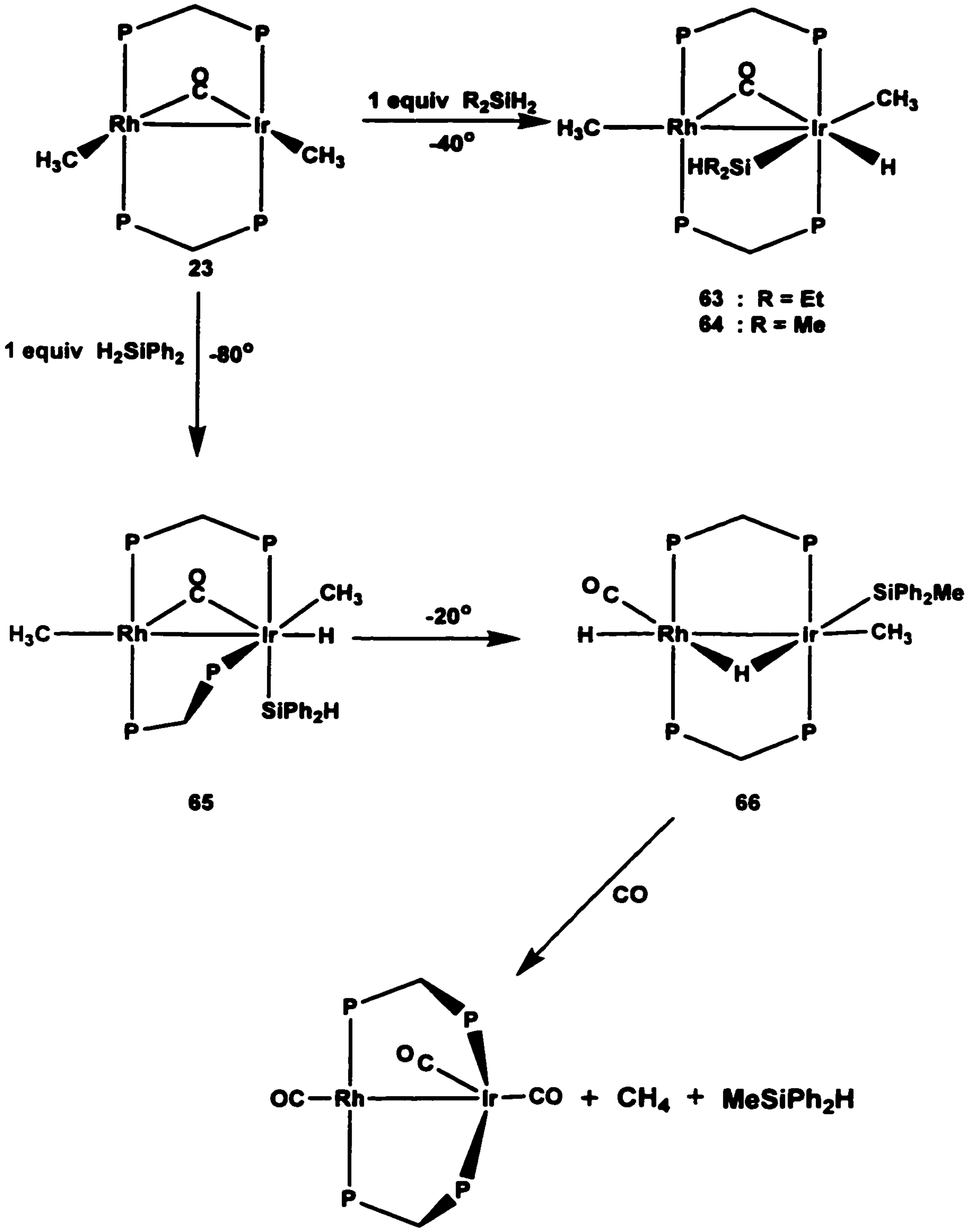
A

terminally to Rh and would necessitate a bridging-silylene moiety. Such a formulation appears unlikely since the coupling observed between the α-carbon of the alkynyl group and Rh (6.0 Hz) is much smaller than anticipated for a Rh-C σ bond (*ca.* 50-60 Hz).[12b,c] Furthermore, the equal coupling of Rh to both the α- and β-carbons of the acetylide moiety would be difficult to rationalize in such a bonding model. In addition, in structure **A** we would expect to observe coupling of the acetylide α-carbon to the Rh-bound ^{31}P nuclei which has previously been observed in the range *ca.* 10-17 Hz.[12a-d,f,13] In view of the absence of mechanistic evidence detailing the transformation of the starting material to **61** as a result of the complexity of the spectra obtained for the initial products of the reaction, we know little about the rearrangements between **42** and **61**, although it would seem to involve at some stage the generation of a silylene-bridged species. Although it is tempting to suggest the intermediacy of a species such as **A**, with migration of the alkynyl group occurring at the more labile Rh, we have no evidence to support this. Like the cationic silyl compound **59**, compound **61** is slowly hydrolysed in solution by adventitious moisture, yielding the same trihydride complex.[5a] The analogous dimethyl silyl species $[RhIr(CO)_2(H)(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SiMe_2C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**62**) can be accessed by treatment of **42** with dimethylsilane. This reaction proved to be much more facile, being complete within a few minutes compared to that involving the bulkier diphenylsilane which took about 3 h for completion. Compounds **61** and **62** have strikingly similar spectral parameters (^{13}C, ^{31}P and ^{1}H) except in the ^{1}H NMR spectrum of **62** which displays peaks at δ -0.08 and -0.10 attributed to the silyl methyl protons. Attempts to release the functionalized silane $Ph_2Si(H)C{\equiv}CCH_2Ph$ or $Me_2Si(H)C{\equiv}CCH_2Ph$ by reacting further with CO have not succeeded.

(b) Dimethyl Complexes.

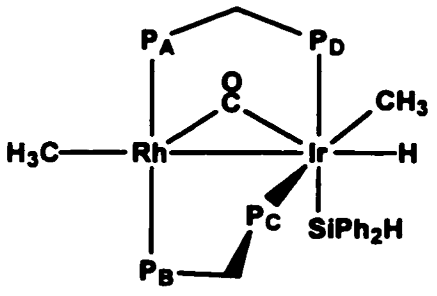
Prompted by the success at inducing Si-C bond formation in the reaction of $[RhIr(CO)_2(\mu\text{-}C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (**42**) with secondary silanes, the reactivity of the dimethyl A-frame complex $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**) with a selection of secondary silanes was attempted in the hope of inducing Si-C coupling of the methyl and silyl fragments. The reaction of diethylsilane (Et_2SiH_2) with **23** at -40 °C provides $[RhIr(CH_3)_2(H)(SiHEt_2)(\mu\text{-}CO)(dppm)_2]$ (**63**), as shown in Scheme 5.4. The hydride ligand in compound **63** is shown to be terminally bound to Ir, as evidenced by its triplet resonance at δ -10.75 in the ^{1}H NMR spectrum. The spectral similarity (^{31}P and ^{13}C) of **63** and the cis dihydride-dimethyl complex $[RhIr(CH_3)_2(H)(\mu\text{-}CO)(\mu\text{-}H)(dppm)_2]$ (**30**) leads us to suggest analogous attack of the silane in the pocket of the A-frame at Ir giving an analogous structure, with the silyl group positioned adjacent to the Rh-Ir bond. The large chemical shift difference of ^{31}P signals for *both* metals in the starting material and **63** ($\Delta\delta$ = 9 and 13 ppm, respectively) is inconsistent with substrate attack outside of the A-frame as was proposed for the η^2-alkyne adduct $[RhIr(CH_3)_2(\mu\text{-}CO)(\eta^2\text{-}DMAD)(dppm)_2]$ (**51**),[7] for which only the Ir-bound ^{31}P nuclei experienced a marked shift in its resonance upon coordination of the

Scheme 5.4


1 equiv R₂SiH₂
-40°
23
63 : R = Et
64 : R = Me
1 equiv H₂SiPh₂
-80°
-20°
65
66
CO
OC—Rh—Ir—CO + CH₄ + MeSiPh₂H

alkyne ligand. Upon warming, compound **63** decomposes to a number of unidentified products, presumably via β-hydride elimination from the silyl ethyl groups followed by further reactivity of resulting hydride products.[5h] A similar instability has been reported for the ethylsilylene species $[Rh_2(CO)_2(H)_2(\mu\text{-}SiHEt)(dppm)_2]$ and $[Rh_2(CO)_2(H)_3(SiH_2Et)(\mu\text{-}SiHEt)(dppm)_2]$.[5d] The dimethylsilyl analogue, $[RhIr(CH_3)_2(H)(SiHMe_2)(\mu\text{-}CO)(dppm)_2]$ (**64**), can also be readily accessed at -40 °C by the corresponding reaction of the starting material with dimethylsilane H_2SiMe_2. The spectral parameters for compounds **63** and **64** are similar, except for the chemical shifts for the protons on the silyl groups, so their structures are assumed to be similar. Unlike **63**, compound **64** can be isolated at ambient temperature.

The more bulky diphenylsilane (H_2SiPh_2) shows a reactivity pattern quite unlike those exhibited by its diethyl and dimethyl analogues. When the reaction is carried out at -80 °C, the NMR spectra indicate the presence of the species $[RhIr(CH_3)_2(H)(SiHPh_2)(\mu\text{-}CO)(dppm)_2]$ (**65**), which although isoelectronic with **63** and **64**, has dramatically different spectral parameters, suggesting a different structure. The ^{31}P NMR spectrum of **65** displays a pattern characteristic of an ABCDX spin system (X = Rh), and simulation of this spectrum gives values of 345 and 15 Hz for the P-M-P couplings at Rh and Ir, respectively, consistent with trans,cis dispositions of the ^{31}P groups at these metals. The calculated coupling constants are summarized below, and



$JRhP_A$ = 145 Hz, $JRhP_B$ = 162Hz

JP_AP_B = 345 Hz, JP_AP_D = 80 Hz

JP_BP_D = 10Hz, JP_BP_C = 85 Hz

J_CP_D = 15 Hz

compare well with those reported (*ca.* 360 and 17 Hz) for the ortho-metalated species [$IrOs(H)_2(CO)_3(\mu_2\text{-}\eta^3\text{-}(o\text{-}C_6H_4PhPCH_2PPh_2)(dppm)$] which was proposed[14] to have a similar trans,cis disposition at Ir and Os, respectively. The $^{13}C\{^1H\}$ NMR spectrum of **65** displays a resonance at δ 210.5 ($^1J_{RhC}$ = 33.1 Hz) consistent with a bridging carbonyl group. The hydride signal appears as a doublet of doublets ($^2J_{PH}$ = 45 Hz, $^2J_{PH}$ = 13 Hz) in the ^1H NMR spectrum, simplifying to a singlet upon broadband ^{31}P decoupling; the lack of Rh-H coupling is consistent with the hydrogen being on Ir. The magnitude of these P-H couplings, is substantially less than that expected for a hydride trans to a phosphine (*ca.* 120 Hz),[5] and is more in accord with a cis orientation of the hydride ligands with each of the dppm ^{31}P nuclei. The significance of the differences in the observed P-H couplings is not clear. The cis diphosphine arrangement probably arises from severe steric interactions involving the silyl ligand. In **63** and **64**, the ethyl and methyl groups on the silyl moiety are sterically less demanding, allowing the trans alignment of the phosphines at Ir. Reaction of **23** at -40 °C with $H_2SiMePh$, having intermediate steric demands, results in the generation of two species: one with an AA'BB'X spin pattern like those of **63** and **64** in the $^{31}P\{^1H\}$ NMR spectrum while the other set of peaks shows an ABCDX spin pattern, paralleling that observed for compound **65**. Presumably, two conformations of the mixed silyl species are obtained with slightly different ground state stabilities. Unfortunately, the methylphenylsilyl species could not be fully characterized due to the complexity of the $^{13}C\{^1H\}$ and ^1H NMR spectrum.

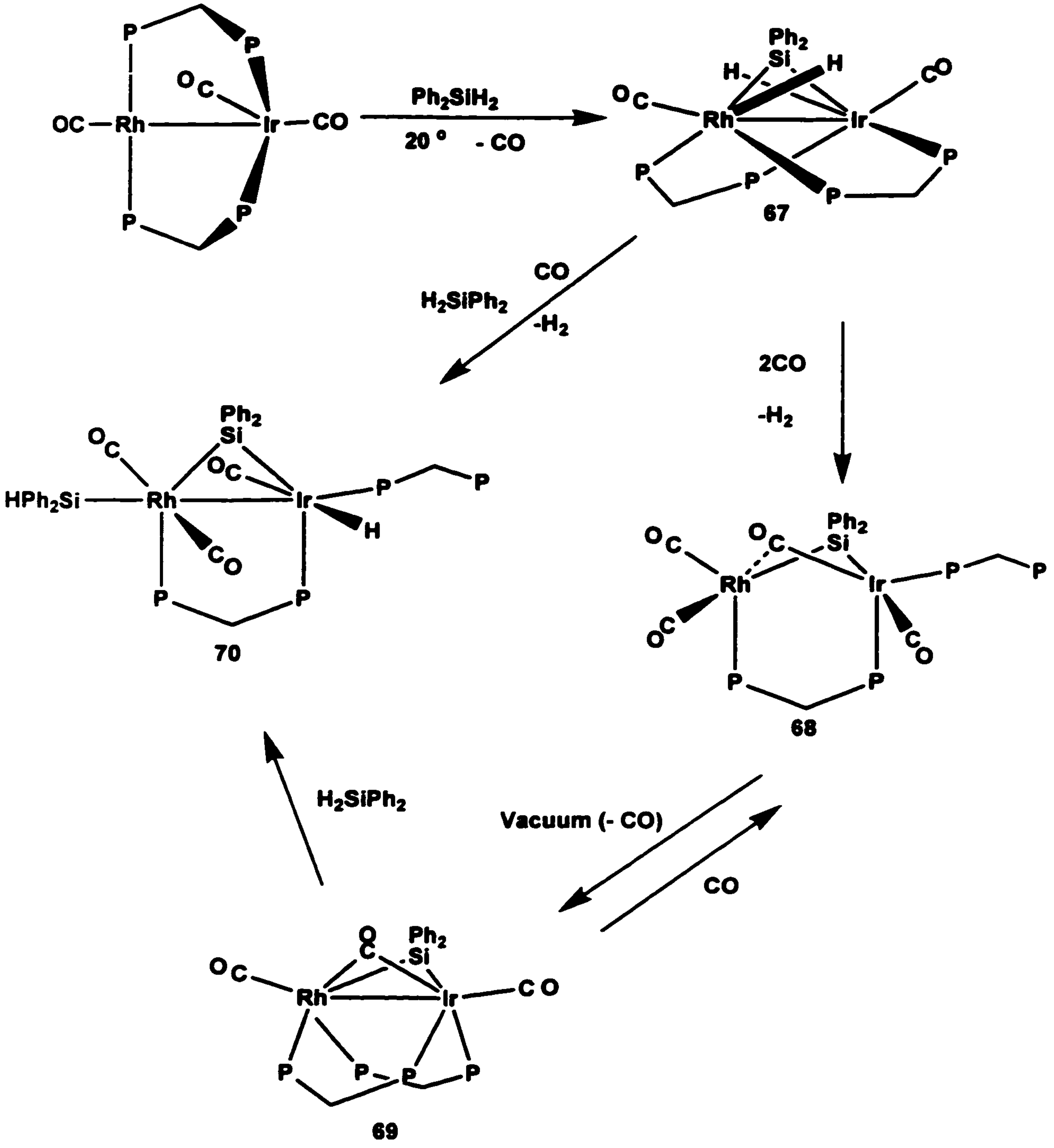
Upon warming the sample to -20 °C, compound **65** transforms to the dihydride complex [$RhIr(CH_3)(H)(SiMePh_2)(CO)(\mu\text{-}H)(dppm)_2$] (**66**) in which oxidative addition of the second Si-H bond has occurred accompanied by methyl migration onto the silyl group. In addition, the carbonyl group has moved from a bridging site in **65** to a terminal one on Rh (δ 190.4, $^1J_{RhC}$ = 68.4 Hz) in **66**. The ^{1}H NMR spectrum for **66** shows the expected resonances for a bridging and terminal hydride, in addition to a triplet (δ 0.32) and singlet (δ -0.26) resonance in the methyl region, each integrating as three protons. The former is assigned to a methyl group on Ir while the latter is assigned to the silyl methyl group on the basis of its lack of P-H coupling. The exact geometry at Ir is unknown. Attempts to prepare $[RhIr(^{13}CH_3)_2(\mu\text{-}CO)(dppm)_2]$ in order to determine the site of the silyl group (the methyl carbon would be expected to display a two-bond coupling to Rh if it were bound to this metal) have not met with success. However, we favor a formulation in which the silyl group binds to Ir rather than Rh. Placing this group on Ir would give both metals octahedral geometries (albeit distorted), as shown, while the alternative formulation in which the silyl moiety is positioned at Rh would leave the Ir center coordinatively unsaturated. Again, as was the case with the alkynyl silyl species **61**,**62** it is probable that the rearrangement of **65** to **66** proceeds through an unobserved silylene-bridged intermediate. It is difficult to explain why oxidative addition of both Si-H bonds to give dihydride species was only observed for the bulky H_2SiPh_2 whereas the reactions involving H_2SiEt_2 and H_2SiMe_2 did not proceed beyond the cleavage of one Si-H bond. It may be that the electron-withdrawing phenyls on H_2SiPh_2 activate the silyl group toward cleavage of the Si-H bonds by rendering these bonds more electrophilic.[13] It seems clear that the formation of a bridging silylene via oxidative addition of both silane Si-H bonds, is pivotal to the Si-C bond-forming steps; so far only diphenylsilane has satisfied this criterion in reactions of the A-frame complex **23**. Further work is warranted to test this theory by investigating the reactivity of the dimethyl complex **23** with secondary silanes containing other electron-withdrawing substituents such as halogens. Migration of a metal-bound alkyl silyl functionality giving an alkyl silyl species, as seen above, is very rare; however, an example of the reverse step involving silyl migration to a carbenic group has recently been reported.[15a]

At ambient temperature, compound **66** loses methane (which was detected in the ^{1}H NMR spectrum of the crude product mixture) and is transformed to two hydride-containing species. One of these is tentatively identified as [RhIr(CO)(H)(SiMePh$_2$)(dppm)$_2$], the product arising from methane elimination. Unfortunately, the structural identity of this species is not known with certainty. The other species is presumably a dihydride formed by hydrolysis reactions involving either **66** or the above monohydride complex. However, in the presence of an atmosphere of CO at 0 °C, compound **66** is quantitatively converted to the tricarbonyl complex [RhIr(CO)$_3$(dppm)$_2$] accompanied by production of methane and the free silane HSiMePh$_2$. These by-products were identified by their proton peaks at δ 2.03 (singlet, C*H*$_4$), 4.92 (quartet, Si-*H*) and 0.64 (doublet, Si-C*H*$_3$). The apparent absence of diphenyldimethylsilane, Ph$_2$SiMe$_2$, one of the possible reductive elimination by-products from **66**, in the product mixture is consistent with the lower tendency for reductive elimination of silyl and alkyl fragments,[3f,5c,h,15] with reductive elimination of alkyl hydride[16] and silyl hydride groups[2c,3e,4a,17] being more common.

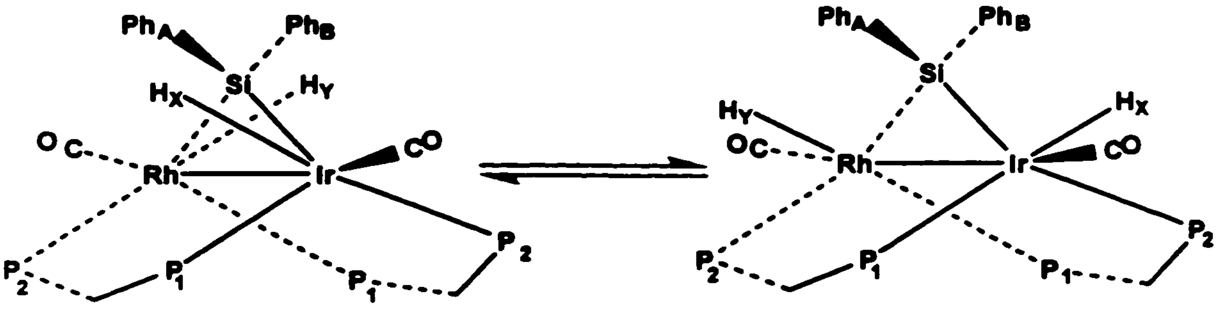
(c) Reactivity Studies with [RhIr(CO)$_3$(dppm)$_2$].

Previous studies carried out by Eisenberg and co-workers[5b,d] and by members of our group[5a] on the reactivity of secondary silanes with the low-vaient homobinuclear complexes [M$_2$(CO)$_3$(dppm)$_2$] (M = Rh, Ir) had shown that activation of both silane Si-H bonds by the adjacent metals had occurred, yielding silylene-bridged dihydride species. It was of interest to extend this study to the mixed-metal combination Rh/Ir, anticipating a unique reactivity pattern due to the different properties of each metal. The reaction of $[RhIr(CO)_3(dppm)_2]$ with 4 equiv of silane at room temperature occurs slowly; new peaks attributed to the silylene-dihydride dicarbonyl complex, $[RhIr(CO)_2(H)_2(\mu\text{-}SiPh_2)(dppm)_2]$ (**67**) begin to appear after 15 min, being present in 25-35% yield as determined by the ratios of the ^{31}P NMR peaks. Like its homobinuclear analogues, $[M_2(CO)_2(H)_2(\mu\text{-}SiR_2)(dppm)_2]$ (M = Rh, R = Et;[5d] M = Ir, R = Ph[5a]), compound **67** is fluxional in solution at room temperature, for which the $^{31}P\{^1H\}$ NMR spectrum shows two broad peaks centered at δ 20.5 and -13.2. Cooling the sample to -40 °C causes each broad signal to split into two sets of peaks (δ 23.4, 14.3, -6.7 and -20.4) with unresolved P-M-P coupling. The ^1H NMR spectrum also shows the same phenomenon, with two sets of broad resonances each for the hydrides (δ -9.72, $^1J_{RhH}$ = 14 Hz; -11.83) and for the dppm methylene protons (δ 4.83 and 3.18) observed at ambient temperature. Upon cooling to -40 °C, the hydride resonances become resolved, each displaying distinct cis (*ca.* 12 Hz) and trans (*ca.* 120 Hz) P-H coupling, suggesting that they have a cis,trans disposition with respect to the ^{31}P nuclei at each metal as depicted in Scheme 5.5. These coupling values fall within the range expected for cis and trans two-bond P-H couplings;[5] in particular, they compare well with values of 12-17 Hz and 120-155 Hz reported[5g] for a series of Ir dihydride complexes. A similar orientation of the hydrides with respect to the dppm ^{31}P has been reported for the Ir_2 analogue $[Ir_2(CO)_2(H)_2(\mu\text{-}SiPh_2)(dppm)_2]$,[5a] the structure of which was determined by X-ray crystallography and proposed for a related carbyne species, $[Ir_2(CO)_2(H)_2(\mu\text{-}COCH_3)(dppm)_2][CF_3SO_3]$.[18] At -40 °C four peaks (*ca.* δ 5.40, 4.97, 3.16 and 2.89) are observed for the methylene protons, integrating equally with each of the hydride resonances. The asymmetry between the two ^{31}P nuclei on each

Scheme 5.5


Ph$_2$SiH$_2$
20 °
- CO
67
CO
H$_2$SiPh$_2$
-H$_2$
2CO
-H$_2$
70
68
H$_2$SiPh$_2$
Vacuum (- CO)
CO
69

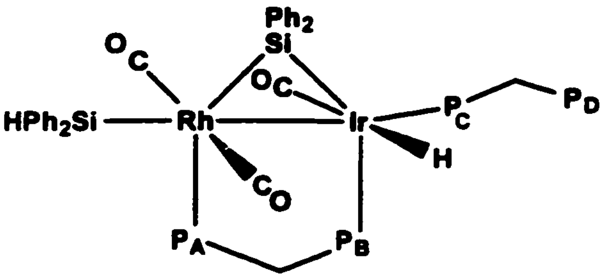
metal disappears at higher temperatures by a fluxional process in which the hydride ligands alternate between the two different faces of the RhIrSi plane, moving from trans to one phosphine to trans to the other, as outlined below.



Dashed lines are used to portray bonds at the backside of the molecule. This view is reinforced by the observation that the chemical shifts for the hydrides changed little between ambient temperature and -40 °C.

Unlike the Ir_2 analogue, compound **67** loses H_2 in the presence of excess Ph_2SiH_2 at room temperature after 1 d yielding the final silyl, silylene complex $[RhIr(CO)_3(H)(SiHPh_2)(\mu\text{-}SiPh_2)(\eta^1\text{-dppm})(dppm)]$ (**70**). Since this compound is shown to be a tricarbonyl, the extra CO (in the absence of added CO) is apparently scavenged from the solution, having been released during the initial formation of compound **67**. The $^{31}P\{^1H\}$ NMR spectrum for compound **70** displays an ABCDX spin pattern (X = Rh), in which all phosphorus nuclei are chemically inequivalent. Only one of these ^{31}P resonances exhibits strong Rh-P coupling, and the up-field doublet of doublets at δ -29.5 ($^2J_{PP}$ = 36 Hz, $^4J_{PP}$ = 7 Hz), is close to that of free dppm (δ -22.3), suggesting that this ^{31}P nucleus is not bonded to any metal but corresponds to a pendent dppm group. This high-field resonance is also close to that reported for the related dirhodium species $[Rh_2(CO)_3(\mu\text{-}CO)(\mu\text{-}SiEt_2)(\eta^1\text{-dppm})(dppm)]$ (δ -26.8, $^2J_{PP}$ = 40 Hz),[5d] and for other known metal complexes having η^1-dppm ligands.[19] The Ir-bound

^{31}P nucleus (P_C) exhibits a through metal-metal coupling ($^2J_{RhP}$) of *ca*. 5 Hz to the Rh center. A simulation of the ^{31}P NMR spectrum of **70** together with the observed spectrum are shown in Figure 5.2, and the derived coupling constants for **70** are given below.



70

$JRhP_A$ = 94.3 Hz, $JRhP_C$= 5.1Hz

JP_AP_B = 102.6Hz, JP_AP_C= 5.6 H

JP_BP_D = 8.3Hz, JP_BP_C = 6.5 Hz

J_CP_D = 35.6 Hz,

The $^{13}C\{^1H\}$ NMR spectrum for **70** shows the presence of two carbonyl groups on Rh (δ 203.9, $^1J_{RhC}$ = 55.8 Hz, $^2J_{CC}$ = 29.1 Hz and 201.7, $^1J_{RhC}$ = 55.3 Hz,) and one on Ir (δ 186.1). The magnitude of the C-C couplings on the CO groups on Rh is consistent with these groups being mutually trans.[20] The silyl hydrogen appears as a doublet at δ 5.38 ($^3J_{PH}$ = 4 Hz), with no resolvable coupling to Rh, in the ^1H NMR spectrum, which collapses to a singlet only upon irradiation of the Rh-bound ^{31}P resonance, indicating that the silyl group is on Rh. The hydride ligand appears as a doublet of doublets at δ -10.46 with approximately 8 and 12 Hz coupling to phosphorus indicating that it has a cis geometry with respect to both Ir-bound ^{31}P nuclei. The absence of Rh-H coupling, together with selective ^{31}P decoupling experiments, clearly establish the hydride as terminally bound to Ir. Although the bridging nature of the silylene group could not be confirmed by NMR spectroscopy, it was established by X-ray crystallographic analysis. The ORTEP diagram for compound **70** is shown in Figure 5.3 with selected bond lengths and angles given in Table 5.3. To a first approximation, the geometry at each metal is distorted octahedral in which severe distortions result from the bridging position of the $SiPh_2$ group. A

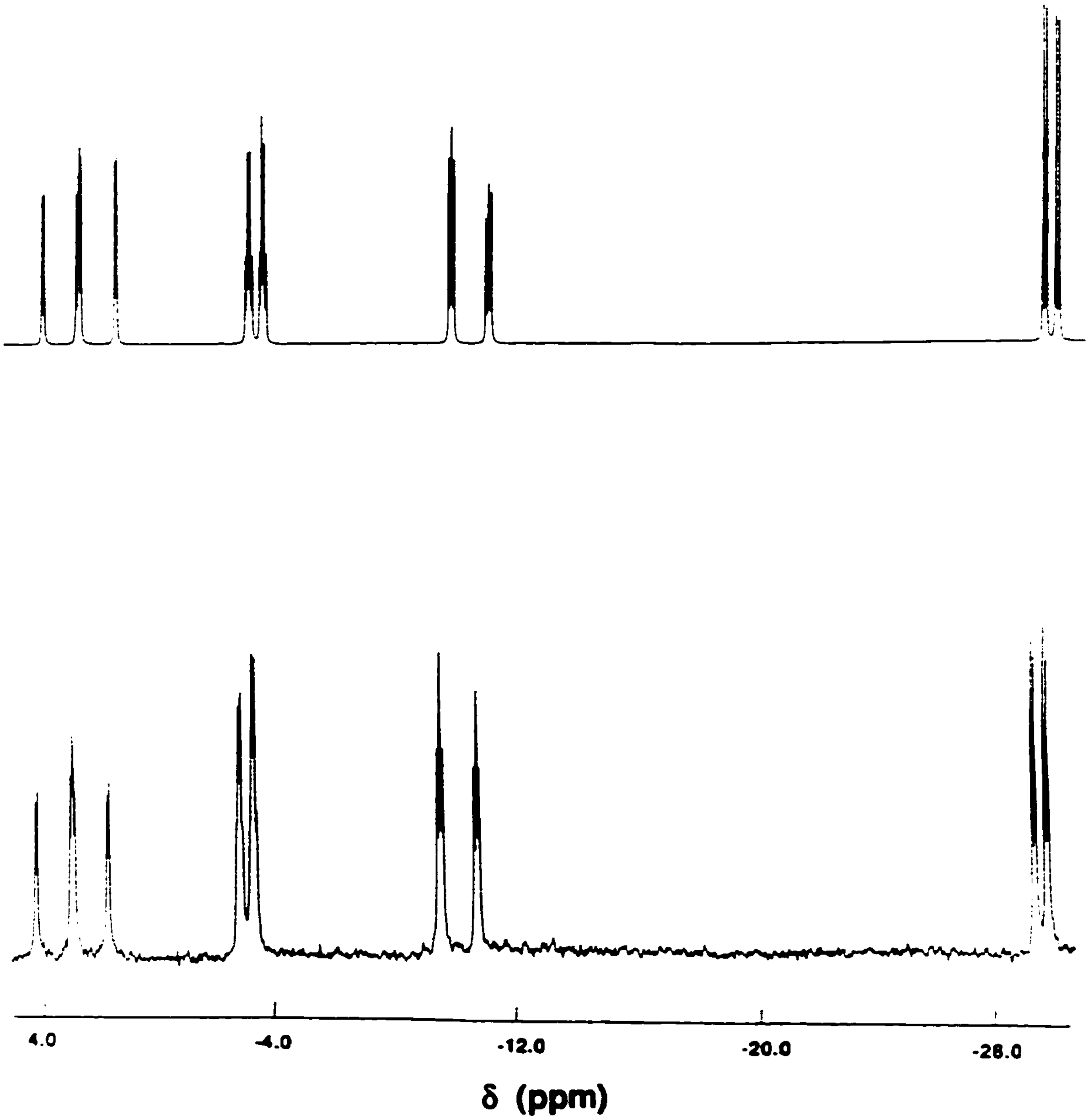


Figure 5.2 Calculated (top) and experimental (bottom) $^{31}P\{^{1}H\}$ NMR spectra of **70** showing the ABCDX spin coupling pattern.

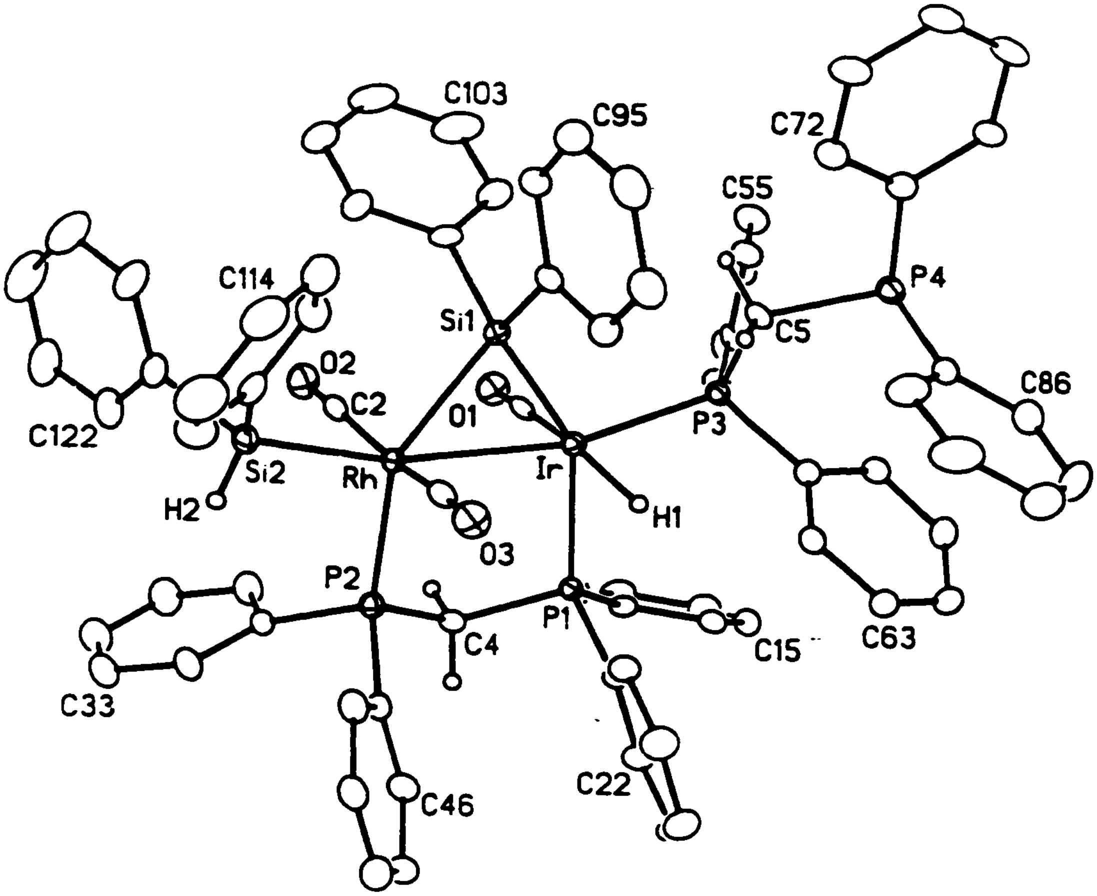


Figure 5.3. Perspective view of the [RhIr(H)(CO)$_3$(SiHPh$_2$)(η^1–dppm)(μ–SiPh$_2$)(μ–dppm)] molecule (**70**) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the hydride, silyl (H(2)) and dppm methylene groups, and are not shown for the phenyl groups.

Table 5.3. Selected Interatomic Distances and Angles for compound 70.

(a) Distances (Å)

Atom1	Atom2	Distance
Ir	Rh	2.8594(6)
Ir	P(1)	2.341(2)
Ir	P(3)	2.273(2)
Ir	Si(1)	2.338(2)
Ir	C(1)	1.905(11)
Ir	H(1)	1.65
Rh	P(2)	2.372(2)
Rh	Si(1)	2.427(2)
Rh	Si(2)	2.398(2)
Rh	C(2)	1.904(10)
Rh	C(3)	1.878(10)
P(1)	C(4)	1.848(8)
P(2)	C(4)	1.832(8)
P(3)	C(5)	1.837(8)
P(4)	C(5)	1.854(8)
O(1)	C(1)	1.141(11)
O(2)	C(2)	1.146(10)
O(3)	C(3)	1.151(10)

(b) Angles (deg)

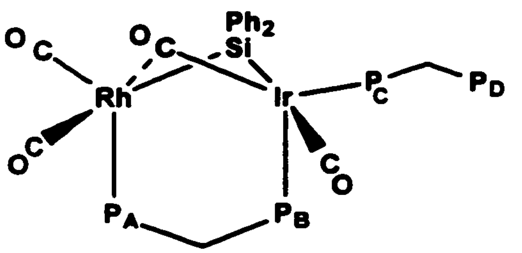
Atom1	Atom2	Atom3	Angle
Rh	Ir	P(1)	91.09(5)
Rh	Ir	P(3)	156.46(5)
Rh	Ir	Si(1)	54.55(5)
Rh	Ir	C(1)	93.6(2)
Rh	Ir	H(1)	99(3)
P(1)	Ir	P(3)	108.28(7)
P(1)	Ir	Si(1)	145.39(7)
P(1)	Ir	C(1)	92.8(3)
P(1)	Ir	H(1)	69(2)
P(3)	Ir	Si(1)	104.38(7)
P(3)	Ir	C(1)	98.6(2)
P(3)	Ir	H(1)	76(3)
Si(1)	Ir	C(1)	93.5(3)
Si(1)	Ir	H(1)	108.7(14)
Ir	Rh	P(2)	93.57(5)
Ir	Rh	Si(1)	51.72(5)
Ir	Rh	Si(2)	165.33(6)
Ir	Rh	C(2)	92.8(2)
Ir	Rh	C(3)	93.2(2)
P(2)	Rh	Si(1)	145.16(7)
P(2)	Rh	Si(2)	101.01(7)
P(2)	Rh	C(2)	93.5(3)
P(2)	Rh	C(3)	97.3(3)
Si(1)	Rh	Si(2)	113.78(8)
Si(1)	Rh	C(2)	86.4(2)
Si(1)	Rh	C(3)	88.5(2)

Table 5.3 (contd).

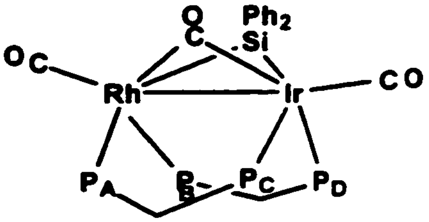
Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Si(2)	Rh	C(2)	88.0(3)	Ir	Si(1)	Rh	73.73(6)
Si(2)	Rh	C(3)	83.5(3)	Ir	C(1)	O(1)	179.3(7)
C(2)	Rh	C(3)	167.3(4)	Rh	C(2)	O(2)	176.9(8)
Ir	P(1)	C(4)	109.9(3)	Rh	C(3)	O(3)	176.9(7)
Rh	P(2)	C(4)	110.0(3)	P(1)	C(4)	P(2)	112.9(4)
Ir	P(3)	C(5)	114.0(3)	P(3)	C(5)	P(4)	116.1(4)

surprising observation is that the Ir-P(3) (2.273(2) Å) bond of the η^1-dppm ligand, which is oriented almost opposite the Rh-Ir bond (156.46(5) Å), is the shortest of the three metal-phosphorus bond distances, contrary to some previous findings[21] of a trans bond lengthening opposite a Rh-Ir bond. The Rh-Si(1) bond length of 2.427(2) Å of the silylene bridge is significantly longer than Rh-Si(2) (2.398(2) Å) for the silyl group. In contrast, the Ir-Si(1) distance (2.338(2) Å) is short, being slightly shorter than 2.371(4) Å reported for the related Ir_2 species $[Ir_2(CO)_2(H)_2(\mu\text{-}SiPh_2)(dppm)_2]$.[5a] The origin of these discrepancies appears to be steric since the bridging silylene is bent back out of the molecular plane presumably to avoid contact of its phenyls with those of the η^1-dppm and silyl (Si(1)-Rh-P(2) = 145.16(7)°, Si(1)-Ir-P(1) = 145.39(7)°) groups. The trans disposition of the two carbonyl groups on Rh as seen in the solution $^{13}C\{^1H\}$ NMR spectrum (*vide supra*) is also noted in the solid, indicating that there is no significant difference in the solution and solid-state structures for **70**.

Upon examination of the formulations for **67** and **70** it is not obvious whether following H_2 loss an initial tricarbonyl silylene intermediate was formed as was observed for the dirhodium case. Such a proposed intermediate could then react with an additional equiv of silane to afford compound **70**. In the dirhodium case, this intermediate reversibly adds one mole of CO to give a tetracarbonyl η^1-dppm species. To test this reasoning, a sample of **67** (actually a 1:2 mix of **67** and unreacted starting material) was treated with CO. The NMR analysis (^{31}P, ^1H, ^{13}C) taken immediately, indicated the formation of the tetracarbonyl species $[RhIr(CO)_4(\mu\text{-}SiPh_2)(\eta^1\text{-}dppm)(dppm)]$ (**68**). The $^{13}C\{^1H\}$ NMR spectrum of this new species displays resonances at δ 212.4 ($^1J_{RhC}$ = 5.6 Hz), 201.7 ($^1J_{RhC}$ = 71.8 Hz), 201.6 ($^1J_{RhC}$ = 73.6), and 185.3, assigned to one weakly bridging and three terminal carbonyl groups, respectively. The absence of hydride signals in the ^{1}H NMR spectrum, together with the characteristic ABCDX (X = Rh) ^{31}P spin system and the chemical shift for the pendent phosphine group, which again appears up-field at *ca.* -27.3 ppm in the ^{31}P NMR spectrum, is consistent with a formulation that resembles that of the Rh_2 species,[5d] as diagrammed in Scheme 5.5. As with the Rh_2 system, compound **68** loses CO reversibly to form the tricarbonyl species $[RhIr(CO)_2(\mu\text{-}CO)(\mu\text{-}SiPh_2)(dppm)_2]$ (**69**) in which both dppm groups now bridge the metals, having a cradle-like structure paralleling that proposed for **67** and reported for the related Rh_2 species $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiHPh)(dppm)_2]$.[5b] The calculated parameters from ^{31}P spectral simulation for compounds **68** and **69** are summarized below.



68



69

J_{RhP_A} = 100.8 Hz, J_{RhP_C}= 11.9Hz

$J_{P_AP_B}$ = 124.7Hz, $J_{P_AP_C}$ = 4.7 Hz

$J_{P_BP_D}$ = 5.0Hz, $J_{P_CP_D}$ = 40.0 Hz,

J_{RhP_A} = 106.7 Hz, J_{RhP_B}= 97.9Hz

$J_{P_AP_B}$ = 30.2Hz, $J_{P_AP_C}$ = 254.9Hz

$J_{P_BP_D}$ = 155.6Hz, $J_{P_CP_D}$ = 22.3 Hz,

The formulation for compound **69** receives support from the $^{13}C\{^{1}H\}$ NMR spectrum which exhibits peaks at δ 227.6 ($^{1}J_{RhC}$ = 40.7 Hz), 200.9 ($^{1}J_{RhC}$ = 70.0 Hz) and 186.0. Not surprisingly, addition of excess diphenylsilane to a solution containing **69** generates **70** after 1 d. $[RhIr(H)(SiHMe_2)(CO)_3(\mu\text{-}SiMe_2)(\eta^1\text{-}dppm)(dppm)]$ (**71**) is prepared in the same way as the reaction of Ph_2SiH_2.

The formation of compounds **68** and **70** and **71**, in which one dppm ligand is apparently displaced by either carbonyl or silyl group is quite unusual.[22] The fact that the dppm dissociation occurs at Rh, rather than Ir, is not unexpected given the greater lability at the former metal. The structure of **70**, in which the two silicon atoms are cis to each other at Rh seems ideally suited for Si-Si bond formation to yield the metal silane dimer. Unfortunately, attempts to induce this transformation by reacting with CO failed, with no reaction being observed after 48 h in solution. Attempts were also made to remove one CO ligand from **70** using Me_3NO, with the intent of forming the analogous dicarbonyl silyl, silylene hydride complex or the corresponding bis silylene species following reductive elimination of dihydrogen. Preliminary results for this reaction indicates the formation of one major ^{31}P-containing species whose formulation is presently unknown. Although the related bis silylene species were obtained for the Rh_2 system, this was only shown in reactions of the dihydride species $[Rh_2(CO)_2(\mu\text{-}H)(dppm)_2]$ with primary silanes such as $RSiH_3$ (R = Ph, Et, n-C_6H_{13}).[5d]

In hopes of inducing Si-C bond formation as was observed earlier with the acetylide and methyl complexes, compound **70** was reacted with 1 equiv of methyl triflate. However, electrophilic attack occurs at the dangling dppm rather than at the metals, yielding the phosphonium compound $[RhIr(CO)_3(H)(SiHPh_2)(\mu\text{-}SiPh_2)(\eta^1\text{-}PPh_2CH_2PPh_2Me)(dppm)][CF_3SO_3]$ (**72**), paralleling a similar result reported by Shaw and co-workers.[19d] Consistent with the substantially deshielded ^{31}P nucleus for the phosphonium cation, its chemical shift in the ^{31}P NMR spectrum appears downfield at δ 14.2. This value can be compared to a similar low-field resonance (*ca.* δ 22.0)[23] for the phosphonium cation $PPh_2(CH_3)_2^+$. The signals for the remaining three ^{31}P nuclei do not appear to change significantly upon alkylation, suggesting similar structures for compounds **70** and **72**. As expected, the phosphonium methyl protons of **72** appear at typically low field, at δ 1.96 ($^2J_{PH}$ = 13.0 Hz), as a doublet, integrating in a ratio of 3:1:1 with the hydride and silyl hydrogen. This resonance collapses to a singlet upon selective irradiation of the low-field ^{31}P resonance while irradiating the Rh- or Ir-bound ^{31}P resonances leaves it unchanged. Methylation of **71** also readily yields the analogous phosphonium species $[RhIr(CO)_3(H)(SiHMe_2)(\mu\text{-}SiMe_2)(\eta^1\text{-}PPh_2CH_2PPh_2Me)(dppm)][CF_3SO_3]$ (**73**) the spectral parameters of which closely resemble those of **72**. Reaction of the electrophile, CH_3+, at the phosphine rather than at the metal has literature precedent,[19c,d] and appears to be dictated by a combination of electronic and steric factors. Presumably, the pendent phosphine center is the more basic site and both metals are sterically congested. The reaction of **70** with HBF_4 was also attempted in order to contrast its reactivity with that of methyl triflate. Unfortunately, the presumed reaction products were rapidly hydrolysed as evidenced by the NMR spectra which showed the presence of a species analogous to the known trihydride $[RhIr(H)(CO)_2(\mu\text{-}H)_2(dppm)_2]$-$[CF_3SO_3]$ in addition to another species analogous to the complex $[RhIr(CO)_2(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2][CF_3SO_3]$ (**59**) on the basis of spectral similarities; both species have BF_4^- as the counterions instead of triflate anions. The apparent formation of the latter species implies an initial proton attack presumably at one of the metals.

Conclusions.

The results of this study have demonstrated facile double Si-H bond activation in the reactions of the mixed Rh/Ir complexes with dihydrosilanes, including the formation of the agostic species **57**. Compound **57** provides a well-defined example of the intermediacy of such species in reactions culminating in complete cleavage of the Si-H bonds of silanes by metal centers.

The realization of our objective of inducing Si-C bond formation through the formation of compounds **61**, **62** and **66**, is believed to hinge on the cooperativity effects of the different metal combination in these systems, possibly aided by the presence of a labile Rh center. The formation of both compounds directly implicates facile 1,2 migrations of the respective methyl and acetylide ligands onto a silyl group, presumably via silylene-bridged species.

In the study of the oxidative-addition reactions of $[RhIr(CO)_3(dppm)_2]$ with dihydrosilanes, the silyl, silylene complexes **70,71** were obtained, presumably via displacement of a dppm ^{31}P nucleus from the labile Rh center. Interestingly, alkylation of **70,71** resulted in formation of the phosphonium complexes **72,73** by apparent attack of the electrophile at the phosphorus atom of the pendent dppm group.

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6. See Chapt. 2 of this thesis.
7. See Chapt. 4 of this thesis.
8. See Chapt. 3 of this thesis.
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22. This reaction represents a formal nucleophilic displacement of the dppm group at Rh by the Si-H functionality of the diphenylsilane. An analogous nucleophilic displacement of one dppm by MeI from the Pt_2 complex

$[Pt_2(\mu\text{-dppm})_3]$ giving $[Pt_2(CH_3)(\mu\text{-dppm})(\eta^1\text{-dppm})][I]$ has been reported by Puddephatt and Co-workers. See reference 19c.

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Chapter 6

Methylene-bridged Complexes

Introduction

Methylene groups are quite versatile owing to their propensity to undergo C-C and C-heteroatom bond formation with an array of substrates culminating in olefin metathesis[1] and homologation processes;[2,3] the latter reactions are at the heart of Fischer-Tropsch chemistry,[4] in which surface-bound methylene groups combine with other hydrocarbyl fragments giving rise to alkanes and alkenes. It is hoped that our Rh/Ir systems might serve as simple conceptual models for studies aimed at improving our understanding of how these C-C bond-coupling steps occur, the factors that influence them and the mediating role of the metal template.

In a previous study,[5] the methoxymethyl complex $[Ir_2(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ was synthesized through oxidative addition of ICH_2OCH_3 to $[Ir_2(CO)_3(dppm)_2]$. Subsequent removal of the methoxy group by reactions with electrophiles yielded a methylene-bridged species. This approach to preparing methylene complexes has literature precedent,[6] and in this chapter the results of its extension to an RhIr system will be described. Another possible entry into methylene complexes is through the double oxidative addition of dihaloalkanes such as CH_2I_2 to the low-valent complex $[RhIr(CO)_3(dppm)_2]$, an approach that has been successfully used in a number of binuclear complexes.[7] In this case, single oxidative addition of one C-I bond, leading to the formation of an iodo methyl complex, is also possible.[8]

In this chapter, we present the results of preliminary studies aimed at the preparation of methylene-bridged complexes involving our dppm-bridged RhIr framework.

Experimental Section

General Comments. General experimental conditions were as described in Chapters 2-5. The compounds [RhIr(CO)$_3$(dppm)$_2$],[9] [RhIr(CH$_3$)(CO)$_2$(dppm)$_2$]-[CF$_3$SO$_3$] (**2**)[10] and [RhIr(CO)$_2$(H)(μ-H)$_2$(dppm)$_2$][CF$_3$SO$_3$],[9] were prepared as previously reported. The characterization of some of the compounds was based on spectroscopic methods owing to difficulties in separating them from side products such as [RhIr(I)$_2$(CO)(μ-CO)(dppm)$_2$],[11] [RhIr(CO)$_2$(μ-I)(μ-CO)-(dppm)$_2$][I][11] and other unidentified species. For this reason, the microanalyses for these compounds (*vide infra*) gave unsatisfactory results. Iodomethylmethylether, iodoacetonitrile, diiodomethane, trimethylsilyl triflate ((CH$_3$)$_3$SiOSO$_2$CF$_3$), and Diazald were purchased from Aldrich. **Iodomethylmethylether is extremely toxic and appropriate safety precautions should be exercised during its handling**. Spin saturation transfer experiments were carried out on a Bruker AM-400 NMR spectrometer operating at 400.1 MHz. Spectroscopic data for the new compounds are given in Table 6.1.

Preparation of Compounds

(a) [RhIr(I)(CH$_2$OCH$_3$)(CO)(μ-CO)(dppm)$_2$] (74). To a slurry of 45 mg (0.039 mmol) of [RhIr(CO)$_3$(dppm)$_2$] in 3 mL of toluene was added CH$_3$OCH$_2$I (3.3 μL, 0.039 mmol) and the resulting mixture was then stirred. The suspension dissolved within 0.5 h and after 1.5 h of stirring, the color of the solution turned yellow from orange. 10 mL of pentane was added, causing the

Table 6.1. Spectroscopic Parameters for the Compounds[a]

		NMR[d]		
Compounds	IR,[b,c] cm^{-1}	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
[RhIr(I)(CH$_2$OCH$_3$)(CO)(μ-CO)(dppm)$_2$] (**74**)	1932(ss), 1745(s)	30.8(dm, $^1J_{RhP}$=163.7Hz) -3.8(m)	4.42(m,2H), 4.20(m,2H) 2.93(td,3H), 2.02(s,3H)	212.7(dm, $^1J_{RhC}$=40.1Hz, $^2J_{CC}$ =6.0Hz,1C), 179.5(m,1C)
[RhIr(CH$_2$OCH$_3$)(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] (**75**)	-	22.2-20.6 (second order multiplet)	4.43(m,2H), 3.98(m,2H) 2.58(b, 2H), 2.27(s,3H)	182.5(bs,1C) 177.7(dt, $^1J_{RhC}$=71.3Hz,1C)
[RhIr(CO)$_2$(μ-CH$_2$)(μ-I)(dppm)$_2$][CF$_3$SO$_3$] (**76**)	1958(bs)[c]	21.6(dm, $^1J_{RhP}$=110.4Hz) -5.8(m)	10.79(qd,2H), 4.80(m,2H) 4.37(m,2H)	191.9(dt, $^1J_{RhC}$=66.3Hz,1C) 183.5(t,1C)
[RhIr(I)(CO)(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**77**)	1957(ss)[c]	10.9(dm, $^1J_{RhP}$=128.9Hz) -10.6(m)	7.75(dq,2H), 4.79(m,2H) 4.58(m,2H)	174.4(t,1C)
[RhIr(CO)(η^2-DMAD)(μ-CH$_2$)(μ-I)(dppm)$_2$][CF$_3$SO$_3$] (**78**)	-	11.3(dm, $^1J_{RhP}$=125.9Hz) -2.9(m)	12.22(qd,2H), 4.48(m,2H) 4.37(m,2H), 3.58(s,3H) 3.26(s,3H)	180.7(t,1C)

Table 6.1 (contd).

		NMR[d]		
Compounds	IR,[b,c] cm^{-1}	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(I)(CO)_2(\mu\text{-}CO)(Ph_2P\text{-}CHPPh_2)(dppm)]$ **(79)**	1953(bs), 1823(m)	P_A 25.3(dm, $^1J_{RhP}$=124.0Hz) P_B 15.7(dm, $^1J_{RhP}$=114.0Hz) P_C –6.1(m), P_D –12.7(m)	4.60(m,1H), 4.41(m,1H) 2.03(tt, $^2J_{PH}$=7.0Hz, $^4J_{PH}$=3.3Hz,1H)	204.3(dm, $^1J_{RhC}$=38.0Hz, 1C), 195.2(dt, $^1J_{RhC}$ =71.1Hz,1C), 182.0 (bs,1C)
$[RhIr(C_2H_4)(\mu\text{-}H)(CO)_2\text{-}(dppm)_2][CF_3SO_3]$ **(80)**	1966(bs)[c]	22.7(dm, $^1J_{RhP}$=114.2Hz) -0.1(m)	4.20(m, 4H), 1.58(m, 4H), -12.18(dm, $^1J_{RhH}$=23.0Hz, 1H)	185.1(dt,1J_{RhC}=74.0Hz,1C) 181.2(b,1C)

[a] IR abbreviations: ss = strong sharp, sb = strong broad, ms = medium sharp, m = medium, w = weak, sh = shoulder. NMR abbreviations: t = triplet, d = doublet, dt = doublet of triplets, dd = doublet of doublets, tt = triplet of triplets, ddt = doublet of doublets of triplets, ddm = doublet of doublets of multiplets, dm = doublet of multiplets, td = triplet of doublets, bs = broad singlet, m = multiplet, q = quartet, s = singlet. [b] Nujol mull except as indicated. Values quoted are ν(CO) except as indicated. [c] CH_2Cl_2 cast. [d] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4 while ^1H and $^{13}C\{^1H\}$ are referenced vs TMS. Chemical shifts for the phenyl hydrogens are not given in the ^1H NMR data.

precipitation of a yellow solid (36 mg, 71%). Anal. Calcd for $IrRhIP_4O_3C_{54}H_{49}$: C, 50.10; H, 3.78; I, 9.82. Found : C, 49.97; H, 4.07; I, 10.65.

(b) Reaction of [RhIr(I)(CH$_2$OCH$_3$)(CO)(μ-CO)(dppm)$_2$] with CH$_3$SO$_3$CF$_3$. 20 mg (0.015 mmol) of [RhIr(I)(CH_2OCH_3)(CO)(μ-CO)(dppm)$_2$] (**74**) was dissolved in 0.5 mL of CD_2Cl_2 in an NMR tube at -78 °C. Methyl triflate (1.8 μL, 0.015 mmol) was added, the reaction mixture was allowed to stand at this temperature for 0.5 h, then gradually allowed to warm to ambient temperature causing a change in the color of the solution from yellow to purple. NMR analysis carried out immediately indicated the presence of [RhIr(CH_2OCH_3)-(CO)$_2$(dppm)$_2$][CF_3SO_3] (**75**) and *ca.* 20-30% of [RhIr(CO)$_2$(μ-CH_2)(μ-I)(dppm)$_2$]-[CF_3SO_3] (**76**) in the solution. Our failure to separate these products precluded elemental analysis. The use of trimethylsilylmethyl triflate in the reaction with **74** gave similar product distribution as above.

(c) [RhIr(CO)$_2$(μ-CH$_2$)(μ-I)(dppm)$_2$][CF$_3$SO$_3$] (76). Compound **74** was prepared as described in (a) using 10 mL of toluene. After 1.5 h of stirring, the mixture was purged with N_2 gas at a rate of *ca.* 0.3 mLs^{-1} for 15 min to remove dissolved CO from the reaction mixture. At this stage, trimethylsilyl triflate ($(CH_3)_3SiOSO_2CF_3$) (7.5 μL, 0.039 mmol) was added causing the yellow solution to become a cloudy, purple suspension within 5 min. After 0.5 h of stirring, the solvent was removed *in vacuo*. Recrystallization from CH_2Cl_2/ether gave a brown-purple solid (44 mg, 80%). Anal. Calcd for $IrRhISP_4O_5C_{54}H_{46}$: C, 45.95; H, 3.26; I, 9.00. Found C, 45.56; H, 3.25; I, 8.12.

(d) [RhIr(I)(CO)(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (77). 30 mg (0.021 mmol) of compound **76** and 3 mg (0.062 mmol) of Me_3NO were charged into a 10 mL flask and dissolved in 3 mL of CH_2Cl_2. The mixture was stirred for 0.5 h under a slow purge of N_2 (*ca.* 0.1 mLs^{-1}) during which time the purple solution turned brown. The solvent was removed *in vacuo*, the brown residue was redissolved in 1 mL of CH_2Cl_2, and 5 mL of ether was added. The resulting brown flocculent solid was recrystallized from CH_2Cl_2/ether. The NMR analysis (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$) indicated the presence of **77** in addition to varying amounts of $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][CF_3SO_3]$ which has similar spectral characteristics with those of the previously characterized $[RhIr(CO)_2(\mu\text{-}I)\text{-}(dppm)_2][BF_4]$.[11]

(e) $[RhIr(CO)(\eta^2\text{-}DMAD)(\mu\text{-}CH_2)(\mu\text{-}I)(dppm)_2][CF_3SO_3]$ (78). Compound **77** was prepared *in situ* as described in (d). DMAD (dimethyl acetylenedicarboxylate, 2.6 μL, 0.021 mmol) was added and stirred for 1 h. Removal of the solvent and recrystallization from CH_2Cl_2/ether gave an orange-brown powder. Microanalysis was not carried out for compound **78** due to difficulties in separating excess Me_3NO and due to co-production of other unidentified minor products.

(f) Reaction of $[RhIr(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ with HBF_4. 30 mg (0.026 mmol) of $[RhIr(CO)_3(dppm)_2]$ was slurried in 2 mL of toluene. CH_3OCH_2I (2.6 μL, 0.026 mmol) was added and the mixture was stirred for 1.5 h. At this stage, HBF_4 (3.3 μL, 0.026 mmol) was added. After 0.5 h an orange precipitate had formed. 10 mL of pentane was added to complete the precipitation and the product was washed (2 x 5 mL) with pentane and dried *in vacuo* (23 mg, 63%). The NMR data indicated that the previously characterized $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$[11] was the only product present in solution. If the reaction was conducted in an NMR tube, dimethylether was identified in the ^1H NMR spectrum.

(g) $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (79). 39 mg (0.034 mmol) of $[RhIr(CO)_3(dppm)_2]$ was dissolved in 5 mL of benzene, CH_2I_2 (2.7 μL, 0.034 mmol) was added and the mixture was stirred for 1 h during which time the color of the solution changed from orange to dull yellow. The solvent was then removed *in vacuo*. Recrystallization from benzene/pentane afforded a yellow microcrystalline solid (28 mg, 64%). Microanalysis results for **79** were always low in % carbon and high in % iodine due to the co-production of minor amounts (between 15% and 25%) of [RhIr(CO)$_2$(μ-CO)(μ-I)(dppm)$_2$][I]. A typical result is given: Anal. Calcd for IrRhP$_4$O$_3$C$_{53}$H$_{43}$: C, 49.86; H, 3.37; I, 9.95. Found: C, 49.17; H, 3.34; I, 10.96.

(h) Reaction of Compound 79 with HBF$_4$. Compound **79** was prepared as described in (g) above except that the reaction was carried out in an NMR tube in 0.5 mL of THF-d$_8$. HBF$_4$.Me$_2$O (4 μL, 0.034 mmol) was added via a syringe. The NMR analysis (^{1}H and ^{31}P{^{1}H}) of the resulting mixture indicated the formation of the previously identified species [RhIr(CO)$_2$(μ-I)(μ-CO)-(dppm)$_2$][BF$_4$].[11]

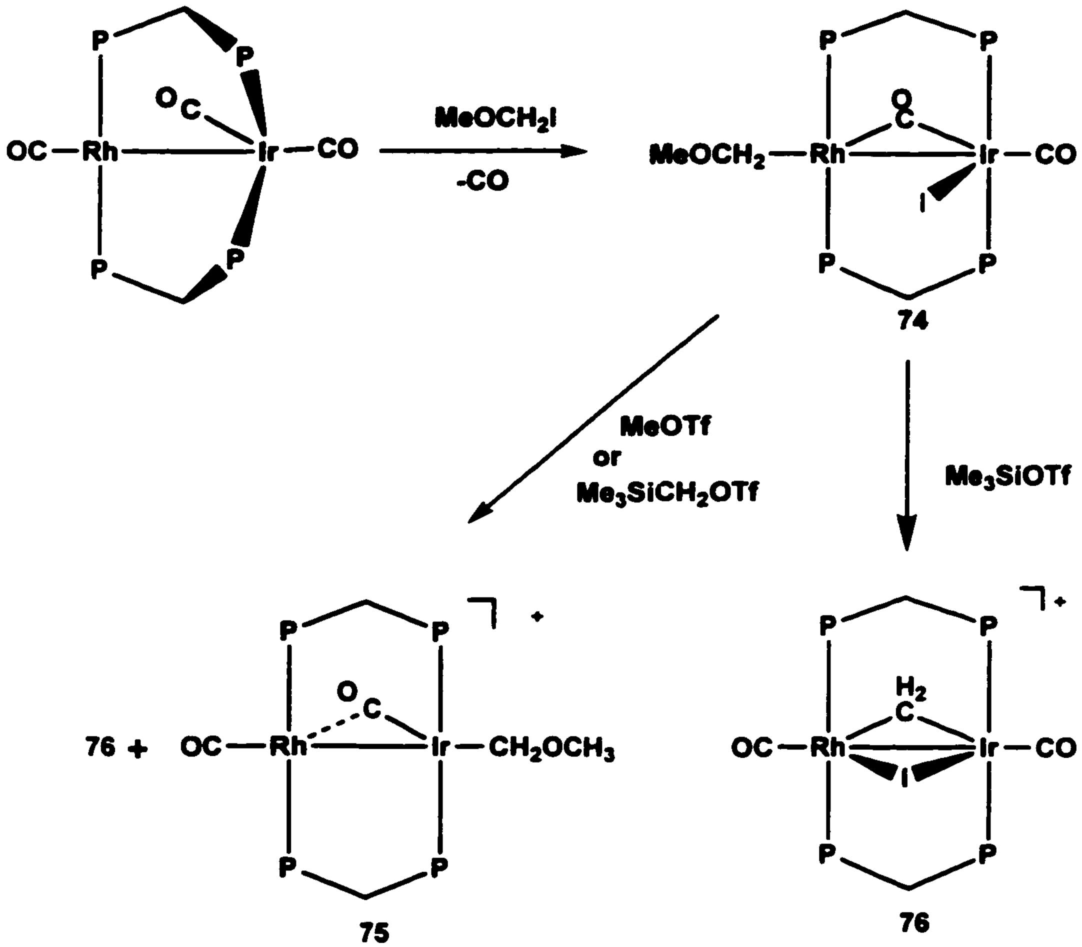
(i) Reaction of [RhIr(CH$_3$)(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] with CH$_2$N$_2$. 30 mg (0.023 mmol) of [RhIr(CH$_3$)(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] (**2**) was dissolved in 0.6 mL of THF-d$_8$ in an NMR tube. Freshly prepared diazomethane gas, obtained by adding 2 mL of a saturated KOH solution to a 1 mL methanolic solution of Diazald (100 mg) in a test-tube equipped with a septum, was bubbled through the solution via a cannula for 5 min and the sample was taken for NMR analysis immediately. The NMR analysis at room temperature showed quantitative conversion to [RhIr(C$_2$H$_4$)(μ-H)(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] (**80**), in addition to 1-butene. Compound **80** was unstable in the absence of ethylene. At temperatures between -80 °C and 0 °C, the NMR data showed several broad and overlapping peaks. Compound **80** may be alternatively synthesized by the reaction of [RhIr(H)(CO)$_2$(μ-H)$_2$(dppm)$_2$][CF$_3$SO$_3$][9] with ethylene. After 7 d in an NMR tube, **80** is formed in about 60% yield as determined by NMR spectroscopy (ratios of ^{31}P signal intensities) in addition to the starting material.

Results and Discussion

Although $[RhIr(CO)_3(dppm)_2]$ does not react with CH_3I, it reacts readily with CH_3OCH_2I, accompanied by CO loss, yielding the oxidative-addition product, $[RhIr(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ (**74**). This is the mixed-metal analogue of the previously characterized $[Ir_2(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$,[5] the structure of which was determined crystallographically. The methylene protons for the methoxymethyl group appear at δ 2.93, as a triplet of doublets, consistent with this group being bound to Rh while the methyl group gives rise to a singlet at δ 2.17. The carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum for **74** displays two peaks at δ 212.7 ($^1J_{RhC}$ = 40.1 Hz, $^2J_{CC}$ = 6.0 Hz) and 179.5, assigned to bridging and terminal carbonyl groups, respectively. This is supported by the IR spectrum which shows two absorption bands at 1953 and 1823 cm^{-1}. Presumably, the presence of the iodo and alkyl ligands, which are good σ donors,[12] leads to increased electron density at the metals, necessitating a bridging carbonyl group. The carbonyl group can better maximize its π acidity in a bridging position where it simultaneously binds to two metals rather than binding terminally to a single metal.[13] Compound **74** is spectroscopically similar and structurally analogous to the previously described iodo methyl complex $[RhIr(I)(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]$,[10] and to the known diiodo complex $[RhIr(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$.[11]

Compound **74** contains several potential sites for electrophilic attack. In addition to direct attack at the metals (which could then be followed by coupling reactions[4-7,14] involving the added electrophile and the organic ligand),

Scheme 6.1



74

75

76

electrophilic attack at the oxygen of the methoxy group may result in transformation of this ligand into a methylene group, which is one of the focusses of this chapter . Alternately, electrophilic attack can occur at the iodo ligand leading to the formation of $[RhIr(CH_2OCH_3)(CO)_2(dppm)_2]^+$ by loss of iodomethane. This species would be analogous to the methyl complex **2**, so it would be of interest to compare the reactivity of this compound having a methoxy substituent on the methyl group.

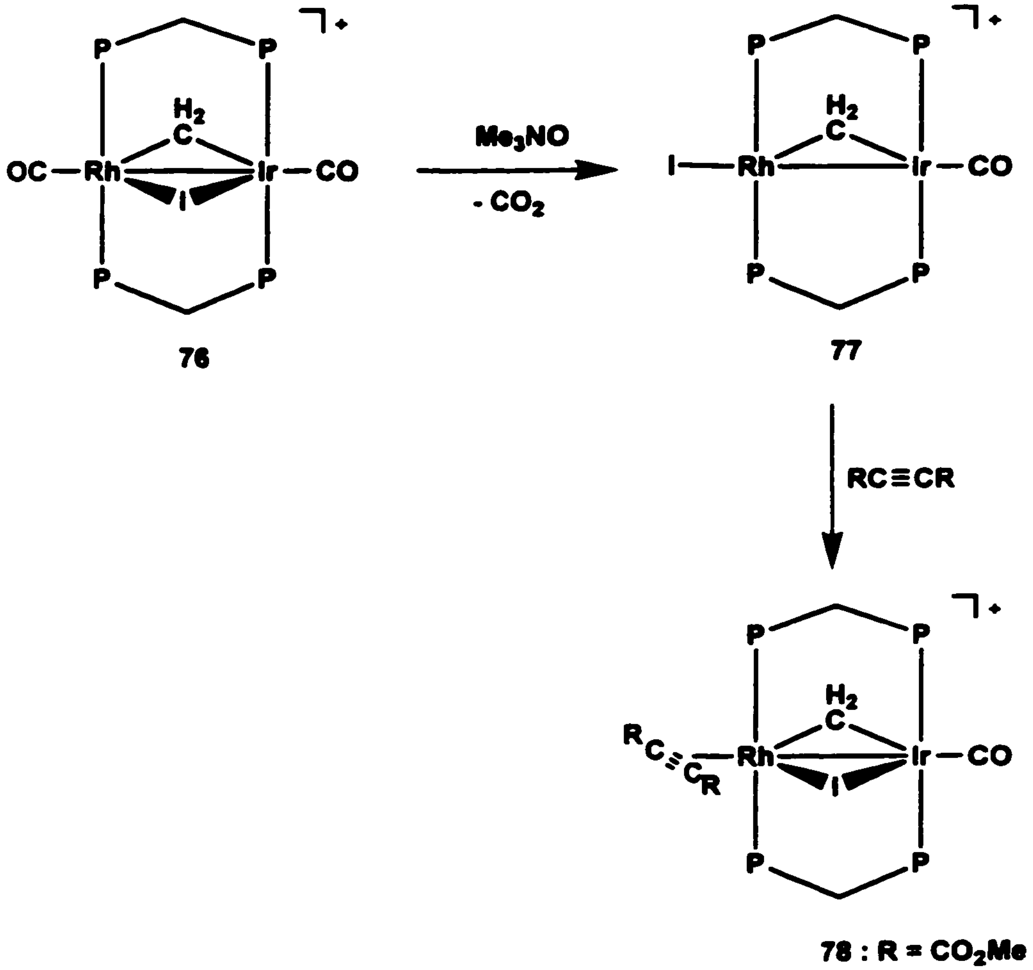
Compound **74** reacts with methyl triflate ($CH_3OSO_2CF_3$) or trimethylsilylmethyl triflate ($(CH_3)_3SiCH_2OSO_2CF_3$) by both pathways suggested above. The major product, $[RhIr(CH_2OCH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**75**), results from iodide abstraction, whereas the minor species $[RhIr(CO)_2(\mu\text{-}CH_2)(\mu\text{-}I)(dppm)_2]$-$[CF_3SO_3]$ (**76**), formed in *ca.* 20-30% yield, occurs through loss of the methoxy group. The $^{31}P\{^1H\}$ NMR spectrum for compound **75** at room temperature displays a complex second-order multiplet centered at δ 21.9, for the Rh-bound phosphines with an overlapping singlet resonance for the Ir-bound ligand (an analogous spectral pattern was shown for compound **2** in Chapter 2). The methylene and methyl protons of the methoxymethyl group appear as broad resonances at δ 2.58 and 2.27 in the ^1H NMR spectrum while the carbonyl groups display resonances in the $^{13}C\{^1H\}$ NMR spectrum at δ 182.6 and 177.7 ($^1J_{RhC}$ = 71.0 Hz). These $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ resonances for **75** closely resemble those observed earlier for the methyl analogue **2**; in particular, both species display a low-field signal for the Ir-bound carbonyl, (which suggests that this group might be involved in a weak semibridging interaction with the adjacent Rh) attesting to the structural similarities of both compounds. Removal of the iodide ion is accompanied by migration of the methoxymethyl group from Rh to Ir, in much the same way as observed in the iodo methyl compound [$RhIr(I)(CH_3)(CO)(\mu\text{-}CO)(dppm)_2$] (**13**) described in Chapter 2. By contrast, the analogous reaction of the diiridium complex [$Ir_2(CH_2OCH_3)(CO)(I)(\mu\text{-}CO)(dppm)_2$] with methyl triflate was reported[5] to give the methoxycarbyne species [$Ir_2(H)_2(CO)_2(\mu\text{-}COCH_3)(dppm)_2$][$CF_3SO_3$], an apparent result of abstraction of the iodo group followed by double C-H bond activation. This finding reflects the greater tendency of the Ir center in this species to undergo oxidative addition.[15] Again, as was noted earlier[10] for the above methyl complex, C-H activation in the diiridium system is not paralleled in the RhIr analogue. It is not entirely surprising that C-H bond cleavage is not favored at Rh, but it is surprising that this process did not at least occur at the Ir center. Presumably, the Ir center in the mixed-metal system has somehow been rendered less basic, relative to the analogous Ir_2 system through interaction with the adjacent Rh center. The chemistry of compound **75** was not investigated since it could not be obtained free from the other reaction product, compound **76**.

In the above reaction with methyl triflate the methylene-bridged complex [$RhIr(CO)_2(\mu\text{-}CH_2)(\mu\text{-}I)(dppm)_2$][$CF_3SO_3$] (**76**), resulting from electrophilic attack at the methoxymethyl oxygen and elimination of dimethyl ether, was only obtained in low yield. It can be obtained as the exclusive product if the more oxophilic electrophile, trimethysilyl triflate ($Me_3SiOSO_2CF_3$) is used instead. The methylene protons of **76** resonate down-field as a doublet of quintets at δ 10.79 ($^2J_{RhH}$ = 1.0 Hz), within the range (5-11 ppm)[16] commonly observed for methylene groups which bridge metal-metal bonds. The formulation assumed for compound **76**, in which the iodo group bridges the metals with both carbonyl groups trans to the Rh-Ir bond, is based on the structure detemined for the analogous Ir_2 complex [$Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}I)(dppm)_2$][$CF_3SO_3$].[5]

Compound **76** is inert to most substrates including phosphines, ethylene, allenes, acetylene and ^{t}BuNC, probably owing to the saturated configuration at each metal. The nucleophile NaC≡CH also fails to react with compound **76** as does divinyl magnesium ($(CH_2{=}CH)_2Mg$). However, MeLi and vinyl magnesium bromide both react with **76** but give irreproducible results. The reaction of **76** with KI in acetone results in the formation of two isomeric products (syn and anti isomers) with the suggested formulations $[RhIr(I)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$. However, the complexity of the spectra due to the presence of two other by-products and insufficient data[17] precluded an accurate identification.

One of the carbonyl groups of compound **76** is labile and treatment with Me_3NO results in the formation of the methylene-bridged monocarbonyl species $[RhIr(I)(CO)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**77**), shown in Scheme 6.2. The ^{1}H NMR spectrum for **77** displays a quintet of doublets at δ 7.75 assigned to the bridging methylene protons. The only carbonyl group present in the molecule appears as a triplet at δ 174.4 in the $^{13}C\{^{1}H\}$ NMR spectrum, consistent with this group being bound to Ir. With the carbonyl substituent at Ir and the methylene group bridging both metals, the iodide ligand is by necessity terminally positioned on Rh. The reactions of compound **77** with acetylene (1 equiv or excess) gave a number of products which have not been fully characterized.[18] Compound **77** also reacts with the activated alkyne DMAD, to afford a methylene-bridge alkyne adduct $[RhIr(CO)(\eta^2\text{-}DMAD)(\mu\text{-}CH_2)(\mu\text{-}I)(dppm)_2][CF_3SO_3]$ (**78**). The bridging methylene protons for this compound show up as a quintet of doublets at δ 12.22 in the ^{1}H NMR spectrum, which also displays singlet peaks at δ 3.58 and 3.26 assigned to the DMAD methoxy protons. The $^{13}C\{^{1}H\}$ NMR spectrum exhibits only a triplet resonance at δ 180.7 attributed to a terminal carbonyl group on Ir. Although the exact coordination

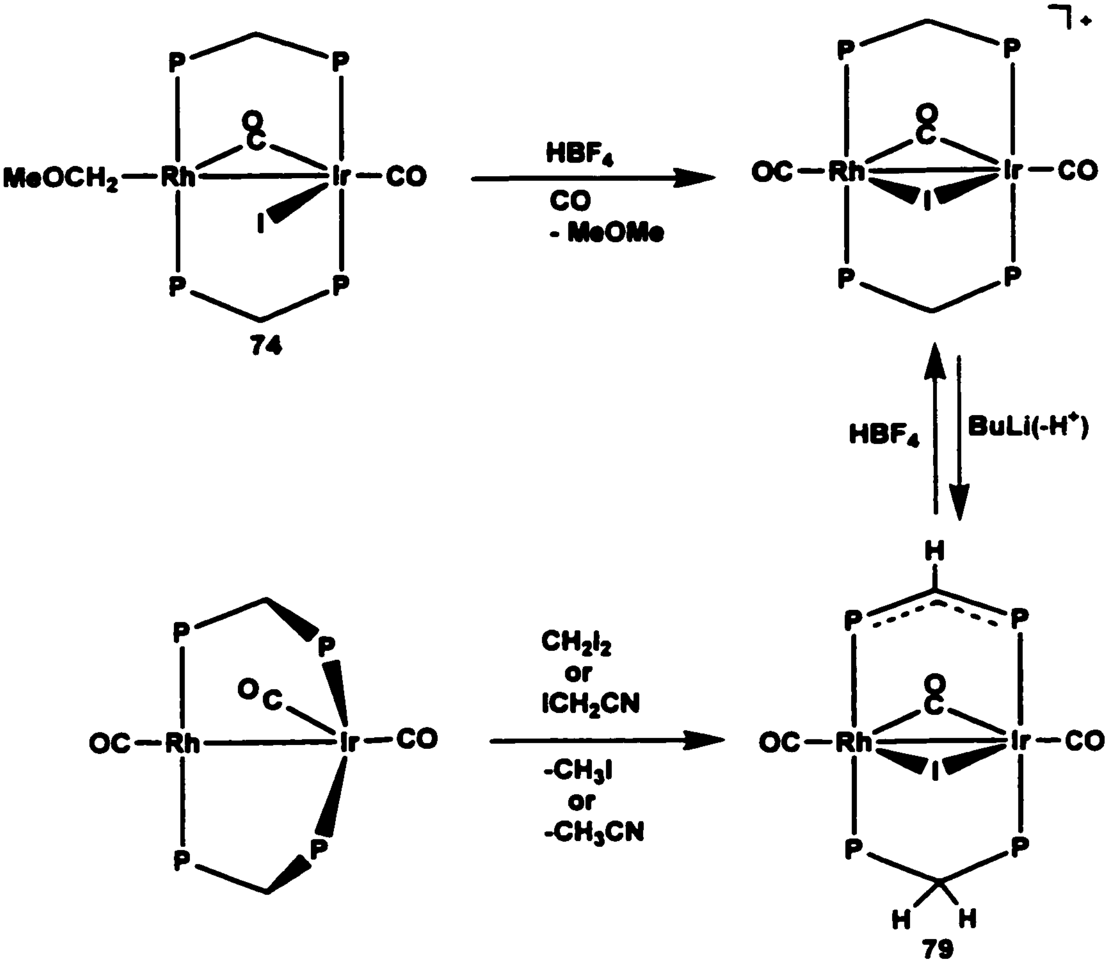
Scheme 6.2


P
P
H₂
C
OC
Rh
Ir
CO
I
P
P
76
Me₃NO
- CO₂
I
Rh
Ir
CO
77
RC≡CR
RC≡CR
Rh
Ir
CO
78 : R = CO₂Me

modes of the iodine and the alkyne ligands could not be unambigously determined from the spectral data, the gross structure, as formulated above, was confirmed by X-ray crystallography. The complete structural data for **78** are not provided due to significant problems associated with the refinement of the structure, resulting from the very poor diffracting ability of the crystal; nevertheless the data clearly show the overall structural features of the complex, confirming the η^2-alkyne coordination on Rh, adjacent to the bridging methylene. Compound **78** is structurally related to the iodo-bridged methylene species **76**, by replacement of its Rh-bound carbonyl with a DMAD group. We had hoped to induce C-C coupling processes with these reactions, but so far this has not been realized.

Addition of HBF_4 to a toluene solution of $[RhIr(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ (**74**), prepared *in situ*, causes an immediate change in the color of the solution from yellow to orange, along with the precipitation of the previously characterized cationic iodo tricarbonyl species $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]$-$[BF_4]$,[11] the extra carbonyl group presumably being scavenged from decomposition products. If the reaction is conducted in an NMR tube, a singlet (δ 3.38) is observed in the ^1H NMR spectrum, which is assigned to the protons of dimethylether. We suggest that protonation at one metal has occurred to give an initial, unobserved hydrido, methoxymethyl species accompanied by facile reductive elimination of dimethylether. Although we have no information about the site of protonation, protonation at Rh, adjacent to the methoxymethyl ligand would be expected to result in facile elimination of dimethylether. This is in contrast to the analogous diiridium species $[Ir_2(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ which gives the methylene species $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}I)(dppm)_2]^+$ upon protonation,[5] presumably through protonation at the methoxy group.

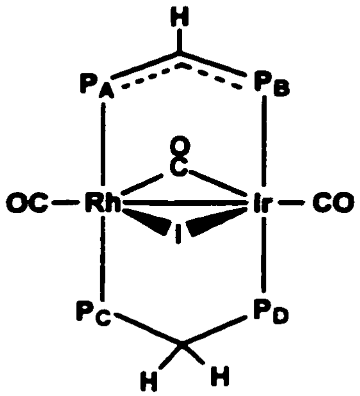
Scheme 6.3



MeOCH$_2$—Rh
Ir—CO
74
HBF$_4$
CO
- MeOMe
OC—Rh
Ir—CO
+
HBF$_4$
BuLi(-H$^+$)
CH$_2$I$_2$
or
ICH$_2$CN
-CH$_3$I
or
-CH$_3$CN
79

Although the oxidative addition of ICH_3 and ICH_2SiMe_3 to $[RhIr(CO)_3(dppm)_2]$ does not occur[10] the facile reaction of ICH_2OCH_3 suggested that other ICH_2X groups, in which one of the methyl hydrogens is substituted by an electronegative group, may also result in oxidative addition. We therefore investigated the reactions of the above tricarbonyl complex with CH_2I_2 and ICH_2CN. Although the single oxidative addition of these species would yield an iodide or cyanide-substituted methyl compound, the diiodomethane is also capable of generating a methylene-bridged diiodide, by a double oxidative addition. The reaction of $[RhIr(CO)_3(dppm)_2]$ with CH_2I_2 or ICH_2CN occurs readily to give the identical product in each case. This product is *neither* of the targeted oxidative-addition species, but instead was identified as $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (**79**), as diagrammed in Scheme 6.3. The other products are CH_3I or CH_3CN, respectively, identified in ^1H NMR spectrum in NMR tube reactions. Clearly in these reactions a hydrogen atom of one of the dppm methylene groups has been abstracted accompanied by coordination of an iodine atom at the metals. The most prominent feature of the ^1H NMR spectrum is the presence a high-field triplet of triplets at δ 2.03, assigned to the methyne hydrogen of the $Ph_2PCHPPh_2$ group. The high-field shift upon conversion of the dppm methylene group to a methyne group has previously been observed.[19] This resonance is also close to that exhibited by the analogous Ir_2 compound (*ca.* δ 2.07).[5] The other two dppm methylene protons appear in the low-field region expected for these groups (δ 4.60 and 4.41), each integrating in a ratio of 1:1 with the high-field signal. The $^{31}P\{^1H\}$ NMR spectrum for compound **79** differs from the normal AA'BB'X spin system for these systems owing to the different P-C-P couplings for dppm and $Ph_2PCHPPh_2$ groups. The P-C-P coupling for the latter group (132 Hz), derived by simulation, is substantially larger than that calculated for the dppm (*ca.* 83

Hz), since the former involves an sp^2 methanide carbon in contrast to the sp^3 hybridization for the methylene carbon. Significantly, these calculated coupling constants, which are summarized below, compare favorably with those reported for analogous Ir_2 complex (*ca.* 129 and 80 Hz),[5] which has been



$J_{P_AP_B}$ = 132 Hz

$J_{P_AP_C}$ = 291 Hz, $J_{P_BP_D}$ = 288 Hz

$J_{P_CP_D}$ = 83 Hz

$J_{P_AP_D}$ = $J_{P_BP_C}$ = 29 Hz

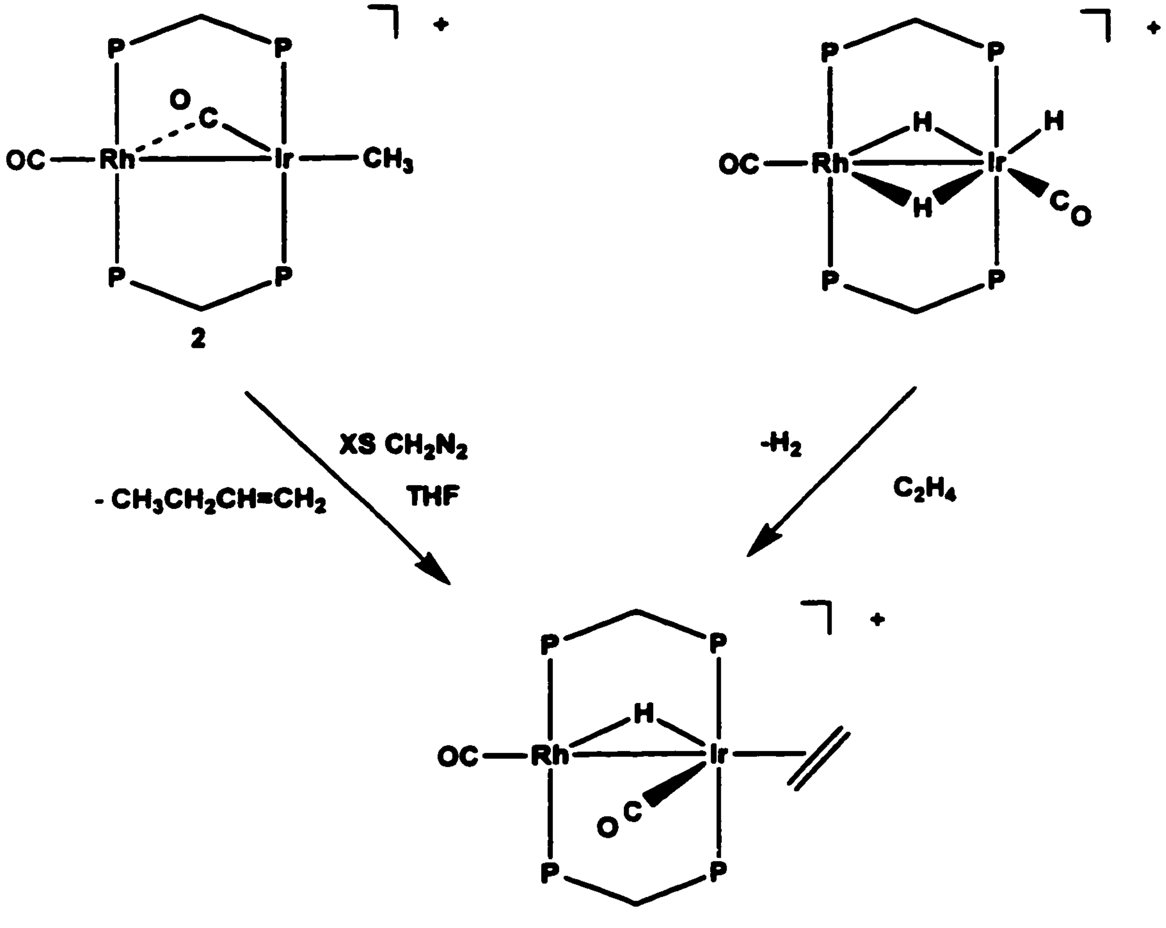
J_{RhP_A} = 124 Hz

J_{RhP_C} = 114 Hz

structurally characterized and those of the related RhOs species [RhOs(CO)$_4$-(Ph_2CHPPh_2)(dppm)] (*ca.* 159 and 96 Hz).[19] In addition, simulation of the spectrum gives values of 291 and 288 Hz for the P-P coupling across Rh and Ir, respectively, consistent with a trans arrangement at each metal. This compound can formally be considered as a deprotonated product of the known $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]^+$, particularly given the acidic tendencies of dppm,[20] therefore the $Ph_2PCHPPh_2$ group can be considered as an anionic donor, conferring upon both metals an 18e configuration and a (+1) oxidation state. Consistent with these ideas, **79** is readily protonated at the methyne carbon with HBF_4 affording the aforementioned iodo tricarbonyl species $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$,[11] and addition of ^{t}BuLi to this product readily reverses the protonation step, regenerating **79**. This reversible protonation/deprotonation cycle is reminiscent of the results obtained for the related RhOs species $[RhOs(CO)_4(Ph_2CHPPh_2)(dppm)]$.[19] In fact, however, the above reactions with CH_2I_2 and ICH_2CN have been previously observed in our group[19] and others,[20] and appear to proceed via a radical process, and not a deprotonation reaction.

Another common route to methylene-bridged complexes is through the use of diazomethane.[21,22] Reaction of **2** with CH_2N_2 at room temperature, resulted in the formation of the hydrido ethylene adduct $[RhIr(C_2H_4)(CO)_2(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**80**), along with a quantity of 1-butene, identified by its peaks in the ^1H NMR spectrum (δ 5.80, 4.96, 4.80, 2.03 and 0.93). The ethylene adduct is analogous to that reported for $[Ir_2(C_2H_4)(CO)_2(\mu\text{-}H)(dppm)_2][CF_3SO_3]$.[23] Compound **80** is also the major product obtained when a solution of the trihydride species $[RhIr(H)(\mu\text{-}H)_2(CO)_2(dppm)_2]^{+}$[9] is pressured with ethylene gas. The ^1H NMR spectrum for **80** at room temperature displays, in addition to a broad signal for the dppm methylene protons (*vide supra*), a multiplet (δ 1.58) for the ethylene protons and a multiplet at δ -12.18 ($^1J_{RhH}$ = 23.0 Hz) for the bridging hydride ligand. Although the results of selective ^{31}P decoupling experiments were equivocal as to which metal the ethylene ligand binds, owing to the broadness of the ethylene proton peaks, we suggest the structure, diagrammed in Scheme 6.4, analogous to that proposed for the tricarbonyl hydrido species, $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2][CF_3SO_3]$,[9] by replacement of one carbonyl on Ir with ethylene. This formulation gives an identical environment at Rh in the two compounds, and a slight difference at Ir, due to CO substitution by C_2H_4. This would be in keeping with the greater tendency for Ir to be coordinatively saturated and receives support from the different spectral parameters at the Ir end seen for **80** and $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ ($^{31}P\{^1H\}$: δ -0.1, vs. -5.5; $^{13}C\{^1H\}$: δ 181.2, vs. 179.5) while those at the Rh end are strikingly similar ($^{31}P\{^1H\}$: δ 22.7, $^1J_{RhP}$ = 114 Hz vs. 22.8, $^1J_{RhP}$ = 112 Hz; $^{13}C\{^1H\}$: δ 185.1, $^1J_{RhC}$ = 74.0 Hz vs. 186.2, $^1J_{RhC}$ = 73.9 Hz). The formulation for

Scheme 6.4

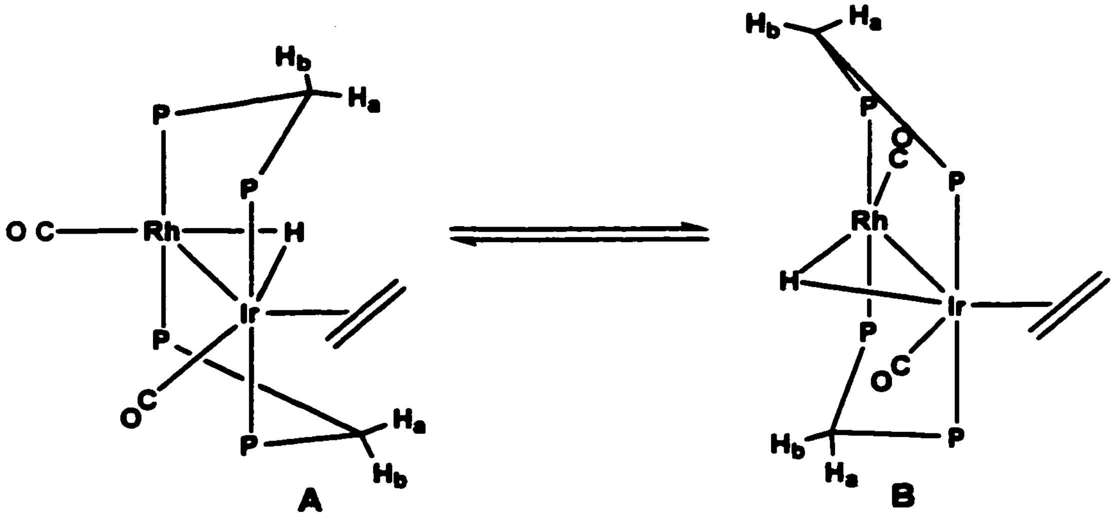


2

80

80 is subtly different from that of its diiridium analogue, in that in the latter species both carbonyl groups are bound to one of the Ir centers with one of this CO group engaged in a semi-bridging interaction with the adjacent metal bearing the olefin ligand. However, both species have +1 d^8 square planar and trigonal bipyramidal configurations at the metals. Unlike the Ir_2 complex which is stable to isolation, **80** loses ethylene in the absence of an atmosphere of the gas. Similar instabilities have been observed for the other known examples of ethylene adducts involving the RhIr framework.[24,25]

The appearance of one signal for the four protons of the ethylene group at room temperature suggests that this group is rapidly rotating about the metal-olefin axis. Similar facile rotation of a coordinated ethylene group is a common phenomenon and has been observed in related binuclear systems involving "Ir_2"[23] and "IrRu"[21] frameworks. However, unlike the "IrRu" system in which there is exchange between the bound olefin and free olefin in solution, spin saturation transfer experiments provide no evidence of a similar exchange occurring in **80**. The observation of one resonance for the dppm methylene protons at room temperature suggests that a fluxional process akin to that observed for the diiridium ethylene species,[23] is occurring, in which the inequivalent protons (H_a and H_b on each CH_2 unit) on opposite faces of the $RhIrP_4$ plane become equivalent through a "tunnelling" of the hydride from one side of the plane to the other. This process presumably occurs in concert with ethylene rotation. A similar "hydride tunnelling" process has also been described for the related species $[Ir_2(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$,[26] $[ReIrCO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$,[27] $[RhCo(CO)_3(\mu\text{-}H)(dppm)_2]$[28] and $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2]\text{-}[CF_3SO_3]$.[9]



In fact, the mechanism as depicted above does not actually exhange environments for H_a and H_b, but we assume that the environment in H_a in structure **A** is similar enough to that of H_b in structure **B** that they have similar chemical shifts. For true exchange between identical environments, the CO and C_2H_4 ligands on Ir would also have to exchange, which would probably require dissociation and recoordination. Certainly our evidence suggests that this is not occurring for ethylene. At -40 °C the ^{31}P NMR spectrum spectrum shows a broad unresolved peak for the Ir-bound ^{31}P nuclei at -1.2 and a doublet of multiplets at δ 23.8 for the Rh-bound phosphorus nuclei; the former peak becomes a multiplet at -80°C and ambient temperature typical of the BB' part of an AA'BB'X (X = Rh) spin system. The above fluxional process appears to be restricted to the Ir metal, and as reflected in the low-temperature limiting specta, may be rationalized in terms of only one environment for the phosphines at Rh (H trans to CO) whereas there are two environments at Ir (H trans to CO or C_2H_4). Both carbonyl resonances are broad at -80 °C while the dppm methylene peaks appear as AB quartets at δ 4.38 and 3.80 which supports the idea of some sort of exchange process which is frozen out at low temperatures. Also not unexpected at this temperature, the ethylene protons show up as two signals at δ 0.96 and 0.53.

When the reaction is carried out at -80 °C, four broad peaks appear at δ 25.4, 23.7, 3.2 and -4.1 in the ^{31}P NMR spectrum, suggesting the presence of two major products in solution. Unfortunately these species could not be identified owing to the broadness and complexity of the ^{1}H NMR spectrum which was further complicated by overlap of peaks. Although, this situation was not redressed at -60 °C, compound **80** was clearly identified by its hydride resonance at δ -12.18 which remained invariant up to ambient temperature. Also at this temperature, peaks attributable to 1-butene were clearly evident. At -40 °C, the ^{31}P{^{1}H} NMR data showed complete conversion to **80**. As mentioned earlier, the complexity of the ^{1}H NMR spectrum frustrated attempts to identify possible intermediates leading to the olefin formation. Therefore the mechanism for the formation of **80** or the organic by-product 1-butene is presently unclear. Unfortunately, preliminary attempts to carry out ^{13}C and ^{2}H labelling experiments aimed at ascertaining the fate of the methyl substituent of **2** in the product mixtures has so far proven inconclusive. In addition, we have been unable to observe a methylene species which is presumably a necessary intermediate in the coupling process. Further studies aimed at elucidating the mechanisms of these reactions are continuing.

Conclusions

The reactivity of the methoxymethyl complex [RhIr(I)(CH_2OCH_3)(CO)(μ-CO)(dppm)$_2$] (**74**) with various electrophiles has yielded products (and in some cases the targeted methylene complexes) arising from attack of the added substrate at the iodide ligand, the methoxymethyl oxygen or at the metal accompanied by expulsion of an organic molecule. One aspect of this study relates to the reaction of the methyl complex $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with diazomethane. This reaction resulted in C-C bond-forming processes, yielding the hydrido-ethylene complex **80** and the C_4 product, 1-butene.

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17. The signals for the methylene protons could not be observed in the ^{1}H NMR spectrum being presumably masked by peaks due to the phenyls.

18. A preliminary reaction of this species with 1 equiv of acetylene gave an insertion product with the plausible formulation RhIr(I)(CH_3)(C≡CH)(CO)-(dppm)$_2$]$^+$.

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Chapter 7

Conclusions

The reactivity of the heterobinuclear methyl complex [RhIr(CH_3)$(CO)_3$-(dppm)$_2$][CF_3SO_3] (**1**) with a number of small molecules (CO, H_2, ^{t}BuNC, PR_3, alkynes, C_2H_4, and SO_2) has been previously investigated.[1] In general, the reactions resulted in CO substitution by the added ligand (PMe_3, C_2H_4, and alkynes) and/or insertion processes involving the methyl group and either the added substrate (^{t}BuNC) or one of the coordinated carbonyls (upon addition of SO_2). However, in the earlier studies none of the intermediates leading to the observed products were identified. One of the goals of this thesis was to conduct low temperature experiments in efforts to establish the initial sites of substrate attack, the ligand migrations that occurred, and the functions of the different metals in influencing subsequent transformations involving the ligand fragments. As expected, based on the 16e/18e configurations of the Rh/Ir metal centers in **1**, substrate attack by phosphines and H_2 was shown to occur at the unsaturated Rh center. Subsequent rearrangements occurred with phosphine migration to Ir in the first case and methane elimination in the second. In contrast, reactions with ^{t}BuNC and ethylene, even at -100 °C, show no evidence of substrate attack at Rh. Either attack does occur at Rh with extremely facile rearrangement and substrate migration to Ir, or attack occurs directly at Ir. This latter scenario can be accommodated if we assume that carbonyl migration from Ir to Rh occurs, creating coordinative unsaturation at the former and allowing for substrate attack at this metal. If there are two different sites of attack, the factors that favor attack at one site over the other are not known. When subsequent CO loss occurs in these reactions, it apparently occurs from Rh. This is not unexpected based on the greater lability of the second-row metal.

The dicarbonyl analogue, $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**), was readily prepared by mild heating of **1** in refluxing dichloromethane. Unlike **1**, compound **2** has a 16e configuation at each metal and coordinative unsaturation at *both* metals. The reactions of **2** with the above substrates, as with allenes and anionic nucleophiles such as H^-, CN^-, and I^-, gave products in which the incoming substrates end up at Ir, thus reflecting the geometries at the metals in the solution structure (**2′**). As noted in Chapter 2, in **2′** each metal has a square planar geometry, in almost perpendicular alignments, so attack appears to be preferred at Ir since end-on attack at this metal seems favored over attack at Rh, which would occur from the side of the molecule and would involve unfavorable interactions with the ligands on the adjacent metal. In all of these reactions, except those involving iodide anion and olefins, the methyl group remained bound to Ir. Although the above trend, with the incoming substrates binding to Ir may also be explained on the basis of the expected stronger bonding to this third-row metal, the possibly subtle involvement of the anciliary ligands cannot be ignored. For instance, the related compounds **2** and $[RhIr(CH_3)(PR_3)(CO)(dppm)_2][CF_3SO_3]$ (**5**), which differ by replacement of a strong π-acceptor (CO) with the basic phosphine ligand, react differently with allenes. Whereas allene attacks **2** at Ir, to give an η^2-allene species (which slowly converts upon standing for several days to a species proposed to have the allene ligand in a bridging site), accompanied by facile methyl migration, the same reaction with **5** cleanly affords the allene-bridged species **22** as the only product, in which the methyl substituent has remained bound to Ir. A close examination of the solution structures of **2** and **5** might provide a reason for the apparent differences in reactivity. The site of attack for **2**, at Ir, is as described earlier. However, for **5** in which the lone carbonyl occupies a bridging site while the electron donating methyl and phosphine groups are positioned at each metal, substrate attack could potentially occur at either of the coordinatively unsaturated metals on the outside of the complex or at the inside, at one metal and adjacent to the other. The observed coordination between the metals suggests that attack is at the inside of the non-A-frame structure, presumably reflecting steric preferences. Certainly in the bridging site both allene π bonds can become involved in the bonding, which might also favor this bonding mode.

At the outset of this study, one aspect of interest to us relates to the possibility of inducing C-H bond cleavage of the methyl group in our RhIr system by varying the electronic and steric properties of the anciliary ligands; facile C-H activation was observed upon addition of a wide range of ligands to the isostructural diiridium species, $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$.[2] Unfortunately, C-H bond activation of the methyl group was not realized in any of our RhIr systems. These results clearly reflect the greater ability of the Ir center in the Ir_2 systems to undergo oxidative addition coupled with the increased thermodynamic stability of the resulting Ir-H and Ir-C bonds formed in these products.

Binuclear complexes, having the metals in close proximity, are prime candidates for facile movements of ligands from metal to metal. Unlike the homobinuclear Rh_2[3] and Ir_2[2] analogues, for which such migrations occur readily in the absence of added substrate, migration of the ligands in compound **2**, illustrated by the methyl and phosphine groups, does not occur under ambient conditions except upon addition or removal of other ligands. For instance, stepwise CO removal from the phosphine adduct $[RhIr(CH_3)(CO)_3(PMe_3)(dppm)_2][CF_3SO_3]$ (**3a**) results in a corresponding step-wise phosphine transfer, first from Rh to Ir upon removing the first CO, then back to Rh from Ir upon removing the second. The fact that these ligands can bind to either metal in these systems, in the phosphine case producing stable Rh-bound adducts, seems at odds with the expected greater metal-ligand bond strengths of Ir over Rh, as observed earlier. However, it must be recalled that *all* metal-ligand bonds must be considered, and the preferences of the methyl group to be bound to one metal or the other results from the most favorable arrangement of all ligands within the coordination sphere of the two metals.

Significantly, although methyl-bridged species were implicated throughout the studies of the diiridium complexes, they were only proposed as transient intermediates and were never observed. As mentioned in Chapter 1, these methyl-bridged species are important intermediates in methyl-transfer processes that appear to occur readily on metal surfaces or in homogeneous systems containing more than one metal. It was reasoned that the lower tendency of Rh to oxidatively add across a C-H bond[4] might permit the observation of such methyl-bridged species, which would model the C-H activation processes in the Ir_2 analogues. Our attempts to induce the terminal methyl group in **2** to adopt a bridging arrangement, through ligand addition, for example using phosphines and phosphites, failed. Clearly, methyl transfers are occurring upon addition of some substrates to **2**, as for example in the low temperature reactions of DMAD and diphenylsilane, in which it was possible to follow the sequence of movements of the methyl subsituents, first from Ir to Rh, then back to Ir to Rh as the sample was warmed. Nevertheless, direct evidence of a methyl-bridged species in this series was not forthcoming. Interestingly, however, the trimethyl species, $[RhIr(CH_3)_3(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**34**), obtained from alkylation of the A-frame dimethyl species $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**23**), did give methyl-bridged species upon reaction with allene and ethylene. Clearly, in these cases, substrate attack at the coordinatively unsaturated Rh in compound **34** may have resulted in methyl migration from a terminal site at this metal to a bridging one, between the metals. We assume that complete methyl transfer to Ir is disfavored by the steric congestion at this metal.

Certainly a few questions remain unresolved in this study. For instance, in the reactions involving compound **2** it is not clear why attack, apparently at Ir, by substrates such as allenes, I^-, H_2 and H_2SiPh_2 is accompanied by methyl group transfer whereas with the corresponding anionic nucleophiles (H^-, CN^-, CH_3^-, CH_2Ph^-, Ph^-) and allyl bromide, the methyl group remained bound to Ir.

One of our objectives was to synthesize hydrido-alkyl or hydrido-acyl complexes that would model important intermediates in olefin hydrogenation and hydroformylation processes. The observation, at ambient temperature, of the rare cis dihydrido-dimethyl species $[RhIr(CH_3)_2(H)(CO)(\mu\text{-}H)(dppm)_2]$ (**30**) (obtained from the reaction of **34** with H_2), fulfils our goal. The above compound in which two sets of methyl and hydride ligands occupy mutually cis geometries at Ir is, to the best of our knowledge, without precedent in a binuclear system. The acetyl species, $[RhIr(COCH_3)(CH_3)(H)(CO)(\mu\text{-}H)(dppm)_2]$ (**31**), obtained by exposing **30** to an atmosphere of CO, proved be unstable at temperatures above 0 °C. Significantly, it represents one of the few well-defined examples of an acetyl hydride species prior to formation of acetaldehyde.[5]

One of our objectives of inducing insertion processes in the reactions of the methyl species **2** and **23** with SO_2 succeeded, as seen in the formation of alkyl sulfonate complexes. Although, for the latter reaction, insertion of SO_2 was only observed at the Rh-CH_3 bond, preliminary results indicate that it was possible to effect similar insertions at the Ir-CH_3 bond upon prolonging the reaction time; however, this also gave several other unidentified products. Interestingly, the above results contrast those observed for the tricarbonyl species **1** which gave a CO migratory insertion product instead,[1] and the analogous Ir_2 dicarbonyl species[2] which afforded a methylene hydride, SO_2-bridged species. The outcome of the reaction involving the tricarbonyl is possibly a reflection of the presence of a competing π acid such as CO (although the mechanism of the insertion process is different for both reactions).

The results of this study have also demonstrated site-specific processes as evidenced by the alkyne insertion (apparently at Rh), in the carbonylation of the alkyne-bridged intermediate $[RhIr(CH_3)(CO)_2(\mu\text{-DMAD})(dppm)_2]^+$, in which the methyl group is bound to Rh. Another example of this is the formation of the rare formyl complex $[RhIr(CHO)(CO)(\mu\text{-H})(C_2CH_2Ph)_2(dppm)_2]$, apparently by direct hydride ($Li[HBEt_3]$) attack at a coordinated carbonyl ligand. It is suggested that the site-specific attack at the Ir-bound carbonyl is facilitated by the trans influence of the bridging hydride in the precursor complex which presumably enhances the electrophilicity of the CO group. On the other hand, the less bulky $NaBH_4$ reacts to give a vinylidene product, presumably via initial attack at Rh. These site-specific reactions may reflect the interplay of steric and electronic factors in the chemistry of these systems.

The reactions of the alkyl complexes **2**, **23**, and **34** with a variety of alkynes and alkenes (having electron-withdrawing groups) have yielded products reflecting the rich diversity of bonding modes possible for these substrates in binuclear systems. With the activated alkynes (DMAD, HFB) or olefin (C_2F_4), the predominant bonding mode was shown to be bridging both metals, although an η^2-bonding mode was proposed for $[RhIr(CH_3)_2(\mu\text{-CO})(\eta^2\text{-}$

alkyne)(dppm)$_2$] (alkyne = DMAD (**51**), HFB (**52**)), obtained at low temperature, and the methylene complex, [RhIr(CO)(μ-CH$_2$)(μ-I)(η^2-DMAD)(dppm)$_2$][CF$_3$SO$_3$] (**78**), which has been crystallographically characterized. However, with the unactivated alkyne, C_2H_2, the results reflect both the steric and electronic environments at the metals of the starting materials. Thus, while the trimethyl species **34** reacts with acetylene to give an alkyne-bridged product, with attack of the substrate occurring between the metals, the reaction with the coordinatively unsaturated dimethyl species **23** resulted in oxidative addition of one of the C-H bonds of the alkyne, yielding a hydrido-acetylide product. This latter mode of reaction is common in these late-metal systems.

With only one exception, the overwhelming majority of the results in this study demonstrate a lower preference for oxidative additions at the second-row Rh than at Ir. This is most evident in oxidative addition reactions of dihydrogen and silanes, and can be exemplified by the observation, at low temperature, of the agostic species, [RhIr(CH$_3$)(CO)$_2$(μ-H)(μ_2-η^1:η^2-SiPh$_2$H)(dppm)$_2$][CF$_3$SO$_3$] (in the reaction of **57** with Ph$_2$SiH$_2$). The subsequent cleavage of the second Si-H bond of the silyl group, giving rise to the hydride species, [RhIr(COCH$_3$)(H)(CO)(μ-H)(μ-SiPh$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**58**) and [RhIr(CO)$_2$(μ-H)(μ-SiPh$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**59**), provides a rare experimental confirmation of the intermediacy of such species in oxidative additions of silanes. In a related study, the reaction of the low-valent complex [RhIr(CO)$_3$(dppm)$_2$] with diphenylsilane yielded silylene-bridged dihydride products, paralleling those obtained for the analogous homobinuclear species. However, a number of similarities and differences show up in this chemistry. The RhIr silylene dihydride species resembled those of its Ir$_2$ counterpart[6] in its fluxional behaviour at ambient temperature while differing from that displayed by the Rh$_2$ analogue,[7] which was shown to implicate facile reversible Si-H oxidative-addition/reductive elimination cycles. It resembled its Rh_2 counterpart in the subsequent displacement of H_2 by CO to give a tricarbonyl silylene-bridged product; no such chemistry was reported for the Ir_2 analogue. Significantly, the RhIr silylene dihydride species reacts further with additional silane to give the silyl silylene hydride species $[RhIr(H)(SiPh_2H)(CO)_3(\mu\text{-}SiPh_2)(\eta^1\text{-dppm})(dppm)]$ (**70**); neither of the analogous Ir_2 nor Rh_2 congeners gave a similar result. The above silyl silylene complex appears to be a promising candidate for effecting Si-Si bond formation, to give a silane dimer. Although this was not achieved under CO pressure, it may be realized by heating at elevated temperatures. Our attempts at inducing Si-C bond formation which would model one of the proposed termination steps of olefin hydrosilation was achieved. Migration of the methyl and alkynyl groups to silicon-containing fragments provided the methyl silyl species, $[RhIr(CH_3)(CO)(H)(\mu\text{-}H)(SiPh_2Me)(dppm)_2]$ (**66**), and the alkynyl silyl species, $[RhIr(CO)_2(H)(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^2\text{-}SiR_2C_2CH_2Ph)(dppm)_2][CF_3SO_3]$ (R = Ph (**61**), Me (**62**)). Although the mechanism for this transformation is not clear, it is believed to involve an unobserved silylene-bridged intermediate. The transfer of metal-bound hydrocarbyl groups to a silylene moiety (assuming silylene-bridged intermediate is involved), as proposed above, giving rise to hydrocarbyl silyl species, to our knowledge, has no literature precedent, and might provide useful insights into the mechanism of Si-C bond formation in transition metal systems. Indeed, to date, all known Si-C bond formations, resulting in production of carbosilanes, have been shown to involve silyl and hydrocarbyl groups. The above 1,2 alkyl/alkynyl migrations mirrors that seen earlier in the formation of the vinyl species in the reaction of the alkyne-bridged species **46** with CO, and highlights the cooperative interaction of adjacent metals.

As a follow-up of recent success in our group[8-10] in utilizing methylene complexes to induce C-C bond formations (in view of its relevance to Fischer-Tropsch chemistry), the reaction of compound **2** with CH_2N_2 was attempted. Although we did succeed in achieving C-C bond formation as evidenced by the detection of the C_4 unit, 1-butene, and the generation of the ethylene hydride species $[RhIr(CO)_2(C_2H_4)(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**80**), no methylene-bridged species, which presumably are the precursors to the final products, were identified, owing to the facile nature of the reaction. Further work aimed at elucidating the mechanism for this reaction is warranted. In related studies, our approach to synthesize methylene complexes from the reactions of the methoxymethyl iodo species $[RhIr(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ (**74**) with electrophiles has led to the generation of the first examples of methylene-bridged complexes involving the mixed RhIr framework. Preliminary results of the reaction of the coordinatively unsaturated monocarbonyl species $[RhIr(I)(CO)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**77**) with acetylene gave products which are proposed to result from hydride insertions, demonstrating the potential of these species to undergo insertion processes. An extension of this study would be to synthesize the neutral methylene species $[RhIr(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ with the goal of investigating its C-C coupling chemistry with unsaturated substrates such as olefins, allenes and alkynes. Preliminary attempts to obtain this methylene-bridged species, as well as the Ir_2 analogue by reactions of the respective compounds $[MIr(CO)_3(dppm)_2]$ (M = Rh, Ir) with diazomethane have not yielded the targeted species.

A number of features have been encountered in reactions involving RhIr complexes with various substrates which merit further comment. One of these is the prevalence of two structural types in the majority of the compounds in this thesis. The first which has been noted earlier, is the tendency of anionic ligands to preferentially bind to the third-row metal. A good illustration of this is the series of neutral complexes [RhIr(CH_3)(R)(CO)$_n$(dppm)$_2$] (n = 2 for R = H, CN, I, CH_3, Ph, CH_2Ph; n = 3 for R = acyl), in which the anionic moities are bound to Ir, yielding a formally Rh(0)/Ir(+2) configuration. This finding is in contrast to what was observed for a series of related monoalkyl complexes [RhM(R)(CO)$_3$(dppm)$_2$] (M = Os, Ru; R = CH_3, vinyl, acyl, acetylide, CH_2CN),[8] and in related RhW,[11] RhMo,[11] RhMn,[12] and RhRe[13] systems, in which the anionic groups were bound to Rh, irrespective of whether the other metal was second or third row. In the RhOs and RhRu cases, the observed structures were rationalized in terms of a more favored Rh(+1)/M(0) configuration, as opposed to Rh(0)/M(+1). In the present study, however, there is at least one example, [RhIr(I)(CH_3)(CO)$_2$(dppm)$_2$] (**13**), having the preferred Rh(+1)/Ir(+1) configuration, having the methyl group on Rh. In this case it is assumed that methyl, rather than iodide, migration to Rh occurs owing to a more favorable Ir-I bond that is formed, and to the more crowded environment at Ir by virtue of the larger iodo ligand. However, it is not clear why one structure type should be favored over the other, although the tendency of the third-row congener to in the higher oxidation state is well known.[14] The second recurring theme is the presence of bridging or semi-bridging carbonyls in these compounds, a feature that was also noted in several related compounds involving the mixed Rh/M (R = Os, Ru, Mo, W, Re, Mn) combination in our group. Interestingly, the above RhIr compounds have essentially Ir-bound carbonyls which engage in a weak semi-bridging interaction with the adjacent Rh center, as shown by the low-field chemical shifts for this carbonyl compared to those of the Rh-bound CO. Similar bridging or semi-bridging interactions were observed for all the trimethyl complexes obtained in this study. Clearly, the build-up of electron density at Rh (in the trimethyl complexes) as a result of the presence of the methyl group can be alleviated by semi-bridging carbonyl interactions. In the case of the symmetrical dicarbonyl compound $RhIr(CH_3)_3(CO)_2(dppm)_2]$-$[CF_3SO_3]$ (**36**), the octahedral geometry at Ir places both carbonyls in ideal positions to bridge with the adjacent Rh center. Moreover, the observation of a greater number of bridging carbonyls in these RhIr complexes, compared to the analogous Ir_2 system, is consistent with the lower trend of third-row metals supporting bridging carbonyls, and reflects the role of the Rh center in influencing these bridging modes.

One significant finding of this study has demonstrated that the mixed-metal RhIr binuclear complexes can exhibit reactivity patterns which often do not reflect the known tendencies of each metal in their mononuclear analogues. For instance, Rh and Ir complexes tend to have 16e and 18e configurations, with the latter having a preference to be coordinatively saturated. However, for the complex, $[RhIr(CH_3)(CO)_2(\mu\text{-}DMAD)(dppm)_2]$-$[CF_3SO_3]$ (**46**), in which the methyl group is bound to the Rh, this trend is reversed, with the Rh center having a 18e octahedral geometry while Ir has a 16e configuration and is the site of coordinative unsaturation. In this context, it was also surprising to observe that migratory insertions and reductive eliminations apparently occurred at the third-row Ir rather than at Rh, and in some cases, oxidative-additions apparently occurred at the second-row Rh. Thus methane and 1-butene loss appeared to have occurred at Ir in reactions involving the silyl species, ($[RhIr(CH_3)(CO)_2(\mu\text{-}H)(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}SiPh_2H)(dppm)_2]$-$[CF_3SO_3]$ (**57**), and the η^1-allyl species, $[RhIr(Br)(CH_3)(CO)_2(\eta^1\text{-}CH_2C(H)\text{=}CH_2)$-$(dppm)_2][CF_3SO_3]$ (**17**), respectively. In addition, all but two migratory insertions involving CO and CH_3 groups seen in this study appear to have occurred at Ir rather than at Rh; the exceptions were for $[RhIr(COCH_3)(CH_3)(H)(CO)(\mu\text{-}H)(dppm)_2]$ (**31**) and $RhIr(COCH_3)(CO)_2(\mu\text{-}DMAD)(dppm)_2]^+$ (**50**). A clear explanation for these findings cannot be given, although it is probable that the lability at the Ir center in these mixed-metal complexes may have been enhanced by the adjacent Rh, and presumably the proximity of Ir has modified the chemistry that occurs at Rh as well.

This study has also demonstrated that in addition to the more common trans,trans arrangements for the dppm ligand in binuclear systems, it can adopt a variety of other alignments, as alluded to in Chapter 1, such as cis,cis ([RhIr(CO)$_2$(H)$_2$(μ-SiPh$_2$)(dppm)$_2$] (**67**)), cis,trans ([RhIr(CO)$_2$(μ-H)(μ-η^3-(o-C$_4$H$_6$P(Ph)CH$_2$PPh$_2$)(dppm)$_2$] (**12**)) and [RhIr(CH$_3$)(PMe$_3$)(μ-CO)(μ-η^2:η^2-C$_3$H$_4$)-(dppm)$_2$][CF$_3$SO$_3$] (**22**)), and trans,cis ([RhIr(CH$_3$)$_2$(H)(SiHPh$_2$)(μ-CO)(dppm)$_2$] (**65**)). In addition to the favored bridging mode of the dppm ligand in these systems, it can be forced to adopt an η^1-bonding mode, in which one of the phosphines is pendent as illustrated by the two silyl silylene complexes obtained in this study. Furthermore, although these dppm groups are normally spectators in the reaction chemistry of these complexes, they can become involved as demonstrated by the abstraction of a dppm methylene hydrogen in the reaction of [RhIr(CO)$_3$(dppm)$_2$] with I$_2$CH$_2$ and ICH$_2$CN, and in the ortho-metallation of one of the dppm phenyl hydrogens, following methane loss from the hydrido-methyl species [RhIr(CH$_3$)(H)(CO)$_2$(dppm)$_2$].

Overall, this study has shown a rich display of cooperativity effects between adjacent metals in the alkyl complexes involving the mixed RhIr framework. These findings are capable of mimicking important processes such as oxidative-addition, reductive elimination, ligand association and dissociation, ligand transfers, and migratory insertions leading to C-C (and the reverse, de-insertion leading to C-C bond cleavage) and C-heteroatom bond formations, occurring on metal surfaces of mixed-metal catalysts.

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Appendix

Solvents and Drying Agents

Acetone	Calcium sulphate
Benzene	Sodium benzophenone ketyl
Dichloromethane	Phosphorus pentoxide
Diethyl ether	Sodium benzophenone ketyl
pentanes	Sodium benzophenone ketyl
n-Hexane	Sodium benzophenone ketyl
Methanol	Magnesium
Tetrahydrofuran	Sodium benzophenone ketyl
Toluene	Sodium