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METAL-METAL COOPERATIVITY IN THE REACTIONS OF HETEROBIMETALLIC COMPLEXES.

by

David Michael Antonelli

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN THE PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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University of Alberta
Edmonton
Canada T6G 2G2

Department of Chemistry
Faculty of Science
E3-44 Chemistry Bldg., Tel. (403) 492-3254 Fax (403) 492-8231

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Yours sincerely,

Martin Cowie

Martin Cowie
Professor of Chemistry

MC/co

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Metal-Metal Cooperativity in the Reactions of Heterobimetallic Complexes submitted by David Michael Antonelli in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

M. Cowie (Supervisor)

W.L. Gladfelter

J. Takats

R.A. Cavell

K.R. Kopecky

I.A. Dalla Lana

Date: Feb. 7th '91

To My Father

Abstract

The heterobimetallic bis-dppm (dppm= bis-(diphenylphosphino)-methane) complexes of the general form, $[RhM(CO)_x(H)_n(dppm)_2]$ (M= Co; x=3, n=0: M= Fe, Ru, Os; x=3, n=1: M=Mn, Re; x=4, n=0: M= Cr, W; x=4, n=1) were prepared via the chloride displacement reaction of $[RhCl(dppm)_2]$ with the appropriate metal-carbonylate or hydrido-metal-carbonylate anion. All of these complexes contain two bridging dppm ligands and one carbonyl ligand on Rh. The cyclopentadienyl-containing anions, $[FeCp(CO)_2]^-$ and $[MoCp(CO)_3]^-$, however, yielded products in which only one dppm ligand had moved into a bridging orientation, while the other remained chelating on Rh. Crystallographic studies suggest that these complexes are best formulated as mixed valent Rh(I)/M(-I) species with a coordinatively unsaturated Rh center. The low valence of these complexes, as well as the vacant coordination site on Rh, make these complexes very reactive towards oxidative addition.

The reactions of $[RhRe(CO)_4(dppm)_2]$ with molecules of the form XY [X=Cl, Y=Cl; X=Cl, Y=H; X=H, Y=H; X=H, Y=SR(R= Et, Ph)] gave the respective products of the form $[RhRe(\mu\text{-}X)(\mu\text{-}Y)(CO)_3(dppm)_2]$, while the reactions with H^+ and H_2S yielded tetracarbonyls with bridging hydrido and sulfido ligands, respectively. The reactions with the activated alkynes, hexafluorobutyne and dimethyl acetylenedicarboxylate, gave tetracarbonyls with bridging dppm ligands. These complexes reversably lose CO at ambient temperature with concomitant formation of a $Rh \rightarrow M$ dative bond.

Low temperature studies were conducted in the reactions with hydrogen sulfide and thiols in order to determine the mechanism leading to loss of H_2 in the former. It was established that all three reactions (H_2S, HSPh, and

HSEt) proceed via a common mechanism up to the formation of [RhRe(μ-SR)(μ-H)$(CO)_4(dppm)_2$] (R= H, Et, Ph), however the H_2S reaction goes on further to lose H_2. The mechanism of this process was not unequivocally established, however, it appears on the basis of preliminary results that the complex first loses CO, then loses dihydrogen, and finally regains CO.

The complexes [RhMn$(CO)_4(dppm)_2$] (M= Mn, Re) and [IrRe$(CO)_5(dppm)_2$] also react with O_2 to form unusual carbonate-bridged tricarbonyl species via a rare oxidation of coordinated CO. Low temperature mechanistic studies failed to reveal any intermediates in these reactions.

The reactions of [RhRe$(CO)_4(dppm)_2$] and [IrRe$(CO)_5(dppm)_2$] with methyl triflate yielded the rare Rh(I) and Ir(I) alkyl complexes, $[MRe(CH_3)(CO)_4(dppm)_2]^+$, which have four carbonyl ligands on Re and a methyl group on the group-9 metal. These complexes react with CO to form acyl products, and also with H_2 or $LiHB(Et)_3$ to yield, respectively, the hydrido-tetracarbonyl cation and the neutral tetracarbonyl species with loss of methane. The Rh analogue reacts with one or two equivalents of Me_3NO in acetonitrile to form the mono and di-acetonitrile adducts, respectively.

The Ir/Re hydrido-tetracarbonyl cation can be protonated with triflic acid and also reacts reversably with dihydrogen to form a cationic trihydride.

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I wish to express my thanks to Professor Martin Cowie for his help and direction during my graduate studies at the U of A. I would also like to extend my thanks to Professor J. Vederas for his encouragement and support during my undergraduate years.

I also thank my fellow workers in the group for helpful discussions, and training in technical matters. Special thanks go to Dr. R. Hilts for his help and friendship during the last two years of my studies. I would like to express my deepest thanks to my Mother and Father for their steady support in personal and family matters and for their help in raising my children, Paul and Rebecca, during my university years.

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List of Abbreviations and Symbols

anal	analyses
av	average
ca	circa(approximately)
calcd	calculated
CH_2Cl_2	dichloromethane
$CH_3SO_3CF_3$	methyl triflate
coeff	coefficient
DMA	dimethyl acetylenedicarboxylate
DPPM	bis-(diphenylphosphino)methane
Et	ethyl
fw	formula weight
h	hours
HFB	hexafluoro-2-butyne
IR	infrared
L	ligand
M	molar (moles/litre)
Me	methyl
MeOH	methanol
min	minutes
mL	millilitres
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
THF	tetrahydrofuran
δ	chemical shift (ppm)

Crystallographic Abbreviations and Symbols

a, b, c	respective lengths of x, y, and z axes of the unit cell
B	isotropic thermal parameter
deg (°)	degrees
F_c	calculated structure factor
F_o	observed structure factor
h, k, l	indices defining lattice planes, expressed as reciprocals of the fraction of a, b, and c being intersected
p	ignorance factor (accounts for instrumental inaccuracies in measurement of intensity)
R	residual index (measure of agreement between observed and calculated structure factors)
R_w	weighted residual index
w	weighting factor (applied to structure factor)
Z	number of formula weights per unit cell
Å	Angstroms (1 Å = 10^{-10} metres)
α	angle between the b and c axes of the unit cell
β	angle between the a and c axes of the unit cell
γ	angle between the a and b axes of the unit cell
2θ	diffraction angle
ρ	density
λ	wavelength
σ	standard deviation

Chapter 1

Introduction

The study of polymetallic transition metal complexes constitutes a large portion of the research conducted in organometallic chemistry today[1]. The interest in this area stems from the potential that two or more adjacent metals may interact in a cooperative manner and in so doing offer reactivity patterns and catalytic properties which are not observed in monometallic systems.[2,3]

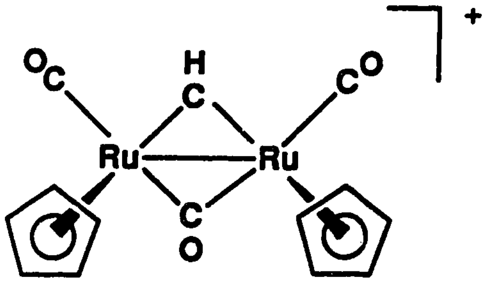
An ensemble of metals can cooperate in several ways. A metal can act in conjunction with an adjacent metal center to stabilize ligands which are too reactive to be observed in monometallic complexes. Secondly, a metal can act as either an electron donating or accepting group with respect to a neighboring metal and thereby alter its electronic environment and hence its reactivity. Adjacent metals in a complex can also act as a means of storage and release of molecular fragments during a catalytic cycle[4] and hence enable processes to occur which would not be possible with monometallic catalysts. Furthermore, a polymetallic complex has several potential coordination sites for incoming ligands. This can give rise to vastly different and more complex chemistry than is observed in monometallic systems.

The importance of transition metal complexes to the understanding of catalysis cannot be overemphasized. In industry, the majority of catalytic processes are conducted using heterogeneous catalysts,[5] or those which are not soluble in the reaction mixture. These are usually metals or metal oxides whose surface is the site of catalytic activity. However, heterogeneous systems are not well understood because they are difficult to study due to the problems involved in applying spectroscopic techniques in situ. Transition metal complexes which function as homogeneous catalysts, on the other hand, are readily studied by Infrared (IR) and Nuclear Magnetic Resonance (NMR) spectroscopies because they are soluble in the reaction media. Furthermore, homogeneous catalysts are normally active under much milder conditions than are their heterogeneous counterparts while also offering a higher selectivity with regards to substrates and products.[6-7]

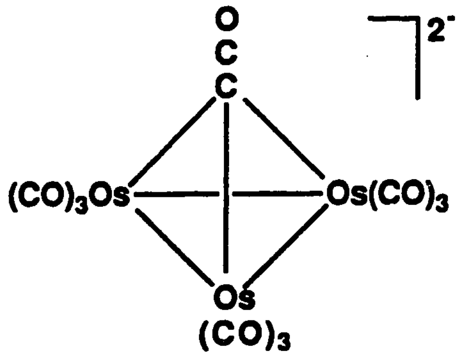
The study of polymetallic homogeneous catalysis has led many to compare these systems to metal surfaces.[8-10]Although the metal-metal bonds on surfaces are stronger than those in bimetallic and cluster compounds, the metal-ligand bonds are thought to be of comparable strength.[11] Muetterties has therefore argued that an ensemble of metal atoms in a polymetallic complex, surrounded by ligands, can act as a useful model for a small portion of a metal surface in a catalytic process, during which small organic fragments are presumably bound to proximate metal atoms for long enough to react in some way with one another.[12] This is generally called the "metal-surface" analogy and has been the driving force for many of the studies involving polymetallic complexes in the last ten years.

Nowhere has the power of this analogy been more evident than in the study of Fischer-Tropsch chemistry[13] which involves carbon monoxide reduction by dihydrogen and carbon-carbon chain growth on a metal surface. It has been postulated that this process occurs via the coupling of high energy organic fragments such as "C", "CH", and "CH_2" on the metal surface. These fragments are in themselves too unstable to isolate. The fact that they have been observed as ligands in polymetallic homogeneous systems does, however, offer some support to the proposal that they may exist on metal surfaces for brief periods of time.

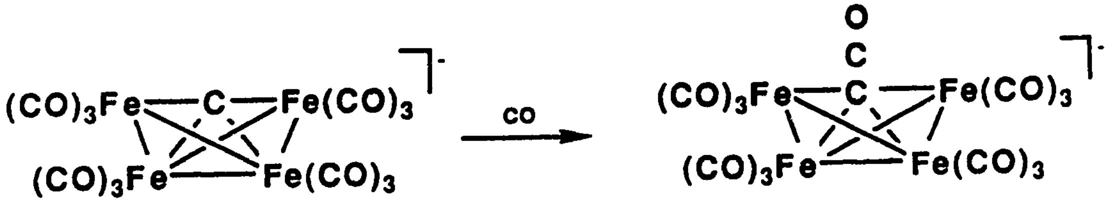
While several trimetallic complexes containing a "CH", or methylidyne, unit bridging all three metal centers have been characterized,[14] diruthenium and diiron complexes with a bridging "CH+" unit as shown below have also



been isolated.[15,16] Furthermore, trinuclear complexes of the rare CCO or ketenylidene ligand,[17] which has never been observed in complexes of lower nuclearity, have recently been prepared. This ligand is thought to be important in the Fischer-Tropsch C-C chain building process.[13a] Such a complex, in which the ketenylidene ligand is bound to a triosmium framework, is shown below. Bradley[18] has isolated multinuclear complexes of the iron triad which contain an exposed "C", or carbide ligand which acts



like a bare carbon in many of its reactions.[19] In one case this ligand was found to coordinate CO to give a ketenylidene unit[20] in a reaction proposed to model the pivotal C-C bond formation step in a Fischer-Tropsch carbon chain growth sequence as shown below.

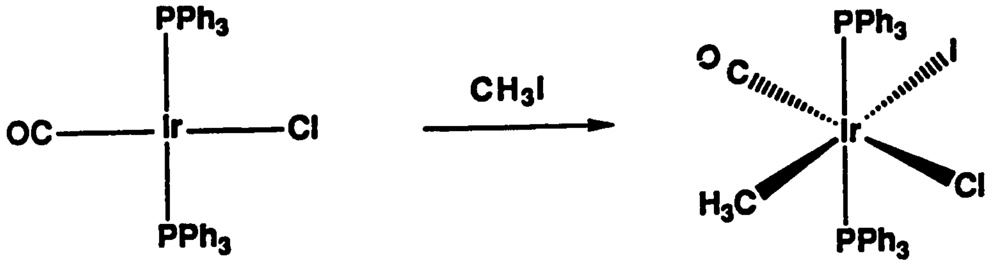


The chemistry in this area continues to expand with the ultimate goal being, perhaps, not only the elucidation of the mechanisms of heterogeneous catalysis and metal surface chemistry, but the development of a selective polynuclear homogeneous catalyst for CO reduction which may be more efficient than the often unselective heterogeneous systems now in use.

The simplest and, therefore, most easily studied of all polymetallic complexes are those containing only two metals. These bimetallic complexes offer the advantages of other polynuclear transition metal species in that they display metal-metal cooperativity effects which lead to richer reactivity patterns and a greater range of possible ligand coordination modes. However, they also have the added convenience of being more easily characterized and studied due to their greater simplicity as compared to higher nuclearity clusters. The IR and NMR spectra are therefore more easily interpreted than those of higher nuclearity clusters due to the fact that the former usually have fewer ligands and thus displays simpler spectra.

Much of the research concerning bimetallic complexes involves the study of oxidative-addition reactions since they have been shown to be important in several homogeneous catalytic processes in which the catalyst is bimetallic in nature.[21] Water gas shift catalysis[22,23] and the hydroformylation process involving dicobalt systems[24] are common examples. The oxidative-addition of H_2S to bimetallic systems is of special interest to catalysis since sulfur-containing compounds are known to act as poisons for both homo and heterogeneous catalysts[25] and also because of the potential use of hydrogen sulfide as a feedstock for H_2 production.[26-28] There is also much interest in the use of transition metal complexes as a means of forming C-S bonds in organic synthesis.[29]

An oxidative-addition reaction is one in which a substrate molecule, of the general form AX, binds to a metal, M, to form a new complex of the form AMX, in which the creation of new M-A and M-X bonds is accompanied by a cleavage of the original A-X bond and a formal oxidation of the metal by two electrons. For example, Vaska's compound, $[Ir(Cl)(CO)(PPh_3)_2]$, reacts with CH_3I to form $[Ir(CH_3)(I)(Cl)(CO)(PPh_3)_2]$ with the formal oxidation of Ir from $^{+}1$ to $^{+}3$ and the creation of new Ir-C and Ir-I bonds.

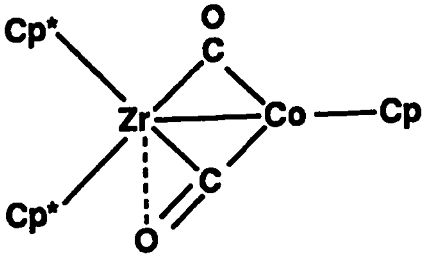


In some cases the substrate molecule may be a species, such as O_2 or an alkyne, which contains a reactive multiple bond. When such a species oxidatively adds to a metal center, the product is normally one containing a three membered ring involving the metal and the two atoms which were previously multiply bonded to one another in the substrate.

For an oxidative-addition reaction to occur an open coordination site must first be available to accommodate the incoming AX molecule. Some complexes, such as Vaska's complex and related Rh(I), Pd(II), and Pt(II) systems already have a vacant coordination site because they have a strong tendency to adopt a 16 rather than an 18-electron configuration. However, the majority of systems require that coordinative unsaturation be induced by adding energy in the form of heat or U.V. radiation to force ligand dissociation.

The microscopic reverse of oxidative-addition is termed reductive-elimination and is also the subject of much interest.[30] It is an important step in most homogeneous catalytic systems[31] as it regenerates an open coordination site on the metal which frees it for further activity. Also, the molecule reductively-eliminated may be the desired product of the process. Together, oxidative-addition and reductive-elimination reactions are responsible for the majority of the transformations that occur during a homogeneous catalytic sequence. Insertion, elimination, and various rearrangement reactions are also important to catalysis, but are not central to the theme of this thesis.

Although the reactivity and catalytic potential of homonuclear bimetallic species have been extensively studied for several years,[32] the chemistry of heterobimetallic systems, in which the two metals are different, has only recently become the object of much attention.[33] It has been suggested[34] that two metals of distinctly different character, held together in close proximity, may offer an even greater variety of chemistry than their homobimetallic counterparts due to the combination of their differing reactivities in the same system. For example, there is much interest in early-late transition metal complexes because of their potential in reducing polar molecules.[34a] The basis for this interest lies in the fact that early transition metals are Lewis acidic and oxophilic and therefore may coordinate the oxygen of a molecule such as CO, while late transition metals can bind to the other end, which in this case is the carbon. Since later transition metals are known to activate dihydrogen in catalytic processes it is thought that such a heterobimetallic system is then capable of further reaction with H_2 leading to reduction of the coordinated CO. Bercaw has isolated the Co/Zr complex shown,[35] which demonstrates the capacity for early-late transition metal systems to coordinate CO at both the oxygen and the carbon ends of the molecule.



There are several existing general methods available for the synthesis of heterobimetallic complexes. Geoffroy divides these into four categories.[33] These are: (1) ligand substitution reactions, (2) addition reactions, (3) condensation reactions, and (4) metal-exchange reactions. The first three of these involve the combining of two monometallic fragments while the fourth technique starts with two polymetallic species which can exchange metal units to form new heterobimetallic systems. Often the first three types of reaction can be aided by the presence of a ligand on one of the monomeric fragments which can bridge the two metals in the product and hence impart increased stability to the metal-metal interaction. These reactions are called bridge-assisted reactions for this reason.[33]

Ligand substitution reactions are those in which a ligand, neutral or charged, on a monometallic complex, is replaced by another metal fragment. An example of such a reaction, in which a halide is replaced by a metal anion, is the reaction of $[Re(CO)_5]^-$ with $[WBr(CO)_5(CR)]$ to form $[WRe(CO)_9(CR)]$ and bromide ion with loss of CO.[36] In some cases the displaced ligand may be neutral, as in the reaction of $[Mn(CO)_5]^-$ with $[Cr(CO)_6]$ to form $[CrMn(CO)_{10}]^-$ and CO.[37] The success of this method largely depends on the nucleophilicity of the incoming metal fragment, the lability of the exiting ligand, and the steric bulk of each metal unit.

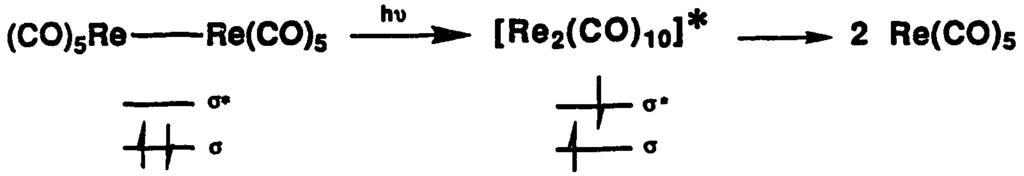
The second class is the simple addition reaction in which a Lewis basic metal fragment bonds with a Lewis acidic metal center with a vacant coordination site. These reactions are identical in concept to the latter class although there is no ligand loss *required*. A good example is the attack of $[Mn(CO)_5Me]$ by $[Re(CO)_5]^-$ to yield $[MnRe(CO)_9(COMe)]^-$.[38] In this reaction the open coordination site is generated by the migration of the Me to an adjacent carbonyl. The reaction of $[Pt(PPh_3)_2(C_2H_2)]$ with $[FeCl(CO)_2(\eta^5\text{-}C_5H_5)]$ to form *trans* -$[Pt(Fe(CO)_2(\eta^5\text{-}C_5H_5))(Cl)(PPh_3)_2]$[39] in which the bis-triphenylphosphine-platinum unit, generated by the loss of C_2H_2, has inserted into the Fe-Cl bond.

Condensation reactions comprise the third general method of synthesizing heterobimetallic complexes. In these reactions two or more monomeric fragments combine to form a new metal-metal bonded species with concomitant loss of a small molecule such as CH_4 or H_2 whose parts come from each of the initial monomers. An example from this class is the bridge-assisted condensation of $[Fe(CO)_4(PMe_2H)]$ with $[Co(CO)_3(\eta^3\text{-}C_3H_5)]$ with loss of C_3H_6 to yield $[FeCo(\mu\text{-}PPh_2)(CO)_7]$[40] which contains a bridging phosphido ligand.

Finally, the fourth class of reaction is termed the metal-exchange reaction and involves the rearrangement of two homobimetallic complexes of different metals to form two equivalents of a new heterobimetallic complex. For example, $[Re_2(CO)_{10}]$ and $[Mn_2(CO)_{10}]$ react at 220° to generate two molar equivalents of $[MnRe(CO)_{10}]$.[41] These reactions frequently require energy in the form of U.V. radiation or heat in order to occur.

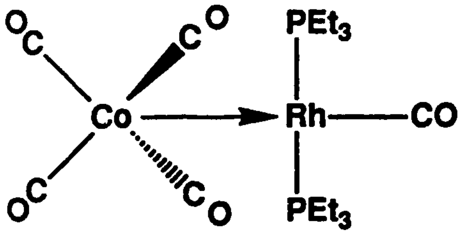
Other methods of generating heterobimetallic dimers exist although most of them involve the combination of several reactants in the presence of extreme heat or ultraviolet radiation. The mechanisms of these reactions are not well understood and the techniques are rarely general enough to be applied to a broad range of systems. Because of this, the usefulness of these methods, loosely categorized as pyrolysis reactions, as a synthetic strategy is greatly limited.

An interesting feature of many heterobimetallic complexes is the nature of the metal-metal bond. In most homobimetallic complexes such as $[Re_2(CO)_{10}]$ the two metals are linked by a nonpolar covalent sigma bond similar to a C-C single bond. A molecular orbital description of this bonding interaction would show two electrons in a low-lying sigma orbital with an empty high-



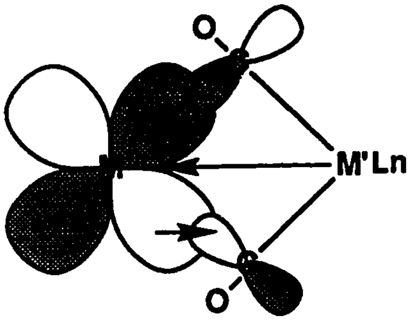
energy sigma antibonding orbital lying above. Promotion of an electron into the antibonding orbital results in a reduction in the bond order from 1 to 0 which leads to homolytic cleavage of the dimer into two 17-electron fragments. Heterobimetallic compounds, on the other hand, often contain a metal-metal bond which is best viewed as a donor-acceptor or dative bond.[42] Such a bond can be compared to that between a Lewis acid such as BEt_3 and a Lewis base such as tetrahydrofuran (THF). In the BEt_3-THF complex the oxygen of THF donates two electrons into the empty boron p orbital to complete the 8 valence electron requirement of this center. The nature of this bond is highly polar as the two electrons are largely localized around the oxygen atom.

A clear example of a dative bond between two metals is found in $[(\eta^5\text{-}C_5Me_5)IrW(CO)_7]$[42b] in which an $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ unit donates two electrons in a dative fashion to a $[W(CO)_5]$ unit. Another example, in which the nature of the metal-metal bond is less straightforward, is $[CoRh(CO)_5(PEt_3)_2]$, whose X-ray crystal structure has been recently determined.[43] This complex has the structure shown below in which a square planar $[Rh(CO)(PEt_3)_2]$ unit is metal-metal bonded to a tetrahedral $[Co(CO)_4]$ unit. These geometries are typical of Rh(I) and Co(-I) rather than Rh(0) and



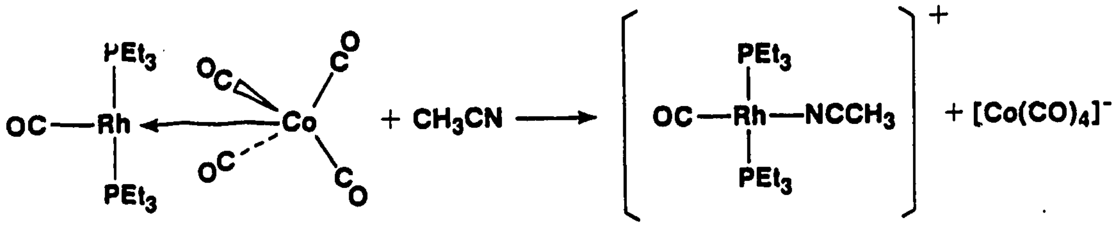
Co(0) and therefore strongly suggest that the bonding is most accurately viewed as Co→Rh donor-acceptor interaction rather than a classical covalent bond, although the latter possibility can not be unequivocally dismissed. In other words, rather than formulate this complex as containing a nonpolar covalent bond between zero-valent Co and Rh centers, the local geometries suggest a dative bond between a Co(-I) center and a Rh(+1) center. Thus, the $[Co(CO)_4]^-$ fragment acts as a "pseudohalide" in donating two electrons to the adjacent $[Rh(CO)(PEt_3)_2]$ unit. For this reason, this complex can readily be compared to $[Rh(L)_3X]$ (X=halide) systems in which the anionic chloride ligand donates two electrons to the Rh center.

Complexes with weak dative metal-metal bonds are often stabilized by back-donation of electron density from the non-bonding orbitals of the acceptor metal into the π-antibonding orbitals of the carbonyl ligands on the donor metal.30 In these systems the carbonyls are said to be sembribridging and the donor fragment can be thought of as a "supercarbonyl" since it acts



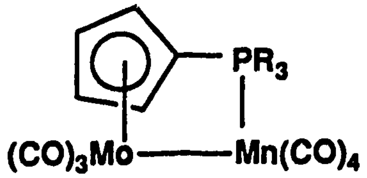
as both a sigma donor and a π- acceptor with respect to the adjacent metal as does a coordinated carbonyl.

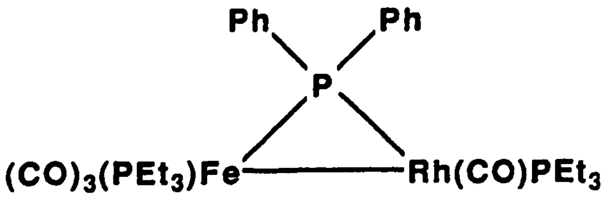
In spite of the stabilizing effects of bridging carbonyls, many homo and heterobimetallic complexes are unstable with regards to the cleavage of the metal-metal bond. The dative bond in many heterobimetallic complexes, is labile, and replacement of the metal donor unit is easily accomplished with even weak donor ligands such as THF and acetonitrile.[44] This inherent weakness, however, can act as a source of incipient coordinative unsaturation and therefore can render these systems more reactive towards an incoming ligand. Geoffroy has established that the complex [CoRh(CO)$_5$(PEt$_3$)$_2$] reacts with even weak donor ligands (L) to form the tetracarbonyl cobaltate anion and [Rh(L)(CO)(PEt$_3$)$_2$]$^+$,[43] as shown below.



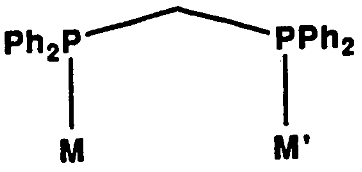
In order to avoid these often undesirable cleavage reactions while studying the chemistry of a dimeric system, bridging ligands other than carbon monoxide can be employed to maintain the bimetallic integrity of the complex. Such ligands must be bidentate in order to coordinate to both metals and have a flexible bite size which can accommodate a variety of intermetallic distances. Furthermore, they should be relatively sterically unencumbering to allow the approach of incoming substrate molecules which may react with the metal centers.

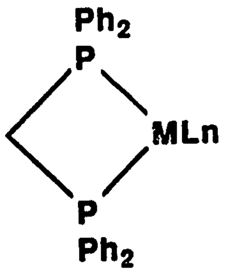
Several ligand systems have been used to bridge heterobimetallic complexes.[33] Casey has employed the heterobifunctional CpPPh$_2$ ligand in many early-late transition metal systems.[45,46] While the cyclopentadienyl portion of the molecule binds in an η^5-fashion to the early transition metal, the phosphorus end coordinates to the later one. Phosphido ligands have also been used extensively[47] but they do not easily accommodate a wide variety of metal-metal distances due to the fact that they form a rigid 3-membered ring with the two metals when bridging a metal-metal bond.





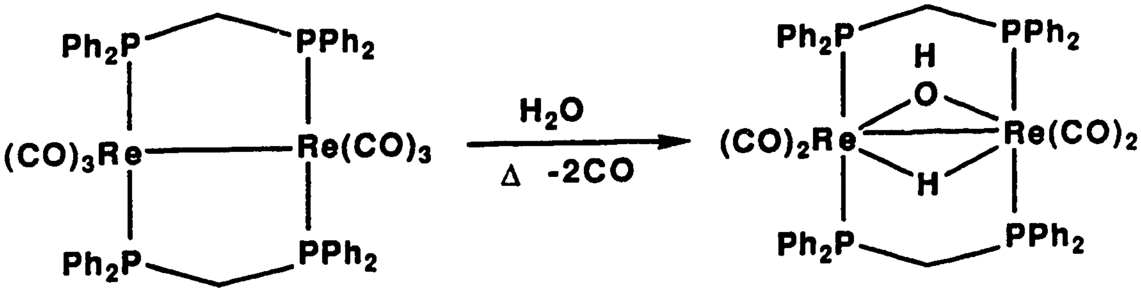
One of the most versatile classes of bridging ligands is that of the diphosphine ligand. This is because steric and electronic factors[48] can be easily controlled by varying the substituents on the phosphorus nuclei and the nature and length of the chain attatching the two basic centers. Because of its flexible bite size and preference to bridge rather than chelate, bis-(diphenylphosphino) methane (dppm) has become a popular ligand.[49] The presence of the phenyl groups also tends to facilitate crystallization which is necessary in order to conduct X-ray crystallographic studies. Furthermore, dppm is a good sigma donor and therefore tends to increase the electron richness and hence oxidizability of the metal(s) to which it is coordinated.[50] Thus, dppm complexes are ideal in many respects for the study of oxidative-addition reactions.





Much of the dppm chemistry explored to date has focused on systems with two dppm moieties bridging the metals. This further increases the stability of the metal-metal interaction while still allowing for facile identification by ^{31}P NMR spectroscopy.[51] Although the greater portion of this work has centered around the study of homobimetallic systems there is an increasing number of heterobimetallic dppm complexes under investigation.[49]

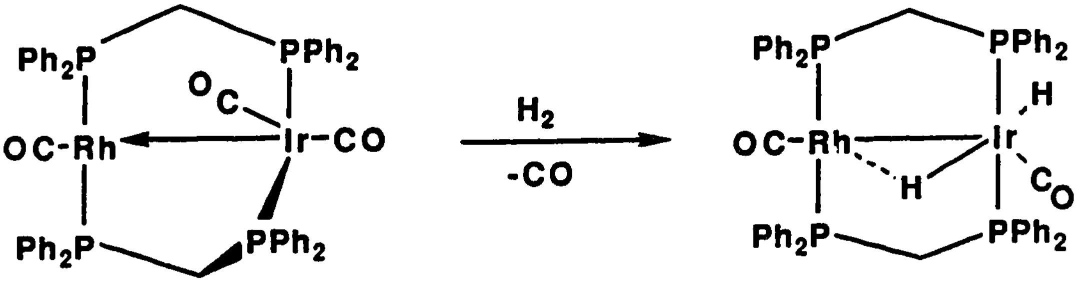
A great deal of this research has proven fruitful. In many cases the presence of the dppm group has enabled reactions to occur which were unsuccessful in the unbridged metal-carbonyl analogues. For example, where $[Re_2(CO)_{10}]$ reacts with H_2O at high temperatures to give only fragmentation products, the dppm-bridged analogue, $[Re_2(CO)_6(dppm)_2]$, reacts with H_2O to give a bimetallic species containing a bridging hydride and a bridging hydroxide.[52] Apparently, the analogous species is first formed in the reaction with $[Re_2(CO)_{10}]$, but it is too unstable and readily fragments to form monomeric products.[53]



Of the heterobimetallic chemistry conducted in this area, some of the most reactive complexes have been shown to be those which contain Rh or Ir.[49]

This is because of the tendency of these metals to adopt coordinatively unsaturated configurations in relatively low oxidation states. This makes them ideal for the study of binuclear oxidative-addition reactions. Moreover, dppm complexes of Rh have the added advantage of being more easily characterized by NMR techniques due to the 100% natural abundance of the NMR-active ^{103}Rh nucleus.[54] Thus, Rh-coupling can be observed in the ^{13}C, ^{31}P, and ^{1}H NMR spectra of these complexes. This is invaluable to the unambiguous assignment of resonances in these spectra. Furthermore, recent advances have now made it possible to obtain ^{103}Rh spectra indirectly through ^{31}P-correlation experiments involving rhodium-phosphine complexes.[55,56] Therefore, it is possible to obtain direct information concerning the electronic environment of a rhodium nucleus through the ^{103}Rh chemical shift.

The heterobimetallic complex [RhIr(CO)$_3$(dppm)$_2$] has been extensively studied by our group.[57] It reacts with dihydrogen, acetylenes, H^+, H_2S and silanes at ambient temperature to form oxidative-addition products. The reaction with H_2 is shown below. The reactivity of this tricarbonyl complex can be rationalized by the fact that it consists of a coordinatively unsaturated



$[Rh(CO)(P)_2]^+$ unit and a pseudohalidic $[Ir(CO)_2(P)_2]^-$ fragment. The presence of the open coordination site on Rh allows small molecules to oxidatively add to the system. The products of these reactions are generally Rh(I)/Ir(I) systems which frequently have one or both parts of the oxidative addend in a bridging position. The enhanced reactivity of this complex as compared to complexes of the general form $[RhX(CO)(P)_2]$ (X=Cl, P= a phosphine ligand) has been attributed to the strong electron donating ability of the low-valent iridium fragment which increases the electron richness of the rhodium center and hence promotes oxidative addition at this site.[57] Furthermore, the neighboring Ir center can participate by stabilizing the initial Rh(III)/Ir(-1) oxidative-addition product.

This system may also undergo two successive oxidative-addition reactions involving the same substrate provided that it has two labile bonds. Thus, molecules of the form H_2X ($X=R_2Si,S$) react to form dihydrido products with bridging X moieties.[58] In some cases, these oxidative-addition products can further go on to reductively eliminate H_2. The mechanism of the second oxidative-addition step and the subsequent loss of dihydrogen is of some interest since the two metals must cooperate to create a vacant coordination site after the initial oxidative addition. This site enables the second H-X bond to be activated. After this step, the ligands must migrate such that the two hydrides are mutually cis, as required prior to reductive-elimination. Although the study of the reaction of the Rh/Ir dimer with hydrogen sulfide conducted at low temperature has only revealed a bridging sulfhydryl species with a terminal Ir hydride, the diiridium system has revealed several intermediates . However, the picture is far from complete as several proposed key intermediates in this system are presumably too short lived to be detected.

In order to extend the studies of reactivity and metal-metal cooperativity in heterobinuclear dppm complexes the synthesis of a series of low valent bis-dppm dimers containing Rh and an earlier transition metal was undertaken. It was hoped that the examination of the oxidative-addition reactions of these complexes might lead to some unique chemistry not observed in the Rh/Ir system. The potential of these complexes to activate dioxygen[59,60] is also of special interest since organometallic species with oxo, peroxo, and superoxo ligands are important to the understanding of the catalytic oxidation of CO [61,62] as well as the oxidation of organic substrates by transition metal complexes.[63] Furthermore, the possibility that these complexes could display Fischer-Tropsch related chemistry due to the rich alkyl chemistry of earlier transition metals, seemed worth exploring.

The object of this thesis, therefore, is to first characterize and study a series of low-valent Rh/M (M= a metal other than Rh) bis-dppm metal-carbonyls and then to thoroughly investigate the chemistry of one of these systems. Rhenium was chosen as the earlier metal because of its rich alkyl and oxo chemistry which we felt could compliment the tendency of low valent Rh complexes to undergo oxidative addition. Complexes of Re also tend to maintain an eighteen electron configuration whereas monovalent Rh and Ir complexes often favor a sixteen electron configuration with a vacant coordination site. It was thus hoped that this combination of these two metals with distinctly different properties would give rise to reactivity patterns not observed in either $[Re_2(CO)_6(dppm)_2]$, $[Rh_2(CO)_3(dppm)_2]$, or $[RhIr(CO)_3(dppm)_2]$.

After the synthesis and characterization of a series of heterobimetallic dppm complexes containing Rh, the reactions of the Rh/Re system with acetylenes, dihydrogen, H^+, and other small molecules will be examined in order to establish the general pattern of oxidative-addition reactions in this particular system. Next, the reactions of H_2S and thiols with this system will be investigated, in hopes of elucidating the mechanism of oxidative-addition involving both S-H bonds of hydrogen sulfide, the possible ligand rearrangements occurring, and subsequent loss of H_2 discussed earlier; the thiols will be investigated as models for the oxidation of the first S-H bond in H_2S. The presence of the Re metal in place of the Ir might tend to stabilize certain intermediates whose analogues were not observed in the studies of the Rh/Ir system. The reaction of the Rh/Re dimer with dioxygen will also be discussed because of its potential importance to the understanding of the catalytic oxidation of organic molecules. Finally, the chemistry of alkyl derivitives of this Rh/Re dimer will be investigated in order to expand the understanding of the properties of bimetallic alkyl complexes and possibly gain insights into carbon-carbon coupling reactions and CO reduction on metal surfaces. Ultimately, then, the goal of this thesis is to establish how the two neighboring metals cooperate in the reactions of the Rh/Re system and how these reactions contrast to the analogous reactions with related systems.

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Chapter 2

A Convenient General Route to a Series of Diphosphine-bridged Heterobinuclear Complexes Which Contain Rhodium, and Structures of the Mixed-Valent Complexes, $[RhM(CO)_4(Ph_2PCH_2PPh_2)_2]$ (M = Mn, Re).†

Introduction

The current interest in heterobimetallic complexes arises from their promise of displaying unique chemistry by virtue of the differing properties of the two distinct metals. In such complexes not only can the ligands be varied to achieve a range in reactivities but the metals can also be changed, allowing an even wider reactivity range to be explored.

As pointed out by Geoffroy and coworkers,[1] the metal-metal bond (M-M') in heterobimetallic complexes is not purely covalent, but can have significant donor-acceptor character. Such bonds have been shown to be relatively weak, being readily cleaved by nucleophiles.[2] Although this property is often not desirable when investigating binuclear reactivity, since it results in cleavage to mononuclear fragments, the labile M→M' bond does have the benefit of yielding a source of incipient coordinative unsaturation. In order to make use of the labile M→M' bond while still maintaining the binuclearity of the complex, we have chosen to use bis(diphenylphosphino)methane (dppm) as a bridging group in order to hold the metals in close proximity during the reactions of interest.

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† A version of this chapter has been published. Antonelli, D.M. and Cowie, M. *Organometallics*, 1990, *Vol. 9*, 1818-1826.

Dppm has been widely used in homobinuclear complexes[3] but has been much less used in heterobinuclear species.[4] Several approaches have been used to synthesize dppm-bridged heterobinuclear complexes,[4] most notably byShaw and coworkers.[4,5] In one approach, complexes containing chelating dppm groups were used, with unwinding of these groups upon reaction with the second metal to yield the dppm-bridged species.[5a-c]

In this chapter we describe a general route to a series of dppm-bridged heterobinuclear complexes through the exchange of the halide ligand in [RhCl(dppm)$_2$] by a series of metal carbonylate anions. This method yields complexes in which the metals are in low formal oxidation states, in which a potentially labile M→Rh dative bond can be formulated. Rhodium is chosen as one of the metals owing to its tendency to adopt a coordinatively unsaturated 16e configuration.[6] The effect of this site of unsaturation on the chemistry of the other, coordinatively saturated metal center will be of subsequent interest. A similar approach has previously been used to prepare a limited number of Pd[7] and Ru[8] complexes.

Experimental Section

General Experimental Conditions

All solvents were dried and deoxygenated before use and transferred directly to the reaction flask by cannula. Reactions were conducted using standard Schlenk procedures. Prepurified argon was used without further drying or deoxygenating. The hydrated rhodium(III) and ruthenium(III) chlorides were obtained from Johnson Matthey Ltd., $Co_2(CO)_8$, $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, $W(CO)_6$, $Cr(CO)_6$, $Os_3(CO)_{12}$, and $Fe(CO)_5$ were purchased from

Strem, while $Mo_2Cp_2(CO)_6$, $Fe_2Cp_2(CO)_4$, $[(Ph_3P)_2N]Cl$ and $Ph_2PCH_2PPh_2$ (dppm) were obtained from Aldrich. $Ru_3(CO)_{12}$[9] and $[RhCl(dppm)_2]$[10] were prepared by the literature procedures, except that in the latter case the reaction in benzene was allowed to proceed for *ca.* 1 h then the benzene was removed and the solid used without further purification. The compound, $Re_2(CO)_{10}$ was sublimed before use and $Fe(CO)_5$ was vacuum distilled. The 99% carbon-13 enriched carbon monoxide was obtained from Isotec Inc.

The ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and the $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer and infrared spectra were run on either a Nicolet 7199 Fourier transform interferometer or a Perkin Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr disks) or solutions (KCl windows, 0.5 mm path length). Elemental analyses were performed by the microanalytical service within the department.

The compounds, $Na[Co(CO)_4]$,[11] $Na[Mn(CO)_5]$,[12] $Na[Re(CO)_5]$,[13] $Na[FeCp(CO)_2]$,[14] and $Na[MoCp(CO)_3]$[15] were all prepared by the reduction of the parent metal carbonyl dimers in THF with 2.3% Na/Hg. In all cases the anions were used *in situ*. The compound $(PPN)[HFe(CO)_4]$[16] (PPN = $[(Ph_3P)_2N]^+$) was prepared by the reaction of NaOH with $Fe(CO)_5$ in MeOH followed by addition of PPNCl, the salts, $(PPN)[HM(CO)_4]$ (M = Ru, Os)[17] were prepared by the Na/NH_3 reduction of $M_3(CO)_{12}$ (M = Ru, Os) followed by treatment with MeOH and PPNCl, and the compounds $(PPN)[HM(CO)_5]$ (M = Cr, W)[18] were synthesized by the reaction of $M(CO)_5PIP$ (PIP = pipyridine) with $(PPN)(BH_4)$ in THF.

Preparation of Compounds

a) [RhCo(CO)$_3$(dppm)$_2$] (1).

The compound [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) was dissolved in 5 mL of THF and Na[Co(CO)$_4$] (21 mg, 0.11 μmol) was then added in 10 mL of THF *via* cannula. The solution gradually turned from light orange to dark orange-brown over 1/2 h. After an additional 18 h stirring the mixture was filtered under argon to remove NaCl and the THF was removed *in vacuo* to yield a dark brown solid which was recrystallized from CH_2Cl_2/Et_2O to yield 82 mg (73%) of a deep brown powder which was spectroscopically identified as (1). Anal. Calcd. for $C_{53}H_{44}CoO_3P_4Rh$: C, 62.68; H, 4.33. Found: C, 62.12; H, 4.16. The spectroscopic parameters for all compounds are given in Table 2.1.

b) [RhFe(μ-H)(CO)$_3$(dppm)$_2$] (2).

The compound [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) was dissolved in 5 mL of THF to which (PPN)[HFe(CO)$_4$] (78 mg, 0.11 μmol) was added by cannula in 10 mL of THF. The color instantly turned dark green and a white precipitate of PPNCl formed. The mixture was stirred for an additional 4 h after which the THF was removed *in vacuo*. The green solid was redissolved in toluene, filtered to remove the PPNCl and the solvent was removed under vacuum. Recrystallization from CH_2Cl_2/Et_2O yielded 84 mg (76%) of a dark green-brown powder (2). Anal. Calcd. for $C_{53}H_{45}FeO_3P_4Rh$: C, 62.81; H, 4.34. Found: C, 62.41; H, 4.13.

c) [RhRu(μ-H)(CO)$_3$(dppm)$_2$] (3).

The compound [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) was dissolved in 5 mL of THF and (PPN)[HRu(CO)$_4$] (83 mg, 0.11 μmol) was added by cannula in 10 mL of THF . The mixture turned dark brown immediately and a white precipitate of PPNCl formed. After 8 h of additional stirring the solvent was

Table 2.1 Spectral Data[a]

	IR, cm^{-1}	NMR	
		$\delta(^{31}P\{^{1}H\})^{d}$	$\delta(^{1}H)^{e}$
$[RhCo(CO)_3(dppm)_2]$ (1)	1944(m), 1922(s), 1830(m)[b]	35.2(m), 22.2(dm, $^{1}J_{Rh\text{-}P}$ = 133 Hz)	
$[RhFeH(CO)_3(dppm)_2]$ (2)	1956(s), 1880(s), 1830(m)[b]	71.1(m), 34.1(dm, $^{1}J_{Rh\text{-}P}$ = 123 Hz)	-12.65(m, $^{1}J_{Rh\text{-}H}$ = 24 Hz, $^{2}J_{P(Fe)\text{-}H}$ = 37 Hz, $^{2}J_{P(Rh)\text{-}H}$ = 12 Hz)[f]
$[RhRuH(CO)_3(dppm)_2]$ (3)	1955(s), 1892(s), 1849(m)[b],	44.8(m), 28.3(dm, $^{1}J_{Rh\text{-}P}$ = 123 Hz)	-9.3(m, $^{1}J_{Rh\text{-}H}$ = 22 Hz, $^{2}J_{P(Ru)\text{-}H}$ = 14 Hz, $^{2}J_{P(Rh)\text{-}H}$ = 12 Hz)
$[RhOsH(CO)_3(dppm)_2]$ (4)	1971(m), 1925(s), 1858(m), ν(Os-H): 2040(w)[b]	-9.2(m), 15.2(dm, $^{1}J_{Rh\text{-}P}$ = 143 Hz)	-7.4(t, $^{2}J_{P(Os)\text{-}H}$ = 20 Hz)
$[RhMn(CO)_4(dppm)_2]$ (5)	1960(m), 1891(m), 1817(s), 1797(s)[b]	81.6(m), 28.6(dm, $^{1}J_{Rh\text{-}P}$ = 131 Hz)	
$[RhRe(CO)_4(dppm)_2]$ (6)	1959(m), 1908(m), 1838(m), 1800(m)[b]	6.2(m), 26.2(dm, $^{1}J_{Rh\text{-}P}$ = 136 Hz)	
$[RhCrH(CO)_4(dppm)_2]$ (7)	1975(m), 1922(m), 1824(s), 1803(s)[b]	70.3(m), 26.2(dm, $^{1}J_{Rh\text{-}P}$ = 121 Hz)	-14.8(m, $^{1}J_{Rh\text{-}H}$ = 23 Hz, $^{2}J_{P(Cr)\text{-}H}$ = 10.1 Hz, $^{2}J_{P(Rh)\text{-}H}$ = 12.2 Hz)
$[RhWH(CO)_4(dppm)_2]$ (8)	1978(m), 1942(s), 1838(s), 1818(s)[c]	21.2(m), 25.5(dm, $^{1}J_{Rh\text{-}P}$ = 121 Hz)	-10.50(m, $^{1}J_{Rh\text{-}H}$ = 25.1 Hz, $^{2}J_{P(W)\text{-}H}$ = 5 Hz, $^{2}J_{P(Rh)\text{-}H}$ = 14.2 Hz, $^{1}J_{W\text{-}H}$ = 49 Hz
$[RhFeCp(CO)(dppm)_2]$ (9)	1679(s)[b]	P_A: d 34.8(ddt, $^{1}J_{Rh\text{-}P_A}$ = 160 Hz, $^{2}J_{P_A\text{-}P_B}$ = 136 Hz, $^{2}J_{P_A\text{-}P_C}$ = 16 Hz); P_B: d 86.9(d); P_C: d -19.2(dd; $^{1}J_{Rh\text{-}P_C}$ = 137 Hz)	
$[RhMoCp(CO)_2(dppm)_2]$ (10)	1684(s), 1960(m)[b]	-22.1(d, $^{1}J_{Rh\text{-}P}$ = 108 Hz)	

[a] Abbreviations used: IR: w = weak, m = medium, s = strong; NMR: m = multiplet, d = doublet, dm = doublet of multiplets, ddt = doublet of doublet of triplets. [b] CH_2Cl_2 solution in KCl cells. [c] Nujol mull in KBr disk. [d] Vs. 85% H_3PO_4, -40°C in CD_2Cl_2 solvent. [e] Vs. TMS, 25°C in CD_2Cl_2 solvent. [f] $J_{P(M)\text{-}H}$ is the coupling constant between the phosphorus nuclei bound to M and hydrogen.

removed *in vacuo* and the residue redissolved in toluene. After filtering this solution to remove the PPNCl the toluene was removed *in vacuo*. The resulting brown residue was recrystallized from CH_2Cl_2 to yield 94 mg (81%) of a dark brown solid (3). Anal. Calcd. for $C_{53}H_{45}O_3P_4RhRu$: C, 60.12; H, 4.16. Found: C, 59.75; H, 4.01.

d) [RhOs(H)(CO)$_3$(dppm)$_2$] (4).

In a procedure identical to part b), 100 mg (0.11 μmol) of [RhCl(dppm)$_2$] was reacted with (PPN)[HOs(CO)$_4$] (92 mg, 0.11 μmol) to yield 109 mg of a fine orange-yellow powder (87%). Anal. Calcd. for $C_{53}H_{45}O_3OsP_4Rh$: C, 55.46; H, 3.92. Found: C, 54.89; H, 4.12.

e) [RhMn(CO)$_4$(dppm)$_2$] (5).

The compound [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) was dissolved in 5 mL of THF and treated with 24 mg (0.11 μmol) Na[Mn(CO)$_5$] in 10 mL of THF. The reaction mixture turned red-orange and was stirred for 8 h after which time some of the product had precipitated. The addition of CH_2Cl_2 (20 mL) caused the product to redissolve. The solution was then filtered under argon to remove the NaCl and the solvent was removed *in vacuo*. Recrystallization of the residue yielded 107 mg (84%) of a yellow powder (5). Anal. Calcd. for $C_{54}H_{44}MnO_4P_4Rh$: C, 56.39; H, 3.83. Found: C, 56.11; H, 4.07.

f) [RhRe(CO)$_4$(dppm)$_2$] (6).

The compound [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) was dissolved in 5 mL of THF and Na[Re(CO)$_5$] (38 mg, 0.11 μmol) in 10 mL of THF was added *via* cannula. The solution turned light orange immediately and was stirred for 6 h. After filtration under argon the solvent was removed *in vacuo* and the residue was recrystallized from CH_2Cl_2/Et_2O. Owing to the high solubility of **6** in CH_2Cl_2 it is important to use a minimum volume of solvent in this step to maximize the yield; 95 mg (74%) of a bright yellow powder of **6** was obtained. Anal. Calcd. for $C_{54}H_{44}O_4P_4ReRh$: C, 55.47; H, 3.76. Found: C, 55.08; H, 4.12.

g) [RhCr(μ-H)(CO)$_4$(dppm)$_2$] (7).

A solution of PPN[HCr(CO)$_5$] (80.7 mg, 0.11 μmol) in 10 mL of THF was added *via* cannula to a solution of [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) in 10 mL of THF. The solution quickly turned dark red-brown over 5 min and was stirred for a total of 8 h. The THF volume was then reduced to 10 mL and the solution was filtered to remove PPNCl. The THF was then removed *in vacuo* and the dark brown residue was recrystallized from THF/Et_2O and washed with 3×5 mL of Et_2O, to yield 85 mg (74%) of a dark brown solid. Anal. Calcd. for $C_{54}H_{45}CrP_4O_4Rh$: C, 62.56; H, 4.37. Found: C, 62.11; H, 4.51.

h) [RhW(μ-H)(CO)$_4$(dppm)$_2$] (8).

The compound [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) was dissolved in 5 mL of THF and (PPN)[HW(CO)$_5$] (95 mg, 0.11 μmol) was added by cannula in 10 mL of THF. The solution rapidly turned dark red-brown and a white precipitate of PPNCl formed. After 6 h of stirring, the THF was removed *in vacuo* to yield a red-brown residue which was extracted into toluene. Filtration of the brown solution to remove the insoluble PPNCl followed by the removal of the solvent *in vacuo* left a red-brown solid which was recrystallized from CH_2Cl_2/Et_2O to give 101 mg (78%) of a dark red-brown powder. Anal. Calcd. for $C_{55}H_{45}O_4P_4RhW$: C, 55.50; H, 3.85. Found: C, 55.17; H, 4.21.

i) [RhFeCp(μ-CO)(dppm)$_2$] (9).

A solution of [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) in 5 mL of THF was treated with a solution of Na[FeCp(CO)$_2$] (22 mg, 0.11 μmol) in 10 mL of THF. The dark green reaction mixture was stirred for 2 h and then filtered under argon. The solvent was removed *in vacuo* and the dark green residue was recrystallized from CH_2Cl_2/Et_2O to yield 74 mg (65%) of a dark green-brown powder. Anal. Calcd. for $C_{56}H_{49}FeOP_4Rh$: C, 65.89; H, 4.80. Found: C, 65.23; H, 4.99.

j) [RhMoCp(CO)(μ-CO)(dppm)$_2$] (10).

The compound [RhCl(dppm)$_2$] (100 mg, 0.11 μmol) was dissolved in 5 mL of THF. Na[MoCp(CO)$_3$] (29 mg, 0.11 μmol) in 10 mL of THF was added *via* cannula and the reaction mixture instantly turned dark brown. After 5 h of stirring the NaCl was removed by filtration under argon and the solvent removed *in vacuo*. The brown product was recrystallized from CH_2Cl_2/Et_2O to yield 80 mg (67%) of product. Anal. Calcd. for $C_{57}H_{49}MoO_2P_4Rh$: C, 62.87; H, 4.50. Found: C, 62.16; H, 4.81.

X-Ray Data Collection

Yellow crystals of [RhMn(CO)$_4$(dppm)$_2$] (5) were obtained from CH_2Cl_2/Et_2O and light orange crystals of [RhRe(CO)$_4$(dppm)$_2$]•THF (6) were obtained from THF/Et_2O. Suitable crystals were mounted and flame-sealed in glass capillaries under argon to minimize decomposition, which was still quite substantial for the Re compound (*vide infra*). Unit cell parameters were obtained from least-squares refinements of 25 well distributed reflections in the ranges $20.0 \leq 2\theta \leq 24.0°$ (compound **5**), $21.9 \leq 2\theta \leq 25.6°$ (compound **6**). For **5** a triclinic cell was established by the usual peak search and reflection indexing programs; the lack of systematic absences established the space group as either P1 or $P\bar{1}$. A cell reduction failed to locate a higher symmetry cell. The centrosymmetric space group was established as the more probable one based on the successful refinement of the structure, although with Z = 1 in this space group the metal carbonyl moieties are disordered about the inversion center (*vide infra*). For compound **6** the space group was established as $P2_1/c$ with Z = 2, so again the metal carbonyl moieties were found to be inversion disordered. Although for **6** there were only two THF molecules per unit cell these were not found to occupy inversion centers but occupy general positions of half-occupancy.

Intensity data for both compounds were collected at 22°C using the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak widths on either side of the scans. Three reflections were chosen as intensity standards and remeasured at 120 min intervals of X-ray exposure. For **5** there was no significant systematic decrease in the intensities of the standards so no correction was applied, but for **6** the intensities decayed by 23.5% so a correction was applied assuming a linear decay. Data were processed in the usual way using a value of 0.04 for p,[19] and absorption corrections were applied to the data using the method of Walker and Stuart.[20,21] See Table 2.2 for pertinent crystal data and details of intensity collection.

Table 2.2 Summary of Crystal Data and Details of Intensity Collection

compound	$[RhMn(CO)_4(dppm)_2]$	$[RhRe(CO)_4(dppm)_2]\cdot THF$
formula	$C_{54}H_{44}MnO_4P_4Rh$	$C_{58}H_{52}O_5P_4ReRh$
fw	1038.7	1242.1
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	10.897(2)	12.963(4)
b, Å	11.046(2)	19.883(3)
c, Å	11.700(2)	11.277(2)
α, deg	68.14(1)	-
β, deg	67.48(1)	99.12(2)
γ, deg	87.69(1)	-
V, $Å^3$	1198.7(4)	2870(2)
Z	1	2
d_{calcd}, g cm^{-3}	1.439	1.437
temp, °C	22	22
radiation, Å	MoKα, 0.71069	MoKα, 0.71069
monochromator	graphite	graphite
μ, cm^{-1}	7.91	25.71
transmission coefft. (min, max)	0.758, 1.101	0.845, 1.230
unique data collected	4169	5463
observed (NO)	3010	3744
no. of variables (NV)	288	188
R[a]	0.054	0.053
R_w[b]	0.082	0.088
error in obs. of unit wt (GOF)[c]	2.573	2.874

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$;

[b] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$;

[c] $GOF = [\Sigma w(|Fo|-|Fc|)^2/(NO\text{-}NV)]^{1/2}$

Structure Solution and Refinement

Both structures were solved by conventional Patterson and Fourier techniques with the assumption that the molecules were statistically disordered about the inversion centers. In fact only two carbonyl groups in each complex are affected since the diphosphine groups are exactly inversion related and one carbonyl group on each metal lies along the Rh-M (M = Mn, Re) axis, and are therefore inversion related. Even within the two carbonyl groups (C(2)O(2) and C(3)O(2)') that do display disorder the oxygen positions of the disordered pairs are superimposable so in fact only the carbons of these two carbonyls show up as two sets of positions having half occupancy. With such minor changes in the carbonyl positions for the two disordered sets it is not surprising that the phenyl ring positions are unaffected and are well behaved.

All non-hydrogen atoms were located. The THF molecule in compound 6 was apparently rotationally disordered since none of the five ring atoms refined acceptably as an oxygen. All five atoms were therefore treated as carbons. Atomic scattering factors[22,23] and anomalous dispersion terms[24] were taken from the usual sources. Hydrogen atoms were included as fixed contributions and were not refined. Their idealized positions were calculated from the geometries of the attached carbon atoms with a C-H distance of 0.95Å being used. Hydrogens were assigned thermal parameters of 20% greater than the isotropic B's of the attached carbon atoms. A summary of positional and isotropic thermal parameters is given in Tables 2.3-2.4.

Table 2.3 Positional and Thermal Parameters for [RhMn(CO)$_4$(dppm)$_2$] (5)

Atom	x	y	z	B (Å^2)^a
Rm^b	0.08893(6)	0.06850(6)	-0.13580(5)	3.62(1)
P(1)	0.0443(1)	0.2671(1)	-0.1231(1)	3.23(3)
P(2)	-0.1549(1)	0.1215(2)	0.1574(1)	3.48(4)
O(1)	0.2855(7)	0.2068(6)	-0.4025(7)	10.1(2)
O(2)	-0.1787(4)	-0.0251(4)	-0.1079(4)	5.4(1)
C(1)	0.2070(7)	0.1530(7)	-0.2972(7)	5.7(2)
C(2)^b	-0.075(1)	0.017(1)	-0.118(1)	3.52(2)*
C(3)^b	0.144(1)	0.041(1)	0.0101(9)	3.2(2)*
C(4)	-0.0293(5)	0.2658(6)	0.0457(5)	3.8(1)
C(11)	0.1984(5)	0.3805(5)	-0.2032(5)	3.5(1)
C(12)	0.2229(6)	0.4932(6)	-0.3157(5)	4.4(2)
C(13)	0.3509(7)	0.5695(7)	-0.3858(6)	5.6(2)
C(14)	0.4493(7)	0.5304(8)	-0.3441(7)	6.5(2)
C(15)	0.4271(7)	0.4143(8)	-0.2329(6)	6.1(2)
C(16)	0.3007(6)	0.3414(6)	-0.1613(6)	4.6(2)
C(21)	-0.0614(5)	0.3633(6)	-0.2041(5)	3.9(2)
C(22)	-0.0965(6)	0.3209(7)	-0.2865(6)	5.3(2)
C(23)	-0.1627(7)	0.4018(9)	-0.3609(7)	8.4(2)
C(24)	-0.2016(6)	0.5152(8)	-0.3491(8)	7.8(3)
C(25)	-0.1744(7)	0.5543(8)	-0.2648(8)	6.9(2)

Table 2.3 (Continued)

Atom	x	y	z	B (Å²)[a]
C(26)	-0.1009(7)	0.4803(8)	-0.1909(7)	6.1(2)
C(31)	-0.1887(6)	0.1205(6)	0.3230(5)	4.0(2)
C(32)	-0.0833(7)	0.1343(8)	0.3575(6)	6.0(2)
C(33)	-0.1080(7)	0.1217(8)	0.4890(6)	6.7(2)
C(34)	-0.2398(8)	0.0916(8)	0.5862(6)	6.7(2)
C(35)	-0.3439(8)	0.0762(9)	0.5516(6)	7.4(3)
C(36)	-0.3206(7)	0.0928(8)	0.4210(6)	6.1(2)
C(41)	-0.3077(5)	0.1710(5)	0.1310(5)	3.4(1)
C(42)	-0.3826(6)	0.0920(7)	0.1116(5)	4.9(2)
C(43)	-0.4977(6)	0.1274(8)	0.0934(6)	6.0(2)
C(44)	-0.5367(7)	0.2486(9)	0.0909(7)	7.0(2)
C(45)	-0.4673(7)	0.3293(8)	0.1144(7)	6.2(2)
C(46)	-0.3497(6)	0.2918(7)	0.1334(6)	5.2(2)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

[b] Atoms Rm is half occupancy Rh and half occupancy Mn, and atoms C(2) and C(3) are half occupancy owing to disorder. See experimental section for details.

Table 2.4 Positional and Thermal Parameters for $[RhRe(CO)_4(dppm)_2] \cdot THF$ (6)

Atom	x	y	z	B (Å^2)^a
Rr^b	0.07431(4)	0.04268(2)	-0.03694(4)	2.98(1)
P(1)	0.1720(2)	-0.0460(1)	-0.0967(2)	3.00(5)
P(2)	0.0265(2)	-0.1377(1)	0.0108(2)	3.04(5)
O(1)	0.2548(6)	0.1333(4)	-0.0804(8)	6.6(2)
O(2)	-0.1088(8)	-0.0213(5)	-0.2414(7)	7.2(2)
C(1)	0.1872(8)	0.1008(5)	-0.067(1)	4.1(2)
C(2)^b	-0.037(1)	0.007(1)	-0.163(2)	3.4(4)*
C(3)^b	0.107(2)	0.033(1)	0.139(2)	4.0(4)
C(4)	0.1021(7)	-0.1264(5)	-0.1115(8)	3.4(2)
C(5)^c	0.429(3)	0.103(2)	0.383(3)	15.4(9)*
C(6)^c	0.387(5)	0.142(3)	0.296(6)	14(2)*
C(7)^c	0.453(3)	0.182(2)	0.280(3)	19(1)*
C(8)^c	0.373(3)	0.194(2)	0.398(3)	12(1)*
C(9)^c	0.439(4)	0.161(3)	0.458(5)	10(2)*
C(11)	0.2037(8)	-0.0334(5)	-0.2479(9)	3.6(2)*
C(12)	0.1267(9)	-0.0400(6)	-0.347(1)	4.6(2)*
C(13)	0.147(1)	-0.0270(6)	-0.467(1)	5.2(3)*
C(14)	0.242(1)	-0.0058(6)	-0.479(1)	5.5(3)*
C(15)	0.319(1)	0.0016(7)	-0.383(1)	5.8(3)*

Table 2.4 (Continued)

Atom	x	y	z	B (Å^2)^a
C(16)	0.3006(9)	-0.0118(6)	-0.265(1)	4.7(2)*
C(21)	0.2978(8)	-0.0663(5)	-0.0076(9)	3.7(2)*
C(22)	0.3638(9)	-0.1123(6)	-0.049(1)	5.1(2)*
C(23)	0.460(1)	-0.1315(7)	0.023(1)	6.3(3)*
C(24)	0.485(1)	-0.1034(7)	0.130(1)	7.3(4)*
C(25)	0.418(1)	-0.0577(7)	0.178(1)	7.7(4)*
C(26)	0.324(1)	-0.0370(6)	0.103(1)	5.2(3)*
C(31)	-0.0433(7)	-0.2160(5)	-0.0339(8)	3.4(2)*
C(32)	-0.0364(9)	-0.2723(6)	0.0411(9)	4.5(2)*
C(33)	-0.095(1)	-0.3298(7)	0.001(1)	6.1(3)*
C(34)	-0.153(1)	-0.3326(7)	-0.111(1)	5.8(3)*
C(35)	-0.162(1)	-0.2757(7)	-0.183(1)	6.4(3)*
C(36)	-0.1087(9)	-0.2168(6)	-0.146(1)	4.9(2)*
C(41)	0.1195(7)	-0.1646(5)	0.1385(8)	3.4(2)*
C(42)	0.202(1)	-0.2037(6)	0.126(1)	5.3(3)*
C(43)	0.279(1)	-0.2239(7)	0.226(1)	6.4(3)*
C(44)	0.262(1)	-0.2043(6)	0.336(1)	5.7(3)*
C(45)	0.176(1)	-0.1703(7)	0.353(1)	6.2(3)*

Table 2.4 (Continued)

Atom	x	y	z	B (Å^2)^a
C(46)	0.1038(9)	-0.1484(6)	0.253(1)	4.8(2)*

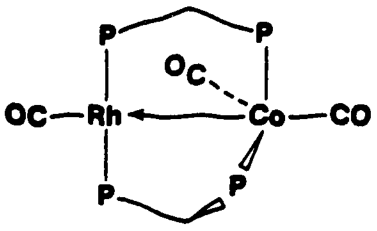
^{a}Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

^{b}Atoms Rr is half occupancy Rh and half occupancy Re, and atoms C(2) and C(3) are half occupancy owing to disorder. See experimental section for details.

^{c}Atoms C(5)-C(9) are the rotationally disordered THF molecule. See experimental section for details.

Results and Discussion

The reaction of [RhCl(dppm)$_2$] with one equivalent of Na[Co(CO)$_4$] occurs readily at room temperature yielding the mixed-metal species [RhCo(CO)$_3$(dppm)$_2$] (**1**). Replacement of the chloride anion by the cobalt carbonylate anion has been accompanied by unwinding of the chelating dppm groups, their transformation to the bridging mode and concomitant loss of one carbonyl group. This reaction can be classed as a bridge assisted ligand substitution reaction, as discussed in Chapter 1. The $^{31}P\{^1H\}$ NMR spectrum is characteristic of a rhodium-containing heterobimetallic complex in which the metals are bridged by two dppm groups, yielding an AA'BB'X spin system. The broad second order multiplet (a pseudo triplet) at δ 35.2 corresponds to the phosphorus nuclei bound to Co and the doublet of pseudo triplets at δ 22.2 represents those bound to Rh ($^1J_{Rh\text{-}P}$ = 133 Hz). The low-field chemical shift for the phosphorus nuclei on Co appears to be typical of these species, in which the chemical shifts move to higher field on progressing down a triad. The carbonyl stretches for **1**, at 1944, 1922 and 1830 cm^{-1} are very reminiscent of those observed for the related complexes, [MM'(CO)$_3$(dppm)$_2$] (M = M' = Rh:[25] 1940, 1920, 1835 cm^{-1}; M = Rh, M' = Ir:[26] 1950, 1934, 1861 cm^{-1}; M = M' = Ir:[27] 1950, 1936, 1857 cm^{-1}), therefore **1** is formulated as having an analogous structure. The assumption that Rh has the coordinatively unsaturated



1

configuration, as shown, is consistent with the structure observed for $[(PEt_3)_2RhCo(CO)_5]$[28] and that proposed for $[F\ \ Co(CO)_7]$,[29] and with the known tendencies of Rh to favour a square-planar 16e configuration[6] and Co to favour 18e species.[30] This formulation very much reflects the method of preparation, with the tetrahedral $[Co(CO)_2L_2]^-$ anion functioning as a pseudo halide in the Vallarino's-type complex, *trans*-$[RhX(CO)L_2]$ (where L represents one end of the diphosphine unit, X = anionic group). The structure of 1 has recently been determined,[31] confirming the above formulation.

Complex 1, like the analogous Rh_2,[25] RhIr[26] and Ir_2[27] complexes, displays temperature dependent fluxionality, as shown by the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra. At -40°C the $^{31}P\{^1H\}$ NMR spectrum is as described earlier, whereas at 23°C the pseudo triplet corresponding to the Co-bound phosphorus nuclei has collapsed to a broad singlet. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample, taken at -40°C displays three equal-intensity resonances at δ 180.4 (doublet of triplets, $^1J_{Rh\text{-}C} = 70$ Hz, $^2J_{P\text{-}C} = 11$ Hz), δ 214.6 (triplet, $^2J_{P\text{-}C} = 20$ Hz) and δ 215.4 (broad singlet). Only the high-field resonance displays Rh coupling, consistent with the structure proposed. At 23°C the high-field resonance remains essentially unchanged, but the other two have collapsed into a broad singlet at δ 215.6, having twice the intensity of the high-field signal. These observations are consistent with a scrambling process occurring only at the Co center.

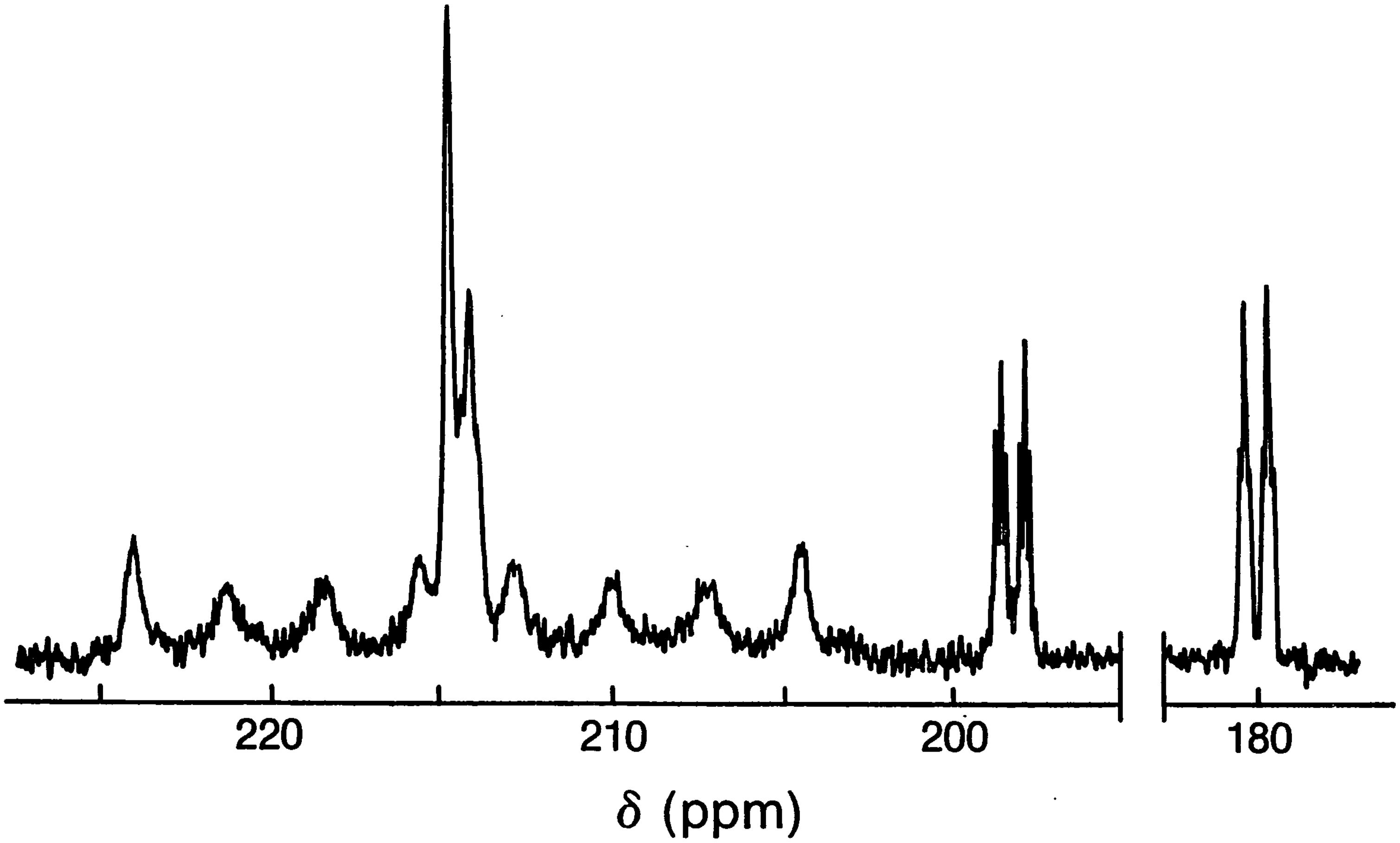
Although CO scrambling over both metals does not occur rapidly on the NMR time scale, addition of ^{13}CO results in enrichment of all carbonyls, indicating complete exchange under these conditions. Scrambling of the carbonyl groups might be expected to proceed through a tetracarbonyl species such as $[RhCo(CO)_4(dppm)_2]$, as was observed for the RhIr[26] and Ir^{27} analogues. Such a species would be reminiscent of $Co_2(CO)_8$, but has not been observed in this study. Instead, under an excess of CO reversible cleavage of 1 occurs slowly, over a 2-4 h period, as shown in eqn. 1. Under one atmosphere of CO at room temperature, the equilibrium still slightly favours the

$$[RhCo(CO)_3(dppm)_2] + 2CO \rightleftharpoons [Rh(CO)(dppm)_2]^+ + [Co(CO)_4]^- \quad (1)$$

dinuclear species, 1, with the ratio of monomer:dimer being about 1:1.25 as monitored by $^{31}P\{^1H\}$ and ^{13}C NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum for the mononuclear rhodium species displays a doublet at δ 22.0 ($^1J_{Rh\text{-}P}$ = 97.5 Hz) essentially as reported,[10] and the $^{13}C\{^1H\}$ NMR spectrum shows a doublet of quintets at δ 198.2 ($^1J_{Rh\text{-}C}$ = 72.4 Hz, $^2J_{P\text{-}C}$ = 14.1 Hz) for the rhodium monomer and an octet for $[Co(CO)_4]^-$, displaying coupling to ^{59}Co (I = 7/2, $^1J_{Co\text{-}C}$ = 281.3 Hz). Figure 2.1 shows the $^{13}C\{^1H\}$ NMR spectrum of a mixture of 1 and the mononuclear species in roughly equal proportions. The resonances at δ 180.4, 214.6, and 215.4 are due to 1, while the octet centered around δ 214.7 and the doublet at δ 198.2 are due to the teracarbonyl cobaltate ion and $[Rh(CO)(dppm)_2]^+$, respectively. In order to regenerate 1 after enrichment with ^{13}CO it is necessary to flush the system with argon for approximately 12 h, since reformation of 1 from the mononuclear fragments is slow. The reaction of 1 with CO confirms the lability of the Rh←Co bond, as previously observed by Geoffroy in an analogous system,[28] although reversible and facile transformation of the bridging dppm mode to the chelating one is highly unusual.

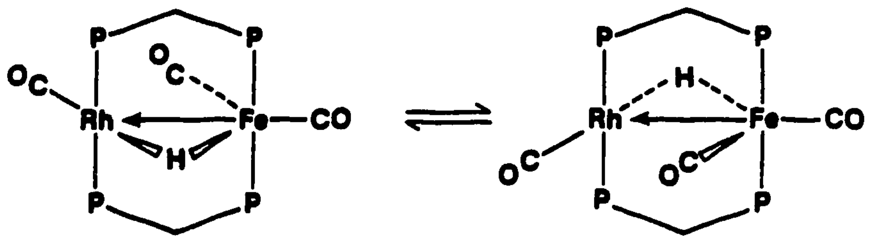
The compound $[RhCl(dppm)_2]$ also reacts with the $[HM(CO)_4]^-$ anions (M = Fe, Ru, Os) as described for $[Co(CO)_4]^-$, to yield the heterobinuclear complexes, $[RhMH(CO)_3(dppm)_2]$ (M = Fe (2), Ru (3), Os (4)). As with compound 1 the $^{31}P\{^1H\}$ NMR spectra of compounds 2-4 are typical of dppm-

Figure 2.1 $^{13}C\{^{1}H\}$ NMR spectrum of a mixture of $[RhCo(CO)_3(dppm)_2]$ and $[Rh(CO)(dppm)_2][Co(CO)_4]$



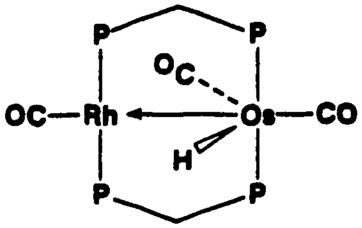
bridged heterobinuclear compounds containing Rh. Species **2**-**4** fall into two structural groups, with the Os complex differing subtly from the Ru and Fe species. This difference shows up clearly in the ^{1}H NMR spectra. For **2** the high-field region of the ^{1}H NMR spectrum displays a complex multiplet which can be shown by selectively decoupling the resonances for the Fe- and the Rh-bound phosphorus nuclei (P(Fe) and P(Rh), respectively), to be a triplet of doublet of triplets ($^{1}J_{Rh-H}$ = 24 Hz, $^{2}J_{P(Rh)-H}$ = 12 Hz, $^{2}J_{P(Fe)-H}$ = 37 Hz), corresponding to a hydride ligand which bridges both metals. The large coupling of the hydride ligand to both the Fe-bound and the Rh-bound phosphorus nuclei suggests that this hydride is strongly bound to both nuclei, and the relatively large coupling to Rh also supports a substantial interaction with this nucleus. By comparison, the isoelectronic complex, $[RhIr(H)(CO)_3(dppm)_2][BF_4]$[26] has a bridging hydride which appears to have a somewhat weaker association with Rh, having $^{1}J_{Rh-H}$ = 19.0 Hz and $^{2}J_{P(Rh)-H}$ = 9.3 Hz. The carbonyl stretches for **2** (1956, 1880, 1830 cm^{-1}) bear a strong resemblance to those of **1** and are again consistent with a mixed-valence formulation with the two lower stretches being associated with the Fe center. These data suggest that **2** has the structure shown, in which a trigonal-bipyramidal $[HFe(CO)_2(L)_2]^-$ center forms a dative bond to Rh(+I). This formulation is analogous to that of **1** except that the additional hydride ligand on Fe results in a TBP structure rather than the tetrahedral coordination of Co. Complex **2** is isoelectronic with the cationic species, $[MM'(H)(CO)_3(dppm)_2]^+$ (M, M' = Rh, Ir),[26,32,33] for which there appear to be two structural forms. The homobinuclear complexes[32,33] have doubly bridged A-frame structures in which the metals are bridged by a hydride and a carbonyl group, whereas the RhIr species[26] has a bridging hydride but only terminal carbonyls. Compound **2** appears to have this latter structure. The

$^{13}C\{^1H\}$ NMR spectrum of **2** displays only two carbonyl resonances at -40°C, at δ 225.5 (triplet, $J_{P\text{-}C}$ = 18 Hz) and δ 183.8 (doublet of triplets, $J_{P\text{-}C}$ = 14 Hz, $J_{Rh\text{-}C}$ = 72 Hz) integrating as 2:1, respectively. At -80°C the higher field, Rh-bound carbonyl resonance is unchanged whereas that at low field appears as a broad (*ca.* 70 Hz at half-height) unresolved peak. We suggest that compound **2** undergoes the fluxional process shown in which tunnelling of the hydride ligand between the metals results in exchange of the two Fe-bound carbonyl groups. Although the low-temperature limiting spectrum of **2** was not obtained, we see no evidence of a bridging carbonyl group, other than the low field ^{13}C shift of one of the cabonyls.



2

The structure of the Ru analogue (**3**) appears to be similar to that of **2**, as evidenced by the ^1H NMR spectrum, which displays a high-field multiplet at δ -9.3. Selective phosphorus decoupling experiments show that, as in **2**, the hydride ligand bridges both metals ($^1J_{Rh\text{-}H}$ = 22 Hz, $^2J_{P(Ru)\text{-}H}$ = 14 Hz, $^2J_{P(Rh)\text{-}H}$ = 12 Hz). The IR spectrum of **3** also resembles that of **2** . Although $^{13}C\{^1H\}$ NMR spectra have not been obtained for **3**, we suggest that it likely undergoes a fluxional process as observed for **2**. The osmium analogue (**4**) however, has a structure different from those of the Fe and Ru species, as shown by the ^1H NMR spectra. Compound **4** displays a triplet in the high-field region of the ^1H NMR spectrum at δ -7.4. Selective phosphorus-decoupling experiments show that this hydride resonance is coupled only to the Os-bound phosphorus nuclei, with no coupling to Rh or the Rh-bound phosphorus atoms observed. This species is therefore formulated as shown, with a terminal hydride ligand bound to Os. The isomer in which the hydride ligand is opposite the Rh←Os bond can be ruled out, since the $^{13}C\{^1H\}$ NMR spectrum displays three equal-intensity resonances, at δ 183.8 (triplet, $^2J_{P\text{-}C}$ = 13.6 Hz), δ 184.9 (triplet, $^2J_{P\text{-}C}$ = 13.6 Hz) and δ 197.6 (unresolved multiplet), showing that all carbonyl groups are inequivalent. This subtly different structure for **4** also gives rise to carbonyl stretches somewhat different from those of **2** and **3**, as shown in Table 2.1. Although for compound **4** an approximately trigonal-bipyramidal geometry for the Os center is shown (ignoring the Os→Rh bond), significant distortions may result through bending of the phosphines toward the sterically undemanding hydride ligand, to give a pseudo-tetrahedral geometry at Os, not unlike the geometry of Co in compound **1**. Such distortions are not uncommon among hydride complexes.[34]



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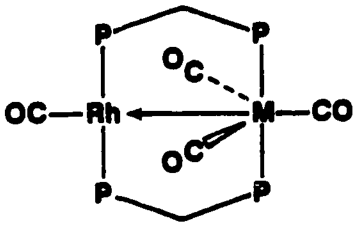
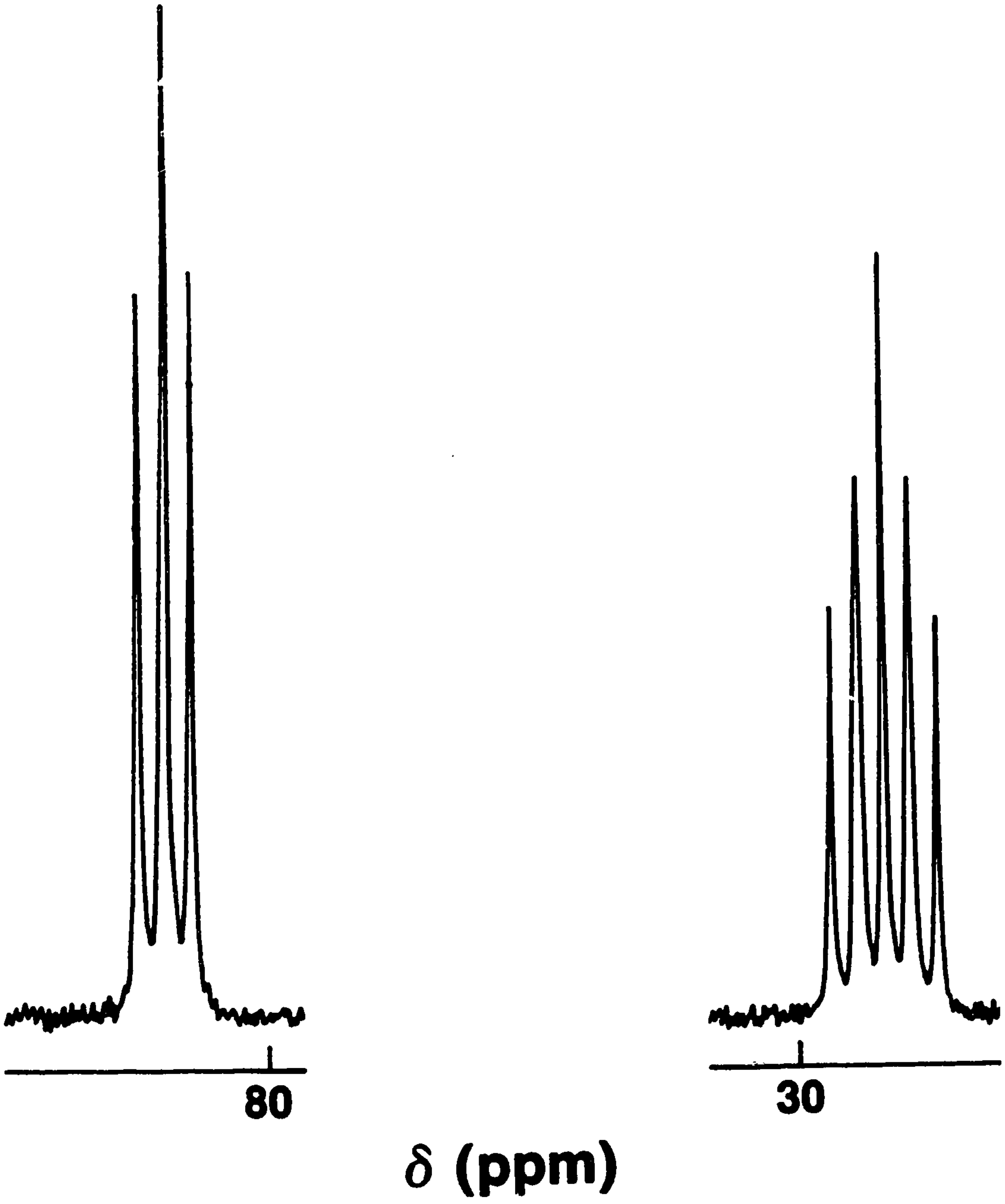
Compound **2** is extremely air sensitive in solution, having a half life of *ca.* 10 min after even brief exposure to air. Although the Ru complex is almost as air sensitive as the Fe analogue, the Os species is slightly more robust and can be handled in air for brief periods of time.

This chemistry can also be extended to Group VII, and the complexes $[RhM(CO)_4(dppm)_2]$ (M = Mn (5), Re (6)) have been prepared by an exactly analogous route utilizing the $[M(CO)_5]^-$ anions. Both products have rather similar $^{31}P\{^1H\}$ NMR (see Figure 2.2 for the spectrum of 5) and IR spectra (except for the lower field ^{31}P NMR chemical shift for the Mn-bound phosphorus nuclei compared to those on Re) consistent with the formulation shown. This formulation has been confirmed by the X-ray structure determinations of both species. Perspective drawings of both compounds are shown in Figures 2.3 and 2.4 with bond lengths and angles given in Tables 2.5-2.8. As noted earlier the metal carbonyl moieties are disordered, however only one set of disordered atoms C(2) and C(3), and one of each of the Rh and Mn (5) or Re (6) positions are shown in these drawings. Although this disorder involves only the metals and two carbonyl groups, it does in principle cast some doubt on the coordination geometries about the metals. However, the interpretation that is most chemically reasonable and the only one that agrees with the ^{13}C NMR data, which clearly indicates that only one of the four carbonyls is bound to Rh (*vide infra*), is that in which Rh has a distorted square planar arrangement and the Mn and Re atoms have trigonal bipyramidal coordinations. The $[M(CO)_3L_2]^-$ (M = Mn, Re) moieties are then



(M = Mn (5), Re (6))

Figure 2.2 $^{31}P\{^1H\}$ NMR Spectrum of $[RhMn(CO)_4(dppm)_2]$



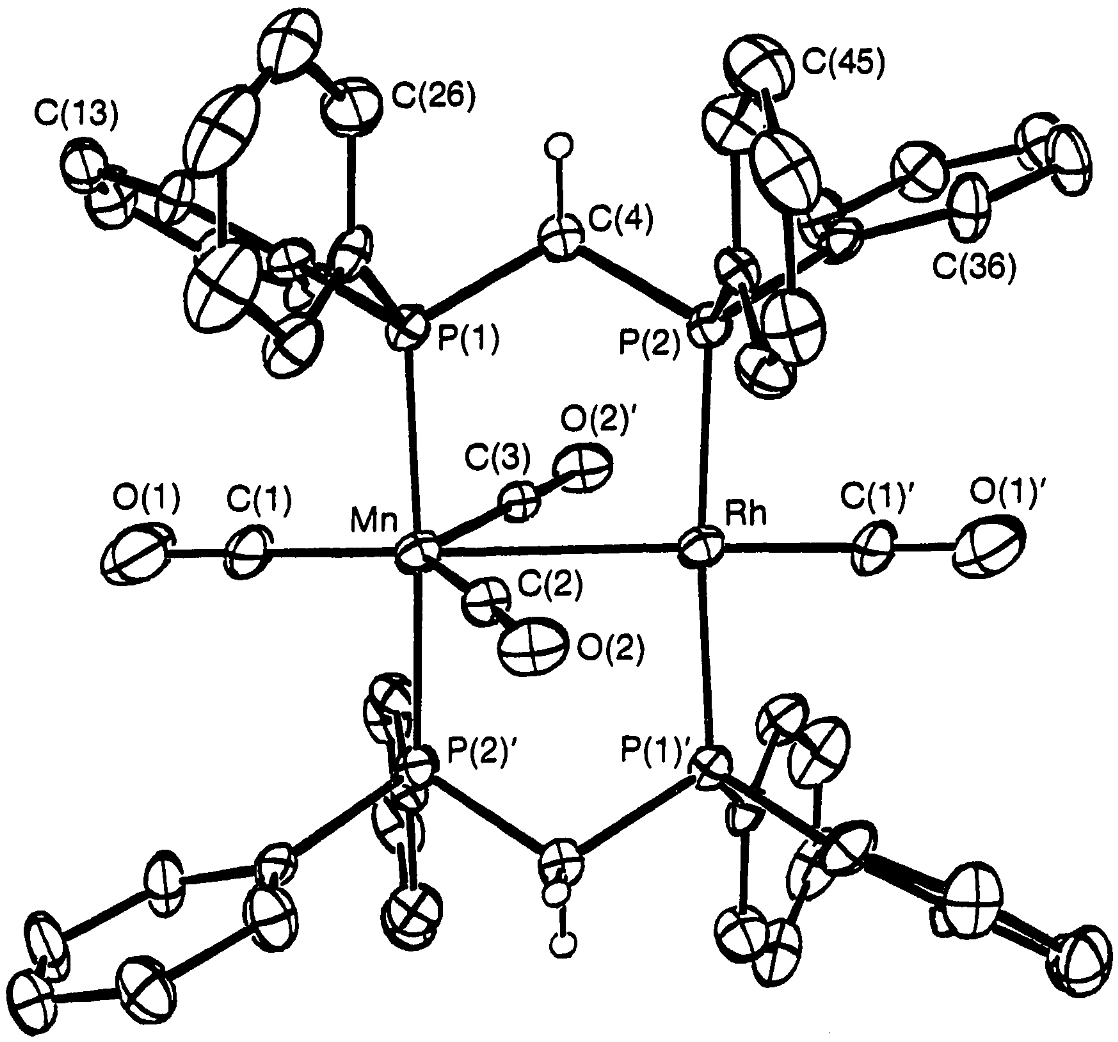


Figure 2.3 A perspective view of [RhMn(CO)$_4$(dppm)$_2$] (5) showing the numbering scheme. Thermal parameters are shown at the 20% level except for hydrogens, which are shown artificially small for the methylene groups but are not shown for the phenyl groups. Although the molecule is inversion disordered only one of the two positions for each of C(2) and C(3) is shown and the two disordered Rh/Mn positions are identified as assumed for the ordered structure.

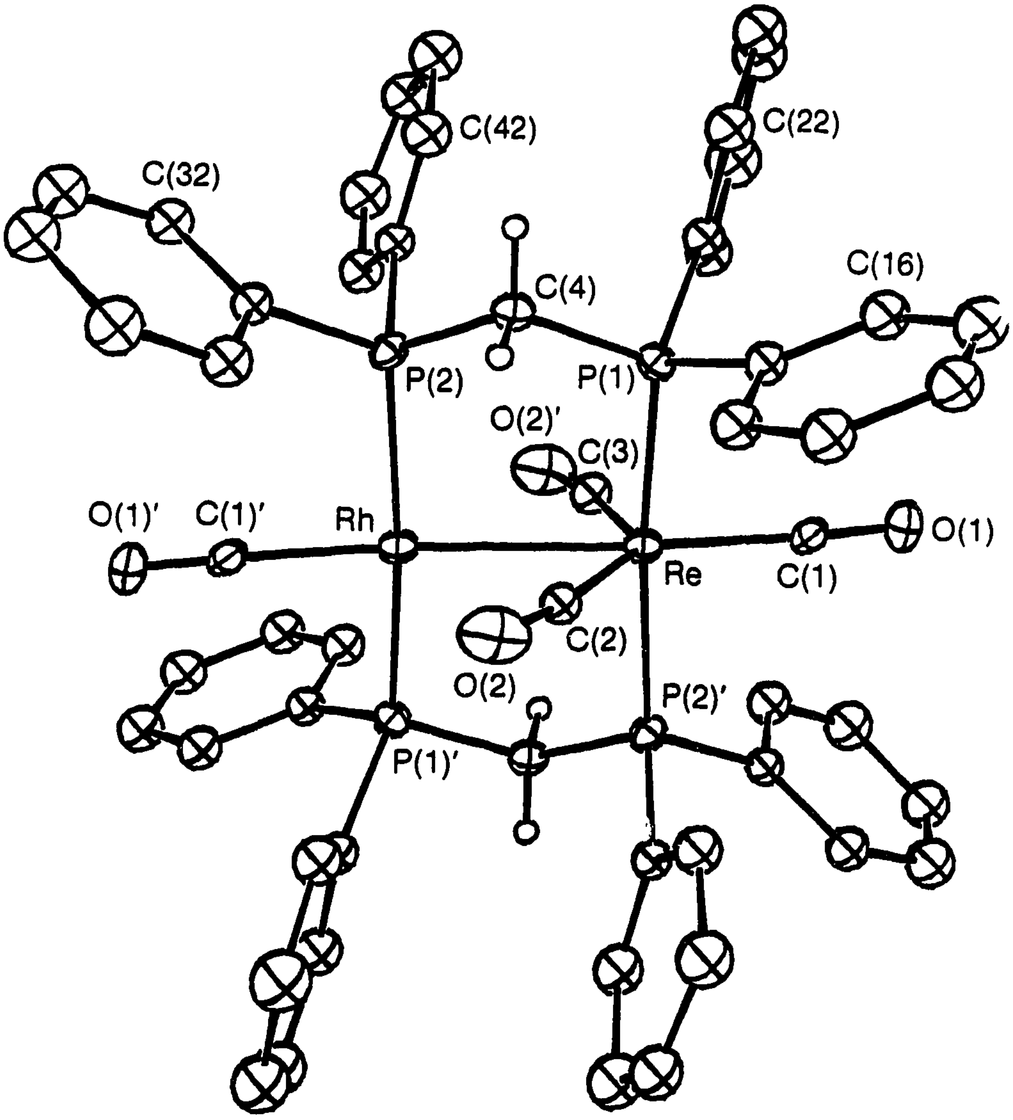


Figure 2.4 A perspective view of [RhRe(CO)$_4$(dppm)$_2$] (6). Thermal parameters and numbering are analogous to that described in Figure 2.3.

Table 2.5 Selected Bond Lengths (Å) for [RhMn(CO)$_4$(dppm)$_2$] (5)

(a) Bonded

Atoms	Distance[a]
Rh-Mn[b]	2.8428(8)
Mn-P(1)[c]	2.275(1)
Mn-P(2)'	2.263(1)
Mn-C(1)[c]	1.737(5)
Mn-C(2)	1.806(8)
Mn-C(3)	1.936(7)
P(1)-C(4)	1.819(4)
P(1)-C(11)	1.833(4)
P(1)-C(21)	1.829(4)
P(2)-C(4)	1.838(4)
P(2)-C(31)	1.823(4)
P(2)-C(41)	1.834(4)
O(1)-C(1)	1.137(6)
O(2)-C(2)	1.188(8)
O(2)'-C(3)	1.289(7)

(b) Non-Bonded

Atoms	Distance
P(1)-P(2)	2.994(1)
Rh-C(2)	2.707(8)
Rh-C(3)	2.475(7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Although the Rh and Mn positions are disordered the atoms are labelled as in Figure 2.3.

[c] Because of disorder Mn-P(1) = Rh-P(1)', Mn-P(2)' = Rh-P(2) and Rh-C(1)' = Mn-C(1).

Table 2.6 **Selected Angles (deg) for [RhMn(CO)$_4$(dppm)$_2$] (5)**

Rh-Mn-P(1)[a]	92.10(3)	Mn-P(1)-C(4)	115.5(1)
Rh-Mn-P(2)'	91.60(3)	Mn-P(1)-C(11)	110.9(1)
Rh-Mn-C(1)	175.6(2)	Mn-P(1)-C(21)	119.1(1)
Rh-Mn-C(2)	67.0(2)	C(4)-P(1)-C(11)	103.5(2)
Rh-Mn-C(3)	58.9(2)	C(4)-P(1)-C(21)	103.8(2)
P(1)-Mn-P(2)'	174.37(4)	C(11)-P(1)-C(21)	102.3(2)
P(1)-Mn-C(1)	87.5(2)	Rh-P(2)-C(4)	114.4(1)
P(1)-Mn-C(2)	96.9(2)	Rh-P(2)-C(31)	113.5(1)
P(1)-Mn-C(3)	84.3(2)	Rh-P(2)-C(41)	116.4(1)
P(2)-Mn-C(1)	88.5(2)	C(4)-P(2)-C(31)	102.6(2)
P(2)-Mn-C(2)	88.4(2)	C(4)-P(2)-C(41)	104.8(2)
P(2)-Mn-C(3)	94.0(2)	C(31)-P(2)-C(41)	103.8(2)
C(1)-Mn-C(2)	117.4(3)	Mn-C(1)-O(1)	179.0(5)
C(1)-Mn-C(3)	116.8(3)	Mn-C(2)-O(2)	174.9(6)
C(2)-Mn-C(3)	125.8(3)	Mn-C(3)-O(2)'	178.2(6)

[a] Labelling is as shown in Figure 2.3.

Table 2.7 Selected Bond Lengths (Å) for $[RhRe(CO)_4(dppm)_2]\bullet THF$ (6)

(a) Bonded

Atoms	Distance[a]
Re-Rh[b]	2.7919(6)
Re-P(1)	2.331(1)
Re-P(2)'	2.343(1)
Re-C(1)	1.936(7)
Re-C(2)	1.99(1)
Re-C(3)	1.97(1)
P(1)-C(4)	1.833(6)
P(1)-C(11)	1.834(6)
P(1)-C(21)	1.820(6)
P(2)-C(4)	1.829(6)
P(2)-C(31)	1.831(6)
P(2)-C(41)	1.806(6)
O(1)-C(1)	1.119(7)
O(2)-C(2)	1.31(1)
O(2)'-C(3)	1.18(1)

(b) Non-Bonded

P(1)-P(2)	3.013(2)
Rh-C(2)	2.58(1)
Rh-C(3)	2.88(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Labelling is as in Figure 2.4.

Table 2.8 Selected Angles (deg) for [RhRe(CO)$_4$(dppm)$_2$•THF (6)

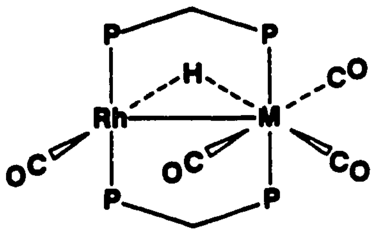
Rh-Re-P(1)[a]	93.36(4)	Re-P(1)-C(11)	112.2(2)
Rh-Re-P(2)'	91.60(4)	Re-P(1)-C(21)	119.2(2)
Rh-Re-C(1)	172.5(2)	C(4)-P(1)-C(11)	102.5(3)
Rh-Re-C(2)	62.6(3)	C(4)-P(1)-C(21)	104.1(3)
Rh-Re-C(3)	72.0(4)	C(11)-P(1)-C(21)	103.3(3)
P(1)-Re-P(2)'	170.29(5)	Rh-P(2)-C(4)	111.8(2)
P(1)-Re-C(1)	86.7(2)	Rh-P(2)-C(31)	117.4(2)
P(1)-Re-C(2)	84.0(3)	Rh-P(2)-C(41)	117.0(2)
P(1)-Re-C(3)	100.3(4)	C(4)-P(2)-C(31)	101.4(3)
P(2)'-Re-C(1)	89.6(2)	C(4)-P(2)-C(41)	105.5(3)
P(2)'-Re-C(2)	90.9(3)	C(31)-P(2)-C(41))	101.9(3)
P(2)'-Re-C(3)	89.3(4)	Re-C(1)-O(1)	177.3(5)
C(1)-Re-C(2)	124.8(4)	Re-C(2)-O(2)	174.6(9)
C(1)-Re-C(3)	100.6(4)	Re-C(3)-O(2)'	167.(1)
C(2)-Re-C(3)	134.5(5)	P(1)-C(4)-P(2)	110.8(3)
Re-P(1)-C(4)	113.8(2)		

[a] Labelling is as in Figure 2.4.

regarded as functioning as pseudo-halide groups. The alternate description, in which both metals are considered to be in the zero oxidation state and joined by a conventional Rh-M covalent bond, would be expected to give rise to octahedral configurations at Mn and Re. Although the geometries about Mn and Re are clearly trigonal bipyramidal (ignoring the M→Rh dative bonds, which can be described as a donation of two electrons from the filled d_{xy} and $d_{x^2-y^2}$ orbitals of the TBP, anionic Mn and Re fragments to the cationic Rh unit.), that about Re is more distorted than that about Mn, with a compressed C(1)-Re-C(3) angle of 100.6(4)° and an expanded C(2)-Re-C(3) angle of 134.5(5)°. By contrast the angles between the carbonyl ligands in the Mn complex are close to the idealized values, ranging from 116.8(3)° to 125.8(3)°. This Mn complex is very reminiscent of the isoelectronic species $[PdMnBr(CO)_3(dppm)_2]$ which has a similar structure.[35] The slight bending of the carbonyl on Re at C(3) is probably not chemically significant, but more likely results from the poorly determined carbon position of this half-occupancy atom and from the single position observed for O(2) which probably in fact represents two closely spaced but unresolved half-occupancy oxygen atoms. The disorder in these compounds negates any detailed comparison of individual metal-ligand bond lengths within each structure, although comparison of the average metal-phosphorus distances is still meaningful. Not unexpectedly the metal-phosphorus distances in the Re complex (2.331(1), 2.343(1)Å) are longer than those in the Mn species (2.263(1), 2.275(1)Å) owing to the larger covalent radius of Re. But surprisingly the Rh-Re distance of 2.7919(6)Å is <u>shorter</u> than the Rh-Mn distance (2.8428(8)Å) indicating a stronger Rh-Re bond. The stronger dative bond involving Re is consistent with its more basic character compared to Mn, as exemplified by the basicities of the $M(CO)_5^-$ (M = Mn, Re) anions,[36] and is again supportive of our mixed-valence formulation. Both distances are significantly shorter than the intraligand P(1)-P(2) distances (2.994(2)Å) (**5**), 3.013(2)Å (**6**)) indicating substantial attraction of the adjacent metal centers. As noted, the coordination about Rh in both complexes is close to square planar as expected for Rh(I) species. Although the carbonyls, C(2)O(2) and C(3)O(2)', in each compound are in positions to be considered as semibridging, and are certainly well within the sum of the van der Waals radii, the contacts involving Rh and these carbonyl carbons (2.475(8), 2.707(8)Å (**5**); 2.58(1), 2.88(1)Å (**6**)) are not unusually short.[37] In addition the essentially linear M-C-O (M = Mn, Re) linkages suggest that interactions of these groups with Rh is not strong. We therefore tend not to consider these groups as semibridging but rather as being forced close to Rh by virtue of the TBP geometries at Mn and Re. This view is supported by the lack of Rh-coupling for these carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectra (*vide infra*).

The reaction of compounds **5** or **6** with ^{13}CO results in enrichment of all carbonyl positions. This facile scrambling over both metals apparently occurs *via* a pentacarbonyl species [$RhM(CO)_5(dppm)_2$] since in the absence of excess CO scrambling in **5** and **6** is not facile at room temperature. For example, raising the temperature of a solution of **6** from -40°C to 30°C causes the carbonyl resonances at δ 217.6 (triplet, $^2J_{P\text{-}C}$ = 9 Hz, 2C), 206.3 (triplet, $^2J_{P\text{-}C}$ = 10 Hz, 1C) and 181.5 (doublet of triplets, $^1J_{Rh\text{-}C}$ = 71 Hz, $^2J_{P\text{-}C}$ = 14 Hz, 1C) to broaden considerably. However even at 30°C coalescence has not occurred and all three resonances are still distinct. The proposed pentacarbonyl species for Mn has not been observed, however the Re analogue, [$RhRe(CO)_5(dppm)_2$] has been characterized in solution (υ(CO): 2010, 1988, 1964, 1918, and 1892 cm^{-1}) as described in Chapter 3 and also as reported,[38] although it loses the additional carbonyl on Rh in the absence of a CO atmosphere. This species is assumed to have a structure analogous to that of the isoelectronic species, $[IrOs(CO)_5(dppm)_2]^+$ which is related to 6 by an additional carbonyl on Ir, which then has a trigonal bipyramidal coordination.[39]

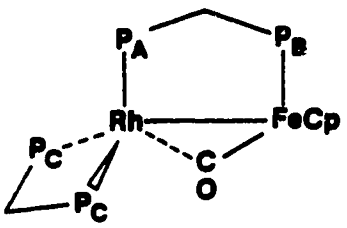
Treatment of $[RhCl(dppm)_2]$ with the $[HM(CO)_5]^-$ (M = Cr, W) anions, yields the analogous mixed-metal complexes involving these group 6 metals, $[RhM(\mu\text{-}H)(CO)_4(dppm)_2]$ (M = Cr (7), W (8)). The $^{31}P\{^1H\}$ NMR spectra clearly establish these species as dppm-bridged mixed-metal complexes involving Rh, and the IR spectra show the expected four carbonyl stretches (Table 2.1). These carbonyl stretches are similar to those of the isoelectronic $[RhReH(CO)_4(dppm)_2][BF_4]$ (ν(CO): 2045, 2000, 1935, 1908 cm^{-1}) discussed in Chapter 3 and as we have reported,[38] except that the cationic species shows the expected shifts to higher frequency. We therefore formulate the structures of 7 and 8 as being like that determined for the above cationic RhRe species. In these structures the geometries about Cr and W are presumed to be pseudo octahedral in which the Rh-H bond can be considered as occupying the sixth coordination site in each complex. The ^1H NMR spectra for these species strongly support these structural formulations displaying complex multiplets



(M = Cr (7), W (8))

at δ -14.8 (8) and -10.5 (7) . The selective decoupling experiments unambiguously show that these hydride ligands bridge the metals, displaying coupling to Rh and to all phosphorus nuclei. In addition, compound 8 also displays coupling to ^{183}W ($^1J_{W\text{-}H}$ = 49 Hz).

The chemistry described above has also been extended to include carbonylate anions which also contain the cyclopentadienyl group. Therefore the reaction of [RhCl(dppm)$_2$] with [FeCp(CO)$_2$]$^-$ yields the compound [RhFeCp(CO)(dppm)$_2$] (9). However, as shown in Figure 2.5, the $^{31}P\{^1H\}$ NMR spectrum suggests a structural type much different than for the previously described species. Three resonances are observed in a 1:1:2 ratio, respectively; the resonance labelled P_A, at δ 34.8, appears as a doublet of doublets of triplets ($^1J_{Rh\text{-}P}$ = 160 Hz, $^2J_{P_A\text{-}P_B}$ = 136 Hz, $^2J_{P_A\text{-}P_C}$ = 16 Hz), the P_B resonance at δ 86.9 is a doublet with coupling only to P_A, and the P_C resonance at δ −19.2 is a doublet of doublets ($^1J_{Rh\text{-}P_C}$ = 137 Hz). The very low carbonyl stretch (1679 cm^{-1}) indicates that this group must bridge the two metals. Based on these data and on the structure of the closely related species [PtMoCp(CO)$_2$(dppm)$_2$]$^+$,[40] we propose the structure shown in which one dppm group remains chelating on Rh and one bridges the two metals. This structure is in agreement with the $^{31}P\{^1H\}$ NMR data which show P_A and



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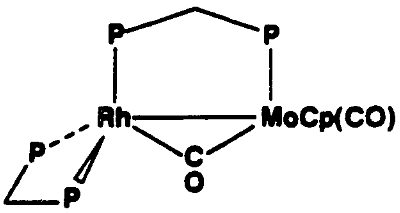

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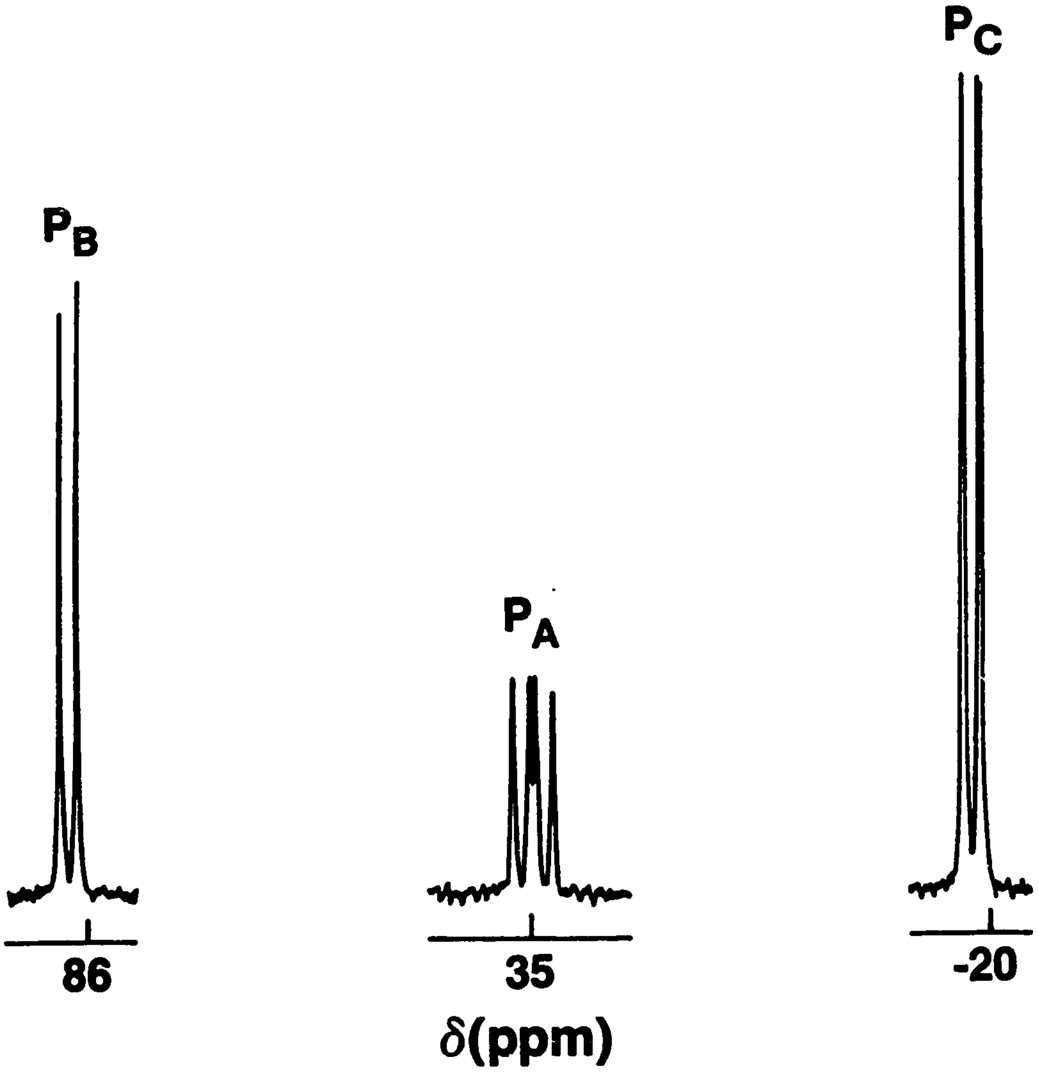
Figure 2.5 The $^{31}P\{^1H\}$ NMR spectrum at 22°C for [RhFeCp(CO)(dppm)$_2$] (9).



both P_C nuclei bound to Rh and coupled to each other, and P_B only coupled to P_A. Based on an assumed piano-stool geometry at Fe, we would have expected to observe two different resonances for each end of the chelating diphosphine (P_C), however even at -80°C only one resonance is observed.

The Rh analogue of the above PtMo complex[40] can also be prepared by reaction of $[RhCl(dppm)_2]$ with $[MoCp(CO)_3]^-$, yielding $[RhMoCp(CO)_2(dppm)_2]$ (**10**). The carbonyl stretches for **10** (1684, 1960 cm^{-1}) are consistent with the structure shown (for the $[PtMo(CO)_2Cp(dppm)_2]^+$ cation carbonyl stretches near 1800 and 1870 cm^{-1} were reported). This RhMo species displays temperature dependent fluxionality as shown by the $^{31}P\{^1H\}$ NMR spectra which appear as a broad (*ca.* 400 Hz) unresolved resonance at δ -22.1, at ambient temperature, as a doublet at δ -22.1 ($^1J_{Rh\text{-}P}$ = 108 Hz) at -40°C, and as three broad resonances having intensity ratios of 2:1:1 at δ -28.1 (2P), -31.2 (1P), -34.8 (1P), respectively at -105°C. The low temperature limiting spectrum that is expected, based on the structure shown, was not observed, although clearly, based on this structure, the two ends of the chelating phosphine must be inequivalent. Again, this proposed structure is very similar to that observed for the Pt analogue,[40] except that we suggest that the carbonyl that was semibridging in the Pt complex is decidedly bridging in our Rh species; this proposal is consistent with the lower carbonyl stretch observed for the Rh species and with the greater tendency of carbonyls to bridge second-row than third-row metals.

Conclusions

The reaction of $[RhCl(dppm)_2]$ with metal carbonylate anions has been shown to be a convenient and general route to a series of dppm-bridged heterobimetallic complexes containing Rh as one of the metals. In the case of anions which contain only carbonyl or carbonyl and hydride ligands, both dppm groups adopt a bridging configuration to yield complexes, all of which contain a coordinatively unsaturated square-planar Rh(I) center and coordinative saturation at the adjacent metal. It appears that these heterobimetallic complexes are best formulated as containing M→Rh dative bonds. Using the cyclopentadienyl-containing anions, $[FeCp(CO)_2]^-$ and $[MoCp(CO)_3]^-$, results in only one of the dppm groups adopting a bridging configuration while the other remains chelating on Rh.

Supplementary Material Available: anisotropic thermal parameters, additional bond lengths and angles, and hydrogen atom parameters (9 pages); listings of the observed and calculated structure factors (35) pages. All Suplementary Data are available from M. Cowie upon request.

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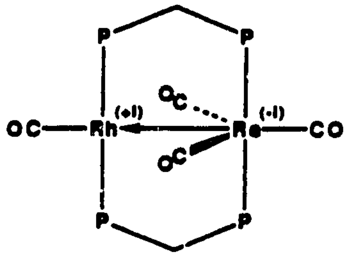
Chapter 3

Oxidative-addition reactions Involving the Mixed-Valence Complex $[RhRe(CO)_4(Ph_2PCH_2PPh_2)_2]$: Influence of the Coordinatively Unsaturated Rh(+I) Center on the Saturated Re(-I) Center.†

Introduction

Oxidative-addition reactions are of fundamental importance in organometallic chemistry,[1,2] and offer additional challenges in polynuclear complexes owing to the possible involvement of the adjacent metals[3-6], as discussed in Chapter 1. As part of an investigation into the reactivity of low-valent diphosphine-bridged heterobinuclear complexes,[7-10] we have undertaken a study of the oxidative-addition and related reactions involving the mixed-metal species $[RhRe(CO)_4(dppm)_2]$ (**1**). The structural characterization of **1**, as discussed in Chapter 2, led to its formulation as a mixed-valence complex in which a donor-acceptor bond links the



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† A version of this chapter has been published. Antonelli, D.M. and Cowie, M. *Inorg. Chem.* 1990, *29*, 4039-4035.

coordinatively unsaturated Rh(+I) center and the saturated Re(-I) center.[11] Whether compound **1** is formulated as a Rh(I)/Re(-I) species, as suggested, or as a more conventional Rh(0)/Re(0) species, it was felt that the low oxidation states of the metals and the coordinative unsaturation at Rh should make the complex prone to oxidative-addition reactions.

We chose to focus our studies on this Rh/Re complex, rather than any of the other heterobimetallic species discussed in Chapter 2, because some of the oxidative-addition reactions of the dirhenium analogue [$Re_2(CO)_6(dppm)_2$][12] had already been investigated, as mentioned in Chapter 1, and it was of interest to investigate the changes in reactivity incurred by the exchange of one of the saturated Re centers in the dirhenium complex for an unsaturated Rh center. Thus, the object of these studies is to establish the influence of each metal on the other, and in particular to establish whether the coordinatively unsaturated Rh(+I) center would increase the reactivity of the otherwise inert $Re(CO)_3P_2^-$ moiety. The related dirhenium complex [$Re_2(CO)_6(dppm)_2$], in which <u>both</u> metals are coordinatively saturated, had been shown to be rather inert, requiring refluxing at 172 ° C for the oxidative-addition reactions of H_2 and phenylacetylene to occur.[12]

Experimental Section

General Experimental Conditions

All solvents were dried and distilled under argon before use. Tetrahydrofuran was dried and deoxygenated with Na/Ph_2CO, as were Et_2O and Hexane. Dichloromethane was dried over P_2O_5. Prepurified Argon was used without further treatment. Carbon monoxide and dihydrogen were used as received. Hexafluoro-2-butyne was used as received from SCM Specialty Chemicals and HCl was used as received from Matheson. Hydrated Rhodium (III) chloride was obtained from Johnson Matthey Ltd. and $Re_2(CO)_{10}$ was purchased from Strem and sublimed before use. Dimethyl acetylenedicarboxylate (DMA) was used as received from Aldrich. All other chemicals were also used as received without further purification. Compound **1**, $[RhRe(CO)_4(dppm)_2]$ (dppm = bis(diphenylphosphino) methane) was prepared as described in Chapter 2., and iodobenzene dichloride was prepared as previously described.[13]

All NMR experiments were conducted on a Bruker AM-400 spectrometer operating at 162.0 MHz for ^{31}P, 400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C. Unless otherwise noted, all $^{13}C\{^{1}H\}$ NMR spectra were obtained in CD_2Cl_2 at -40 ° C except for compound **7**, which was run in d_8-toluene at that temperature. In all cases an internal deuterated solvent lock was used. In general, deuterated solvents were dried over P_2O_5, freeze-pump-thaw degrassed and vacuum distilled into the 5mm NMR tube containing the sample, which was then flame sealed.

Infrared spectra were recorded on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr plates) or solutions (KCl cell windows, 0.5 mm path length). Elemental analyses were performed by the microanalytical service within the department.

Preparation of Compounds

a) $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]\cdot H_2O$ (2).

The complex, $[RhRe(CO)_4(dppm)_2]$ (50 mg, 42.8 μmol), was dissolved in 5 mL of CH_2Cl_2, and $HBF_4 \cdot Et_2O$ (6.75 μL, 47.1 μmol) was added by syringe. The solution turned a lighter shade of yellow and was stirred for 1/2 h. Removal of the solvent and recrystallization of the light yellow product from CH_2Cl_2/Et_2O yielded 52 mg (96%). The one equiv of H_2O apparently originated from wet $HBF_4 \cdot Et_2O$. Anal. Calcd. for $C_{54}H_{47}BF_4O_5P_4ReRh$: C, 50.84; H, 3.71. Found: C, 51.06; H, 3.98. Spectral parameters for the compounds prepared are found in Table 3.1.

b) $[RhRe(CO)_3(\mu\text{-}H)_2(dppm)_2]$ (3).

Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of THF and stirred under 1 atm of H_2. The yellow solution gradually turned dark orange and, after 3 h, a fine yellow precipitate began to settle out. The solution was stirred for an additional 3 h after which the THF was removed *in vacuo*. The yellow residue was recrystallized from CH_2Cl_2/Et_2O to yield 40 mg (82%) of product (3), which is pale yellow in color. Anal. Calcd. for $C_{53}H_{46}O_3P_4ReRh$: C, 55.65; H, 4.05. Found: C, 55.23; H, 4.39.

c) $[RhRe(CO)_3(\mu\text{-}Cl)_2(dppm)_2]$ (4).

Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of THF. Iodobenzene dichloride (11.8 mg, 42.8 μmol) in 50 mL of THF was added by cannula. The solution became slightly lighter in color and, after 2 h, a light yellow precipitate began to settle out. After an additional 2 h the product was collected by filtration and washed several times with Et_2O (5 x 5 mL). Yield = 48 mg (93%). Anal. Calcd. for $C_{53}H_{44}Cl_2O_3P_4ReRh$: C, 52.49; H, 3.66; Cl, 5.85. Found: C, 52.28; H, 3.94; Cl, 6.22.

Table 3.1 Spectral Data[a]

		NMR	
Compound	IR,cm^{-1}	$\delta(^{31}P\{^1H\})^d$	$\delta(^1H)^e$
(2) [RhRe(CO)$_4$(μ-H)(dppm)$_2$] [BF$_4$]	2046 (m), 2003 (s), 1937 (s), 1908 (s)^b; 2010 (s), 1945 (s), 1930 (s)^c	24.5 (dm, $^1J_{Rh\text{-}P}$ = 112 Hz), 3.4 (m)	4.02 (bs, 4 H), -11.94 (m, 1 H, $^1J_{Rh\text{-}H}$ = 22.5 Hz, $^2J_{P(Re)\text{-}H}{}^f$ = 7.0 Hz, $^2J_{P(Rh)\text{-}H}{}^f$ = 12.4 Hz)
(3) [RhRe(CO)$_3$(μ-H)$_2$(dppm)$_2$]	1925 (s), 1838 (s)^b; 1947 (m), 1916 (s), 1838 (vs) ^{c}	31.8 (dm, $^1J_{Rh\text{-}P}$ = 141 Hz), 18.2 (m)	3.89 (bs, 4 H), -8.21 (m, 2 H, 1JRh-H = 25.1 Hz, $^2J_{P(Re)\text{-}H}{}^f$ = 9.8 Hz, $^2J_{P(Rh)\text{-}H}{}^f$ = 10.0 Hz
(4) [RhRe(CO)$_3$(μ-Cl)$_2$(dppm)$_2$]	1967(s), 1905(s), 1820(s)^b		
(5) [RhRe(CO)$_3$(μ-H)(μ-Cl)(dppm)$_2$]	1960(m), 1929(s), 1853(s)^c	23.3 (dm, $^1J_{Rh\text{-}P}$ = 120 Hz), 9.8 (m)	4.32 (m, 2 H), 3.83 (m, 2 H), -9.76(m, 1 H, 1JRh-H = 24 Hz, $^2J_{P(Re)\text{-}H}{}^f$ = 8.1 Hz, $^2J_{P(Rh)\text{-}H}{}^f$ = 12 Hz)
(6) [RhRe(CO)$_5$(dppm)$_2$]	2010 (s), 1988 (s), 1964 (s), 1918 (vs), 1892 (vs)^c	11.4 (dm, $^1J_{Rh\text{-}P}$ = 152 Hz), -1.6 (m)	
(7) [RhRe(CO)$_4$(μ-DMA)(dppm)$_2$]	2001 (m), 1949 (s), 1860 (s), 1831 (w) ^{b}; 1985 (m), 1947 (s), 1863 (m)^c	20.7 (dm, $^1J_{Rh\text{-}P}$ = 155 Hz), 2.0 (m)	4.58 (m, 2 H), 3.19 (s, 3 H), 2.64 (m, 2 H), 1.70 (s, 3 H)

Table 3.1 (continued)

Compound	IR, cm^{-1} [b]	NMR $\delta(^{31}P\{^1H\})$ [d]	NMR $\delta(^1H)$ [e]
(8) [RhRe(CO)$_4$(μ-HFB)(dppm)$_2$]	1987 (m), 1955 (s), 1879 (m)[c] 2005 (m), 1953 (s), 1868 (s), 1839 (w)[b]	15.9 (dm, $^1J_{Rh-P}$ = 144Hz), 1.2 (m)	4.14 (m, 2 H), 3.18 (m, 2 H)
(9) [RhRe(CO)$_3$(μ-DMA)(dppm)$_2$]	2000 (m), 1891 (m), 1811 (s)[c]	17.4 (dm, $^1J_{Rh-P}$ = 124Hz), 7.8 (m)	3.71 (m, 2 H), 3.50 (m, 2 H), 2.70 (s, 3 H), 2.00 (s, 3 H),
(10) [RhRe(CO)$_3$(μ-HFB)(dppm)$_2$]	2009 (m), 1895 (m), 1816 (s)[c]	15.4 (dm, $^1J_{Rh-P}$ = 122Hz), 5.1 (m)	3.73 (m, 2 H), 3.47 (m, 2 H)

[a] Abbreviations used: IR; w = weak, m = medium, s = strong: NMR; m = multiplet, dm = doublet of multiplets, s = singlet, bs = broad singlet. $^{13}C\{^1H\}$ NMR spectral data are given in the text. Unless otherwise noted these were obtained at -40°C in CD_2Cl_2, except for compound 7, which was obtained in d_8-toluene. Chemical shifts are referenced to TMS.

[b] Nujol mull in KBr plates.

[c] CH_2Cl_2 solution in KCl cells.

[d] Vs 85% H_3PO_4, -40°C in CD_2Cl_2 solvent.

[e] Vs TMS, -40°C in CD_2Cl_2 solvent; resonances for the dppm phenyl hydrogens are not given.

[f] $J_{P(M)-H}$ is the coupling constant between the phosphorus nuclei bound to M and hydrogen.

d) [RhRe(CO)$_3$(μ-H)(μ-Cl)(dppm)$_2$] (5).

Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of CH_2Cl_2. Anhydrous HCl (0.94 mL, 42.8 μmol) was added by gas-tight syringe. The yellow solution immediately turned orange and was stirred for an additional 15 min. The solvent was then removed *in vacuo* and the resulting orange residue was recrystallized from CH_2Cl_2/Et_2O to give an orange powder. Yield = 45 mg (92%). Anal. Calcd. for $C_{53}H_{45}ClO_3P_4ReRh$: C, 54.04; H, 3.81; Cl, 3.10. Found: C, 53.79; H, 4.26; Cl, 3.47.

e) [RhRe(CO)$_5$(dppm)$_2$] (6).

Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of CH_2Cl_2 and CO gas was vigorously bubbled through the solution for 5 min, causing the solution to turn from yellow to orange. The rate was then slowed to approximately 0.2 mL/second for 20 min. At this point the IR spectrum of the sample, maintained under a CO atmosphere, showed complete conversion to the pentacarbonyl.

f) [RhRe(CO)$_4$(μ-DMA)(dppm)$_2$] (7).

Compound 1 (50 mg, 42.8 μmol) was dissolved in 2 mL of CH_2Cl_2. Dimethyl acetylenedicarboxylate (5.2 μL, 42.8 μmol) was then added. A yellow precipitate formed instantly. The flask was then purged with CO to prevent formation of 9 and 15 mL of Et_2O was then added to ensure complete precipitation of the yellow product. The solid was collected and washed with 3 x 5 mL Et_2O. Yield = 46 mg (82%). Anal. Calcd. for $C_{60}H_{50}O_8P_4ReRh$: C, 54.93; H, 3.81. Found: C, 55.20; H, 4.17.

g) [RhRe(CO)$_4$ (μ -HFB)(dppm)$_2$] (8).

Compound 1 (50 mg, 42.8 μmol) was dissolved in 2 mL of CH_2Cl_2 to which excess HFB (20 mL) was added. After 5 min of stirring, CO was rapidly passed over the solution and a yellow precipitate began to form. Addition of 10 mL of Et_2O, while maintaining the purge of carbon monoxide, completed the precipitation. The product was collected by filtration under CO and washed with 3 x 10 mL of Et_2O to yield 40 mg (70%) of a light yellow powder. Anal. Calcd. for $C_{58}H_{44}F_6O_4P_4ReRh$: C, 52.30; H, 3.30; F, 8.56. Found: C, 52.49; H, 3.81; F, 8.77.

h) [RhRe(CO)$_3$ (μ -DMAD)(dppm)$_2$] (9).

Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of THF and DMA (5.2 μL, 42.8 mmol) was added by syringe. The yellow solution instantly turned dark maroon and was then refluxed for 1/2 h. The solvent was removed *in vacuo* and recrystallization from CH_2Cl_2/Pentane yielded 46 mg (86%) of an blood-red complex, (9). Anal. Calcd. for $C_{59}H_{50}O_7P_4ReRh$: C, 55.14; H, 3.89. Found: C, 54.57; H, 4.11.

i) [RhRe(CO)$_3$(μ-HFB)(dppm)$_2$] (10).

Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of CH_2Cl_2. Excess (20 mL) hexafluorobutyne was then added by syringe. The light yellow solution quickly turned dark red and was then stirred for an addition 1/2 h. The solvent was removed *in vacuo* and the red residue recrystallized from CH_2Cl_2/Et_2O. Yield = 46 mg (83%). Anal. Calcd. for $C_{57}H_{44}F_6O_3P_4ReRh$: C, 52.51; H, 3.37; F, 8.74. Found: C, 52.83; H, 3.66; F, 8.99.

X-Ray Data Collection

Yellow crystals of $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]\cdot H_2O$ were obtained by slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution of the complex. Several suitable crystals were mounted and flame-sealed under argon in glass capillaries to minimize decomposition. Data were collected on an Enraf-Nonius CAD4 diffractometer with use of MoKα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 well distributed reflections in the range $20.0 \leq 2\theta \leq 24.0°$. A monoclinic cell was established by the usual peak search and reflection indexing programs and the systematic absences established the space group as $P2_1/n$ (a non-standard setting of $P2_1/c$).

Intensity data were collected at 22°C using the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak widths on either side of the scans. Three reflections were chosen as intensity standards and were remeasured at 120 min intervals of X-ray exposure. There was no significant systematic decrease in the intensities of these standards so no correction was applied. A total of 9660 unique reflections were measured and processed in the usual way, using a value of 0.04 for p;[14] of these, 5535 were observed and used in subsequent calculations. Absorption corrections were applied to the data[15] using the method of Walker and Stuart.[16] The crystallographic data are summarized in Table 3.2.

Structure Solution and Refinement

The structure was solved by conventional Patterson techniques to obtain the Rh and Re positions, while all other atoms were located by the usual sequence of full-matrix least-squares and difference Fourier techniques. All atoms of the complex cation and the anion were located. In addition, two peaks appeared on difference Fourier maps in the vicinity of the BF_4^- anion. Based on the ^1H NMR spectrum, which showed the presence of water, and on the locations of these peaks, which were within hydrogen-bonded distances from the BF_4^- anion, these peaks were identified as the oxygen atoms of H_2O molecules. Refinement of their occupancy factors established that each one was of 1/2 occupancy. Although the bridging hydride ligand was clearly located, attempts to refine its thermal parameter resulted in a slightly negative value. Since the positional parameters of this atom were well behaved, its thermal parameter was fixed and its position allowed to refine. All hydrogen atoms of the dppm ligands were included as fixed contributions in their idealized positions at 0.95Å from the attached carbon atoms having the appropriate hybridization. The thermal parameters were fixed at 1.2 times the isotropic B of the attached carbon atom.

Atomic scattering factors[17,18] and anomalous dispersion terms[19] were taken from the usual tabulations. The positional and thermal parameters are summarized in Table 3.3. Bond lengths and angles are given in Tables 3.4 and 3.5, respectively.

Table 3.2 Crystallographic Data for $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]\cdot H_2O$

formula	$C_{54}BF_4H_{47}O_5P_4ReRh$
fw	1275.8
Space Group	$P2_1/n$ (Non-standard setting of $P2_1/c$)
a,Å	17.257(3)
b,Å	12.235(2)
c,Å	26.354(3)
β, deg	102.31(1)
V,Å^3	5436(3)
Z	4
d_{calcd}, g cm^{-3}	1.559
temp, °C	22
radiation, Å	MoKα, 0.71069
monochromator	graphite
μ, (cm^{-1})	27.262
transmission coeft. (min, max)	0.901 - 1.113
unique data collected	9660
observed data (NO)	5535
no. of variables (NV)	388
R[a]	0.043
R_w	0.060
error in obs. of unit wt (GOF)	1.690

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[a] As defined in Table 2.2

Table 3.3 Positional and Thermal Parameters for $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]\cdot H_2O$[a]

Atom	x	y	z	$B(Å^2)$[b]
Re	0.19822(2)	0.16665(3)	0.01131(2)	2.254(7)*
Rh	0.33338(5)	0.32321(7)	0.01506(3)	2.61(2)*
P(1)	0.1455(2)	0.2166(2)	-0.0782(1)	2.47(6)*
P(2)	0.2771(2)	0.3877(2)	-0.0674(1)	2.74(6)*
P(3)	0.2642(2)	0.1003(2)	0.0958(1)	2.60(6)*
P(4)	0.4041(2)	0.2519(2)	0.0931(1)	2.73(6)*
O(1)	0.2154(7)	-0.0732(7)	-0.0280(4)	7.5(3)*
O(2)	0.1778(4)	0.3988(6)	0.0556(3)	3.9(2)*
O(3)	0.0321(4)	0.1130(8)	0.0286(3)	5.2(2)*
O(4)	0.4280(6)	0.5308(7)	0.0331(4)	7.2(3)*
C(1)	0.2106(7)	0.015(1)	-0.0146(4)	4.1(3)*
C(2)	0.1887(6)	0.3168(8)	0.0382(4)	2.8(2)*
C(3)	0.0958(6)	0.1314(9)	0.0229(4)	3.1(2)*
C(4)	0.3922(7)	0.450(1)	0.0259(5)	4.0(3)*
C(5)	0.2198(6)	0.2826(9)	-0.1082(4)	2.8(2)*
C(6)	0.3719(6)	0.1155(9)	0.1067(4)	2.9(2)*
H(1)	0.310(6)	0.177(8)	-0.002(4)	2.0[c]

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[a] Other atom parameters are given in the Supplementary Material.

[b] Starred atoms were refined anisotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

[c] Thermal parameter for H(1) was not refined.

Results and Discussion

Treatment of $[RhRe(CO)_4(dppm)_2]$ (**1**) with one molar equiv of $HBF_4 \cdot Et_2O$ leads to the formation of the protonated species $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ (**2**). Protonation is readily monitored by the increase in carbonyl stretching frequencies, from *ca.* 1800-1959 cm^{-1} in **1**,[11] to *ca.* 1908-2046 cm^{-1} in **2** (see Table 3.1), consistent with oxidation of the complex (*vide infra*) and the resulting positive charge on **2**. The isoelectronic species, $[RhW(CO)_4(\mu\text{-}H)(dppm)_2]$(see Chapter 2), has a very similar pattern of stretches (1978 (m), 1942(s), 1838(s), 1818(s) cm^{-1})[11], which are shifted to lower frequencies in this neutral species. The $^{31}P\{^1H\}$ NMR spectrum of **2** has a doublet of multiplets at δ 24.5 and a multiplet at δ 3.4, corresponding to the Rh-bound and the Re-bound phosphorus nuclei, respectively, essentially as expected for an AA'BB'X spin system, and similar to the spectra previously observed in related dppm-bridged RhRe complexes (see Chapter 2 and later in this Thesis). In the high-field region of the ^1H NMR spectrum a multiplet appears at δ -11.94. Selective phosphorus decoupling experiments clearly indicate that the hydride ligand bridges both metals, displaying coupling to all four phosphorus nuclei and to Rh (see Table 3.1). Whether the precursor, compound **1**, is considered a Rh(0)/Re(0) species or a mixed-valence Rh(+I)/Re(-I) complex, as we favor, protonation has resulted in a formal oxidation of the complex by two units such that both metals can be considered to be in the +I oxidation state.

Although protonation of a metal-metal bonded complex to give a hydrido-bridged species is not unusual, the mixed-valence formulation suggested for **1** does raise some questions regarding the structural changes that might occur upon protonation. Compound **1** is isoelectronic with the species $[MM'(CO)_3(dppm)_2]$ (M , M' = Rh, Ir),[20-22] which have also been formulated as mixed-valence M(+I)/M'(-I) complexes.[22] Protonation of the homobinuclear Rh_2 and Ir_2 complexes resulted in a transformation from their non-A-frame structures, in which the phosphines on one metal were mutually cis, to an A-frame-related structure in which the phosphines on both metals were mutually trans.[23,24] Surprisingly, protonation of the Rh/Ir analogue[22] gave a different structural type in which all carbonyls remained terminal, although again the phosphines appeared to adopt a trans arrangement. It was therefore of interest to establish whether protonation of **1** would result in a significant structural transformation, which might, in our interpretation, be viewed as occurring through oxidation of the trigonal bipyramidal Re(-I) center to give Re(+I).

The X-ray structure determination of **2** clearly shows that a significant structural transformation has indeed occurred, as shown for the cation in Figure 3.1. The diphosphines still adopt a trans arrangement on the metals, having P-M-P angles of *ca.* 172 ° . Although the agreement within each set of Re-P and Rh-P distances is excellent, the former are significantly longer (av. 2.417(2)Å *vs.* 2.325(2)Å) owing to the larger covalent radius of Re. This effect is also displayed in the metal-carbonyl distances which are again longer for Re. In addition, the two mutually trans carbonyls on Re (C(1)O(1), C(2)O(2)), which are in direct competition for π electron density on Re, have longer Re-C distances (2.00(1), 1.989(8)Å)) than that involving C(3)O(3) (1.907(9)Å). The Rh-H(1) and Re-H(1) distances (1.86(8), 2.05(8)Å, respectively) are not significantly different, and owing to the uncertainty involved in positioning the hydrogen in the vicinity of the two heavy metals, little can be inferred about the bonding of this hydride except that it is bridging in an approximately symmetric manner. Protonation has resulted in a substantial

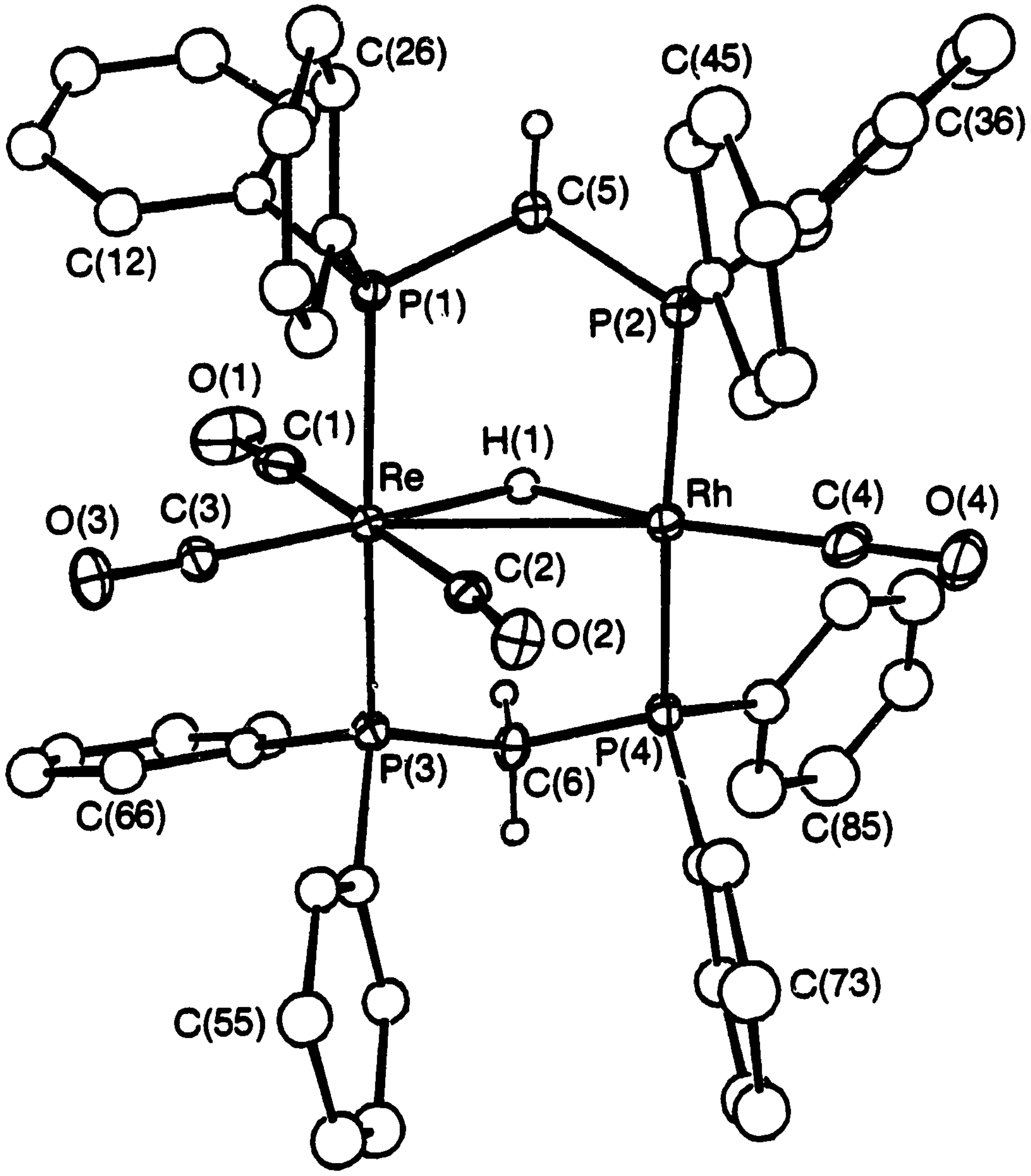


Figure 3.1 A perspective view of the $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$ cation showing the numbering scheme used. Phenyl rings are numbered sequentially around the ring. Thermal ellipsoids are shown at the 20% level except for the methylene hydrogens which are shown artificially small and phenyl hydrogens which are omitted.

increase in the Rh-Re bond length, from 2.7919(6)Å in **1**,[11] to 3.0036(7)Å in **2**, in keeping with the formation of a three-center, two-electron Rh-H-Re bond. In addition to the lengthening of the metal-metal bond, a significant change in the carbonyl positions has occurred upon protonation. The $Re(CO)_3$ moiety is no longer approximately trigonal, and this unit has twisted about the P-Re-P axis with H(1) occupying the sixth site of an approximately octahedral geometry, such that all angles about Re (ignoring the Rh-Re interaction) are close to values expected for an octahedron (see Table 3.5). This transformation, from an approximate trigonal bipyramidal arrangement in **1** to an octahedral environment in **2**, is consistent with an oxidation of Re(-I) to Re(+I). Although carbonyl C(2)O(2) is twisted towards Rh, the Rh-C(2) and Rh-O(2) separations (2.694(9), 3.229(6)Å, respectively) are longer than one set of such interactions in **1**,[11] and therefore appear not to be unusual. We therefore suggest that there is no significant interaction of Rh with this carbonyl group. This view is supported by the lack of Rh coupling to this carbonyl group in the $^{13}C\{^1H\}$ NMR spectrum (vide infra). The geometry at Rh is distorted from square planar such that the fourth coordination site opposite C(4) is actually midway along the Re-H(1) bond. This can be seen from the Re-Rh-C(4) and H(1)-Rh-C(4) angles of 160.1(3) ° and 158(2) °, respectively.

From ambient temperature to -40° C compound **2** is fluxional, so rather than the four expected carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) (see Figure 3.2), only three are observed, at δ 194.6 (triplet, $^2J_{P(Re)\text{-}C}$ = 13 Hz), δ 189.3 (singlet) and δ 182.8 (doublet of triplets, $^1J_{Rh\text{-}P}$ = 72 Hz, $^2J_{P(Rh)\text{-}C}$ = 14 Hz), in a 2:1:1 intensity ratio, respectively. The equivalence of the two mutually trans carbonyls on Re ($(CO)_A$ and $(CO)_B$) apparently results from their exchange which is brought about by movement of the

Table 3.4 Selected Bond Lengths (Å) for $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]\cdot H_2O$

Re-Rh	3.0036(7)	P(2)-C(5)	1.825(8)
Re-P(1)	2.418(2)	P(2)-C(31)	1.819(9)
Re-P(3)	2.415(2)	P(2)-C(41)	1.823(9)
Re-C(1)	2.00(1)	P(3)-C(6)	1.829(8)
Re-C(2)	1.989(8)	P(3)-C(51)	1.835(8)
Re-C(3)	1.907(9)	P(3)-C(61)	1.831(8)
Re-H(1)	2.05(8)	P(4)-C(6)	1.819(8)
Rh-P(2)	2.323(2)	P(4)-C(71)	1.803(9)
Rh-P(4)	2.326(2)	P(4)-C(81)	1.83(1)
Rh-C(4)	1.84(1)	O(1)-C(1)	1.14(1)
Rh-H(1)	1.86(8)	O(2)-C(2)	1.134(9)
P(1)-C(5)	1.832(8)	O(3)-C(3)	1.163(9)
P(1)-C(11)	1.828(8)	O(4)-C(4)	1.16(1)
P(1)-C(21)	1.844(8)		

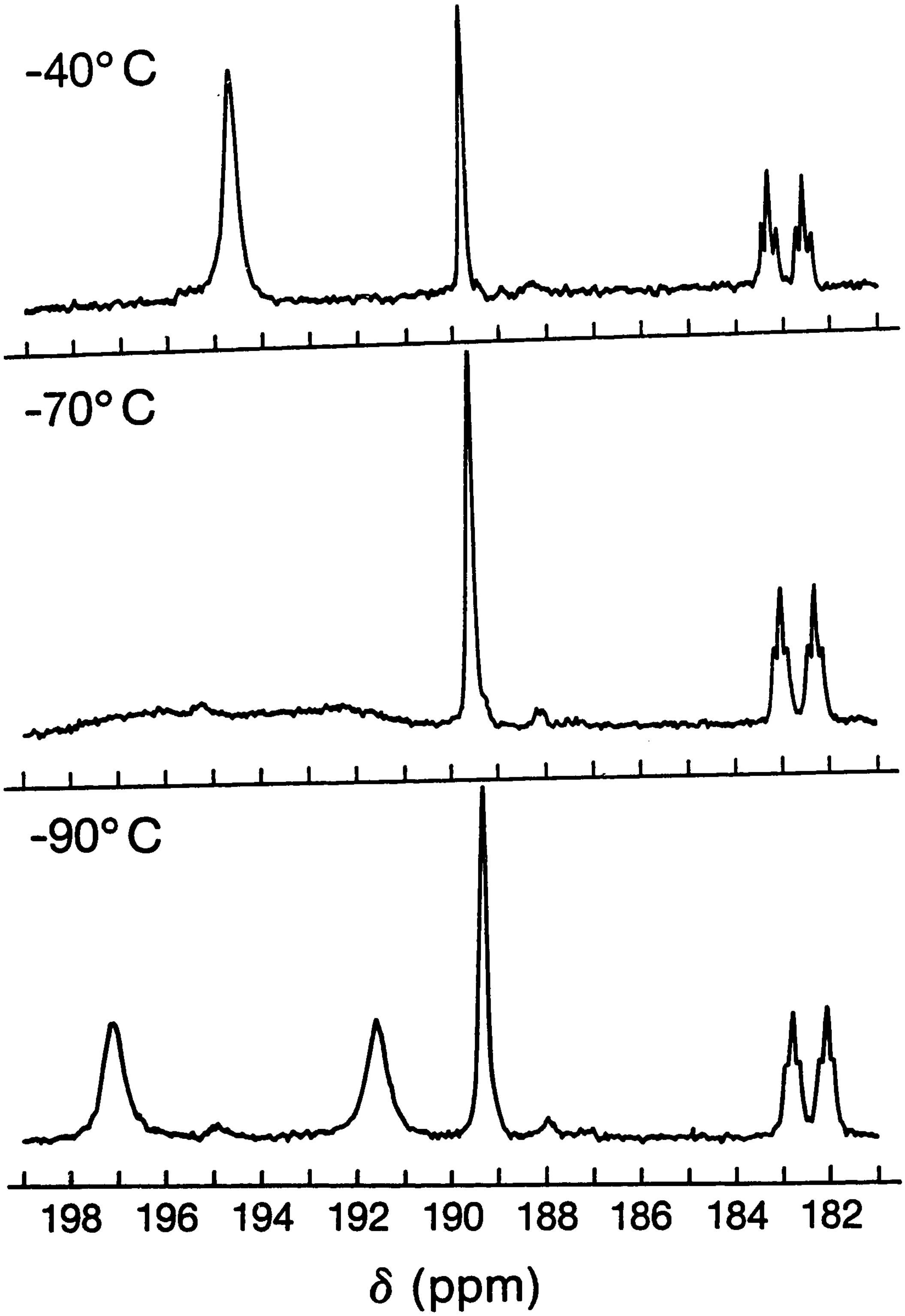
Numbers in parentheses are estimated standard deviations in the least significant digits. Bond lengths for the BF_4^- anion and the phenyl groups are given in the Supplementary Material.

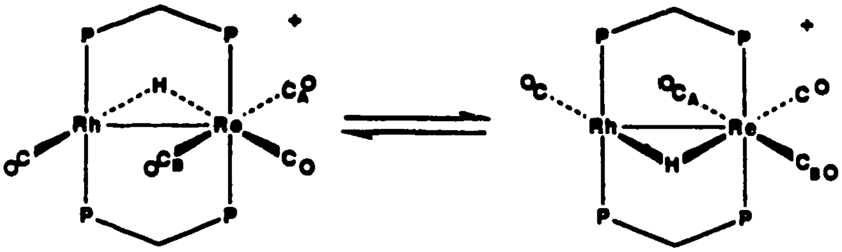
Table 3.5 Selected Angles (deg) for $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]\cdot H_2O$

Rh-Re-P(1)	89.95(5)	Re-Rh-P(2)	91.09(6)	C(31)-P(2)-C(41)	106.8(4)
Rh-Re-P(3)	88.52(5)	Re-Rh-P(4)	92.70(6)	Re-P(3)-C(6)	112.1(3)
Rh-Re-C(1)	117.7(3)	Re-Rh-C(4)	160.1(3)	Re-P(3)-C(51)	118.5(3)
Rh-Re-C(2)	61.5(2)	Re-Rh-H(1)	42(2)	Re-P(3)-C(61)	113.4(3)
Rh-Re-C(3)	151.5(3)	P(2)-Rh-P(4)	172.40(9)	C(6)-P(3)-C(51)	106.1(4)
Rh-Re-H(1)	38(2)	P(2)-Rh-C(4)	88.0(3)	C(6)-P(3)-C(61)	102.9(4)
P(1)-Re-P(3)	171.70(8)	P(2)-Rh-H(1)	95(3)	C(51)-P(3)-C(61)	102.2(4)
P(1)-Re-C(1)	86.9(3)	P(4)-Rh-C(4)	90.6(3)	Rh-P(4)-C(6)	113.2(3)
P(1)-Re-C(2)	94.1(2)	P(4)-Rh-H(1)	84(3)	Rh-P(4)-C(71)	115.6(3)
P(1)-Re-C(3)	92.5(3)	C(4)-Rh-H(1)	158(2)	Rh-P(4)-C(81)	112.4(3)
P(1)-Re-H(1)	90(2)	Re-P(1)-C(5)	112.3(3)	C(6)-P(4)-C(71)	103.9(4)
P(3)-Re-C(1)	86.5(3)	Re-P(1)-C(11)	114.2(3)	C(6)-P(4)-C(81)	102.4(4)
P(3)-Re-C(2)	92.3(2)	Re-P(1)-C(21)	119.9(3)	C(71)-P(4)-C(81)	108.2(4)
P(3)-Re-C(3)	92.7(3)	C(5)-P(1)-C(11)	103.1(4)	Re-C(1)-O(1)	176.9(9)
P(3)-Re-H(1)	84(2)	C(5)-P(1)-C(21)	103.3(4)	Re-C(2)-O(2)	173.6(8)
C(1)-Re-C(2)	178.6(4)	C(11)-P(1)-C(21)	102.0(4)	Re-C(3)-O(3)	177.4(8)
C(1)-Re-C(3)	90.8(4)	Rh-P(2)-C(5)	112.2(3)	Rh-C(4)-O(4)	179(1)
C(1)-Re-H(1)	81(2)	Rh-P(2)-C(31)	112.2(3)	P(1)-C(5)-P(2)	113.5(4)
C(2)-Re-C(3)	90.1(4)	Rh-P(2)-C(41)	118.2(3)	P(3)-C(6)-P(4)	113.9(4)
C(2)-Re-H(1)	99(2)	C(5)-P(2)-C(31)	99.9(4)	Re-H(1)-Rh	100(4)
C(3)-Re-H(1)	170(2)	C(5)-P(2)-C(41)	105.9(4)		

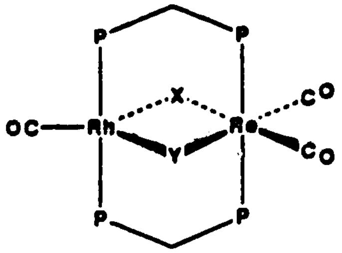
[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Angles involving the BF_4^- anion and the phenyl rings are given in the Supplementary Material.

Figure 3.2 The $^{13}C\{^1H\}$ VT-NMR of $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$ at -40, -60, and -90° C.





hydrido ligand between the metals with accompanying twisting of the metal-carbonyl framework as shown. This fluxionality also results in the appearance of only one resonance for the dppm-methylene protons in the ^1H NMR spectrum owing to the time-average mirror symmetry about the $RhReP_4$ core. Similar fluxional processes have previously been noted in $[RhFe(CO)_3(\mu\text{-}H)(dppm)_2)$, as described in Chapter 2, and in related hydrido-bridged systems.[22,25] At -90 ° C, as shown in Figure 3.2, the two high-field carbonyl resonances have remained essentially unchanged but the low-field signal has split into two broad unresolved signals at δ 197.1 and δ 191.6, resulting in four equal-intensity carbonyl resonances, consistent with the observed solid-state structure. Compound **1** also undergoes facile oxidative-addition reactions with H_2, Cl_2 and HCl to give the structurally analogous species **3**, **4** and **5**, respectively, as shown. In the reaction with H_2 the product, $[RhRe(CO)_3(\mu\text{-}H)_2(dppm)_2]$ (**3**), has two bridging hydride ligands. The $^{31}P\{^1H\}$ NMR spectrum again displays a pattern typical of an AA'BB'X spin system, and the IR spectrum displays the expected three carbonyl stretches in solution. In the ^1H NMR spectrum the resonance for the two chemically equivalent hydride ligands is observed at δ -8.21 and can be shown, through selective ^{31}P decoupling experiments, to display coupling to Rh and to the



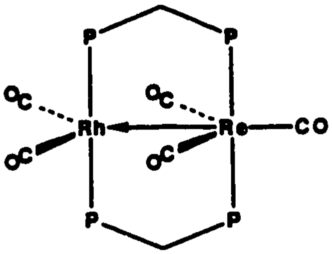
X = Y = H (3)

X = Y = Cl (4)

X = H, Y = Cl (5)

two sets of chemically inequivalent phosphorus nuclei (bound to Rh or Re). Confirmation that 3 is a tricarbonyl species is obtained from the $^{13}C\{^1H\}$ NMR spectrum of a 70% ^{13}CO-enriched sample which shows one resonance (a doublet of triplets, $^1J_{Rh\text{-}C}$ = 69 Hz, $^2J_{P(Rh)\text{-}C}$ = 18 Hz) at δ 191.0 for the single carbonyl on Rh and one resonance (a triplet, $^2J_{P(Re)\text{-}C}$= 7 Hz,) at δ 201.2 for the two carbonyls on Re, having the appropriate integrations. The structure proposed for 3 is a hybrid of the structures proposed for the homobinuclear analogues $[Re_2(CO)_4(\mu\text{-}H)_2(dppm)_2]$ [12] and $[Rh_2(CO)_2(\mu\text{-}H)_2(dppm)_2]$.[26] A structure like that of the related dihydride $[RhIr(H)(CO)_2(\mu\text{-}H)(dppm)_2]$,[22] having one hydride bridging both metals and the other terminally bound to the third-row metal, can be ruled out by the spectral data unless the complex is fluxional, for which there is no evidence down to -80 ° C.

The reaction of 1 with H_2 is reversible, so that under a CO purge compound 1 is regenerated from 3. If 1 is maintained under an atmosphere of CO, a new species (6) having carbonyl stretches in the IR spectrum, at 2010(s), 1988(s), 1964(s), 1918(vs) and 1892(vs) cm^{-1}, is observed. The $^{31}P\{^1H\}$ NMR spectrum of 6 at -40 ° C displays a broad multiplet at δ -1.6 and a doublet of multiplets ($^1J_{Rh\text{-}P}$ = 151 Hz) at δ 11.4, and the $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample shows only one broad peak at δ 202, even at -60 ° C, suggesting that facile carbonyl exchange over both metal centers is occurring. This facile carbonyl exchange is consistent with the ease with which **1** undergoes ^{13}CO scrambling when exposed to ^{13}CO. Although carbonyl exchange in **1** is not observed at ambient temperature, exposure of **1** to ^{13}CO results in total scrambling over both metals, suggesting the involvement of the pentacarbonyl species **6**. The structure proposed for this species is based on the above spectroscopic data and on the structural determination of the isoelectronic species, $[IrOs(CO)_5(dppm)_2][BF_4]$,[27] which displays a trigonal bipyramidal coordination at Ir and a geometry at Os not unlike that at Re in compound **1**. The fifth carbonyl ligand on **6** is very labile and is lost immediately upon flushing the reaction solution with N_2 or Ar, yielding **1**, or upon protonation, yielding **2**. As was the case for compound **1**, we again propose a mixed-valence Rh(+I)/Re(-I) formulation in which a Re → Rh dative bond connects the metals.

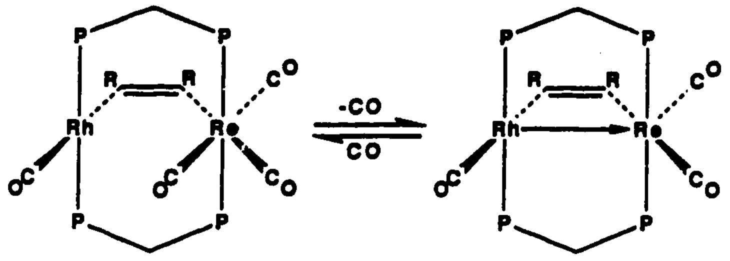


6

Reaction of compound **1** with $PhICl_2$ (a convenient stoichiometric source of Cl_2) results in the formation of the highly insoluble species $[RhRe(CO)_3(\mu\text{-}Cl)_2(dppm)_2]$ (**4**). Although the poor solubility of **4** precluded an NMR investigation, its formulation (as diagrammed earlier) seems clear, based on its elemental analysis and on a comparison of its IR spectrum with that of **3** (see Table 3.1). This structure is similar to that proposed for the diarsine-bridged dirhenium analogue, $[Re_2(CO)_4(\mu\text{-}Cl)_2(dpam)_2]$ (dpam = $Ph_2AsCH_2AsPh_2$),[28] and as observed for the related, $[Re_2(CO)_6(\mu\text{-}Cl)_2(dpam)]$.[29] Compound **1** also reacts instantly with one equivalent of dry gaseous HCl to give $[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}Cl)(dppm)_2]$ (**5**), the mixed hydrido-chloro analogue of compounds **3** and **4**. The spectroscopic data of **5** are comparable to those of **3** and **4** (Table 3.1), and also to the related data for the isoelectronic thiolato-bridged species, $[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SEt)(dppm)_2]$, as reported[9] and as discussed in the following chapter. The structure of this thiolato-bridged species has been determined crystallographically. All evidence suggests the structure for **5** shown earlier. The hydrido-ligand is clearly bridging, as shown by the ^1H NMR spectra with and without selective ^{31}P decoupling, which indicate that the highfield hydride resonance at δ -9.8 is coupled to Rh and to both sets of phosphorus nuclei. Although the chloro ligand cannot unequivocally be identified as bridging, the close similarities between **5** and the ethanethiolato-bridged species strongly supports this formulation. Addition of more than one equivalent of HCl to compound **1** results in formation of the insoluble dichloride species, **4**. Compound **5** is also converted to **4** upon standing in CH_2Cl_2, the half-life being about 85 min at room temperature; however, **5** could be handled briefly in this solvent with no apparent problem.

These facile reactions of H_2, Cl_2 and HCl with **1**, to yield the respective tricarbonyl species **3**, **4** and **5**, are surprising in that in all cases loss of one carbonyl group from Re has occurred. Based on the inertness of the related saturated species $[Re_2(CO)_6(dppm)_2]$ at ambient temperature,[12] it is clear that the coordinatively unsaturated Rh center is pivotal to the reactivity of **1**. Presumably initial reaction is at Rh, with loss of CO being accompanied by movement of the hydrido and chloro groups to the bridging positions, to alleviate the unsaturation at Re brought about by CO loss. For the chloride-containing species, electron precise compounds result owing to the lone pairs of electrons on Cl which can be donated to Re. However, for the dihydride species **3**, an electron deficient structure can be invoked involving three-centered Re-H-Rh bonds.

Reactions of metal complexes with multiple-bond-containing groups, such as alkynes bearing electronegative substituents, can also be regarded as oxidative additions,[30] and we find that compound **1** reacts readily with dimethyl acetylenedicarboxylate (DMA) or hexafluoro-2-butyne (HFB) to yield the respective tetracarbonyl, alkyne-bridged products, $[RhRe(CO)_4(\mu\text{-}RC{\equiv}CR)(dppm)_2]$ (R = CO_2Me (**7**), CF_3 (**8**)). The IR spectra of these species in the carbonyl region look very reminiscent of that obtained for the sulfido-bridged species, $[RhRe(CO)_4(\mu\text{-}S)(dppm)_2]$ ($\nu(CO)$ = 1990, 1953, 1868, 1830 cm^{-1}),[9] suggesting an analogous formulation for the complexes and a dianionic formulation for the bridging alkyne, which would then bind parallel to the Rh-Re axis as a cis-dimetallated olefin. This would yield a square planar geometry for the Rh(+I) center and an octahedral geometry for Re(+I). Consistent with this formulation, the ^1H NMR spectrum of **7** shows two resonances for the chemically inequivalent methyl protons, and the ^{19}F NMR spectrum of **8** displays two quartets ($^5J_{F\text{-}F}$ = 6 Hz) for the two inequivalent CF_3 groups. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of compound **7** is also consistent with the structure shown, displaying four carbonyl resonances at δ 195.8 (doublet of triplets, $^1J_{Rh\text{-}C}$ = 59 Hz, $^2J_{P(Rh)\text{-}C}$ = 12 Hz), δ 197.1 (broad multiplet), δ 197.4 (doublet of doublets, $^2J_{C\text{-}C}$ = 21 Hz, $^2J_{C\text{-}C}$ = 4 Hz) and δ 214.5 (doublet of doublets, $^1J_{Rh\text{-}C}$ = 10 Hz, $^2J_{C\text{-}C}$ = 21 Hz). The high-field signal is clearly established as resulting from the unique Rh-bound carbonyl by its large coupling to this metal. Only this resonance displays resolvable coupling to the phosphorus nuclei. Of the remaining three resonances for the Re-bound carbonyls, the two which are mutually trans are identified by the large carbon-carbon coupling (21 Hz). The higher-field signal of these also displays small cis coupling (4 Hz) to the carbonyl which is opposite the alkyne group, whereas the low-field signal displays slight coupling (10 Hz) to Rh. This Rh-coupling is much less than that expected for a carbonyl group which is bound to Rh either terminally (typically $^1J_{Rh\text{-}C} \cong$ 50-70 Hz) or in a bridging manner (typically *ca.* 35 Hz)[31] and suggests only a weak interaction with this metal. We suggest that this weak interaction results from the carbonyl being forced close to Rh by rotation of the $Re(CO)_3$ framework to accommodate the bridging alkyne. Significantly, when the metals are bridged by a small hydrido group in compound **2**, no coupling between Rh and the related Re-bound carbonyl is observed. Compounds **7** and **8** readily lose CO in the absence of a CO atmosphere to yield $[RhRe(CO)_3(\mu\text{-}RC \equiv CR)(dppm)_2]$ (R = CO_2Me (**9**), CF_3 (**10**)). The $^{13}C\{^1H\}$ NMR spectrum of **10** shows three carbonyl resonances of equal intensity at δ 214.1, 202.7 and 194.3, with only the high-field resonance displaying coupling to Rh ($^1J_{Rh\text{-}C}$ = 55 Hz). This clearly indicates that one carbonyl group has been lost from the Re center. In order to maintain an eighteen electron configuration at Re one might anticipate that the bridging alkyne would twist perpendicular to the Rh-Re axis thereby functioning as a neutral 4-electron donor as has previously been observed in related systems.[32,33] However, the ^1H NMR spectrum of **9** and the ^{19}F NMR spectrum of **10**, which show two different methyl and trifluoromethyl environments, respectively, and the $^{31}P\{^1H\}$ NMR spectra, which still show AA'BB'X patterns similar to those of the respective precursors, **7** and **8**, suggest that the alkynes have remained parallel to the Rh-Re axis. Furthermore, this has been confirmed in an analogous RhOs complex which undergoes CO loss to yield [RhOs(CO)$_3$ (μ-DMA)(dppm)$_2$] [BF$_4$], the structure of which has been determined by X-ray techniques.[34] Previous examples in which an alkyne maintained a cis dimetallated olefin binding mode upon gain or loss of a ligand have been observed,[31,35-40] however in these cases the change in metal-metal bond order was accompanied by a change in the number of bridging carbonyl or related groups. In this example the additional pair of electrons donated to Re comes from Rh, in an unusual electron reallocation in which the coordinatively unsaturated metal functions as the Lewis base, presumably through donation of the pair of electrons in the Rh d_{z^2} orbital, which is directed towards Re. Such a process is not common in such complexes and can be thought of as an inorganic equivalent of the anchimeric or neighboring group effect[41,42] observed in organic chemistry. In this case the neighboring Rh atom donates a pair of electrons to assist in labilizing a carbonyl group on Re. Although the detailed mechanism of this CO loss is uncertain, studies on the analogous Rh/Os system[34] have shown that, rather than direct loss from the Os center, the semibridging CO first migrates to Rh to form a species with two carbonyl ligands on both Rh and Os. This species



R = CO$_2$Me (7)
= CF$_3$ (8)

R = CO$_2$Me (9)
= CF$_3$ (10)

then loses CO from Rh to yield a cationic Os tricarbonyl bridging-alkyne complex. Addition of CO to **9** and **10** regenerates **7** and **8**, respectively. Compound **1** did not react with the non-activated alkynes, diphenylacetylene and 2-butyne, even in refluxing THF.

Attempts to observe oxidative addition of the C-H bond of phenylacetylene to **1** to give a hydride acetylide species, as was observed at 172 °C for $[Re_2(CO)_6(dppm)_2]$[12] did not meet with success. At ambient temperature reaction with **1** was slow, yielding a complex mix of products after 48 h, including 30% starting material. Refluxing in THF again produced a mixture of species. In both cases hydride resonances were not observed in the ^1H NMR spectra. Furthermore, compound **1** did not react with water or alcohols at temperatures below 110 ° C (toluene reflux), in contrast to the above dirhenium species, which at 172 ° C yielded the respective hydrido hydroxide and hydrido alkoxide complexes, via oxidative addition of an oxygen-hydrogen bond.[12] Presumably the low affinity of Rh(I) for hard, oxygen-donor ligands[43] inhibits these reactions.

Conclusions

The presence of the coordinatively unsaturated Rh(+I) center adjacent to the saturated Re center appears to be instrumental in the chemistry of such species. So, for example, $[RhRe(CO)_4(dppm)_2]$ (**1**) undergoes facile reactions at ambient temperature with H_2, Cl_2, HCl, and activated alkynes, whereas the analogous complex, $[Re_2(CO)_6(dppm)_2]$, which has no site of unsaturation, required vigorous heating at *ca.* 172 ° C before similar reactions were observed.[12] Although the reactions of **1** with alkynes did not result in carbonyl loss at ambient temperature, the products in the other reactions resulted from facile carbonyl loss from Re. Carbonyl loss in these species is facilitated by the bonding involving the bridging hydride and halide species which can alleviate the coordinative unsaturation at Re (most simply for the halides by dative bond formation utilizing a lone pair of electrons on Cl). However, subsequent CO loss from the alkyne-bridged complexes does occur without a realignment of the bridging alkyne group. It appears that this carbonyl loss is facilitated by the effect of the neighboring Rh which donates a pair of electrons to Re forming a Rh→Re dative bond, regenerating coordinative saturation at Re.

Supplementary Material Available: Tables containing crystal data and details of intensity collection, anisotropic thermal parameters, positional and thermal parameters for the hydrogen atoms, bond lengths and angles within the phenyl groups, positional and isotropic thermal parameters for all atoms (10 pages), and structure factor Tables (28 pages). All Supplementary Data are available from M. Cowie upon request.

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Chapter 4

Ascertaining the Roles of Each Metal in the Activation of S-H Bonds in Hydrogen Sulfide and Thiols by the Heterobinuclear Complex, $[RhRe(CO)_4(Ph_2PCH_2PPh_2)_2]$. †

Introduction

The current interest in binuclear complexes is based on the assumption that the presence of the two adjacent metals will give rise to reactivity patterns that differ substantially from those of the mononuclear analogues. With this idea in mind we have chosen to investigate chemistry that might clearly benefit from the presence of two adjacent metals, and as part of this study we have been examining the activation of adjacent heteroatom-hydrogen bonds in H_2X molecules ($X = S, Se, SiR_2, SiHR$).[1,2] We are interested in the initial sites of substrate attack in various binuclear complexes, the involvement of the adjacent metals in X-H bond activation processes, the chemically significant ligand rearrangements that occur, and the possibility of subsequent binuclear reductive elimination reactions. In this chapter we present details about the activation of H_2S and thiols. Hydrogen sulfide is of interest to us because of its potential use as a source of H_2[3-6] and organosulfur compounds,[7] whereas thiols may serve to model unstable intermediates both in the initial S-H activation processes involving H_2S and in the subsequent formation of organosulfur products.

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Although our initial studies involved homo- and hetero-binuclear complexes of Rh and Ir,[1-2] we have recently turned to heterobinuclear complexes in which Rh is combined with an earlier transition metal (see Chapter 2). The compound of interest in this study, $[RhRe(CO)_4(dppm)_2]$ (1) (dppm = $Ph_2PCH_2PPh_2$), has the structure shown in Chapter 2, in which a dative bond between the coordinatively saturated Re(-I) center and the unsaturated Rh(+I) center can be formulated.[8] Consistent with the coordinative unsaturation at Rh and the low oxidation states of the metals, compound **1** has been found to be active towards oxidative-addition reactions, involving substrates such as H_2, Cl_2 and HCl, as discussed in Chapter 3 and as reported,[9] so seemed a good candidate for oxidative addition reactions of H-S bonds in H_2S and thiols. It was hoped that the strong tendency of Re to maintain an eighteen-electron configuration might allow the characterization of intermediates that were difficult to observe when the second metal was Rh or Ir.[1,2]

In a related study involving the reaction of H_2S with $[Pd_2Cl_2(dppm)_2]$,[3] activation of both H-S bonds followed by facile H_2 loss to yield $[Pd_2Cl_2(\mu\text{-}S)(dppm)_2]$ was observed. However, the mechanistic details necessary to outline the involvement of the metals were not elucidated. In the present study we attempt to address the questions relating to the involvement of the adjacent metals in H-S bond activation.

Experimental Section

General Experimental Conditions

All solvents were dried and distilled under argon before use. Sodium-benzophenone was used as a drying agent in all cases except for CH_2Cl_2 which was dried over P_2O_5. Prepurified argon and hydrogen sulfide, obtained from Matheson, were used without further treatment. Carbon monoxide also was used as received. Hydrated rhodium (III) trichloride was obtained from Johnson Matthey Ltd. and $Re_2(CO)_{10}$ was purchased from Strem and sublimed before use. Benzenethiol and ethanethiol were obtained from Aldrich. All other chemicals were used as received without further purification. The 99% carbon-13 enriched carbon monoxide was obtained from Isotec Inc. The compound, $[RhRe(CO)_4(dppm)_2]$ (1), was prepared as in Chapter 2.

All NMR experiments were conducted on a Bruker AM-400 spectrometer operating at 161.9 MHz for ^{31}P. In all cases an internal deuterated solvent lock was used. In general, deuterated solvents were dried over P_2O_5, freeze-pump-thaw degassed and vacuum distilled into the 5 mm NMR tube containing the sample. These tubes were flame sealed with the contents at -196°C for the variable temperature NMR experiments.

Infrared spectra were recorded on either a Nicolet 7199 Fourier transform interferometer or a Perkin Elmer 883 spectrophotometer, either as solids (Nujol Mulls on KBr discs) or solutions (KCl cell windows, 0.5 mm path length). Elemental analyses were performed by the micro analytical service within the Department.

Preparation of Compounds

a) $[RhRe(CO)_4(\mu\text{-}S)(dppm)_2]$ (2).

The compound, [RhRe(CO)$_4$(dppm)$_2$] (1) (50 mg, 42.8 µmol) was dissolved in 5 mL of THF to which 2 mL of H_2S (~ 40 µmol/mL, 2 equiv.) was added by gas-tight syringe. The solution slowly turned from yellow to dark orange-red over 1/2 h. The solvent was then removed in vacuo to yield an orange residue which was recrystallized from CH_2Cl_2/Et_2O to give 49 mg (95%) of an orange powder. Anal. Calcd for $C_{54}H_{44}O_4P_4ReRhS$: C, 53.96; H, 3.69; S, 2.67. Found: C, 53.62; H, 3.91; S, 2.95. See Table 4.1 for the spectral parameters of all compounds.

b). [RhRe(CO)$_3$(µ-H)(µ-SEt)(dppm)$_2$] (5).

Compound 1 (50 mg, 42.8 µmol) was dissolved in 5 mL of THF to which EtSH (3.2 µL, 42.9 µmol) was added by syringe. The yellow solution quickly turned dark orange-red and was stirred for 1/2 h. Removal of the solvent in vacuo and recrystallization from CH_2Cl_2/Et_2O yielded 43 mg (84%) of an orange-red powder. Anal. Calcd for $C_{55}H_{50}O_3P_4ReRhS$: C, 54.80; H, 4.18. Found: C, 54.92; H, 4.33.

c). [RhRe(CO)$_3$(µ-H)(µ-SPh)(dppm)$_2$] (6).

Compound 1 (50 mg, 42.8 µmol)was dissolved in 5 mL of THF and PhSH (4.4 µL, 42.9 µmol) was added by syringe. The solution immediately turned from yellow to dark red but was stirred for an additional 1/2 h. Removal of the solvent in vacuo and recrystallization from CH_2Cl_2/Et_2O yielded 47 mg (89%) of an orange-red powder (6). Anal. Calcd for $C_{59}H_{50}O_3P_4ReRhS$: C, 56.60; H, 4.03. Found: C, 57.27; H, 4.29.

Table 4.1. Spectral Data[a]

Compound	IR, cm^{-1} [b]	NMR		
		$\delta(^{31}P\{^{1}H\})$[c]	$\delta(^{1}H)$[d,e]	$\delta(^{13}C)$[d]
$[RhRe(\mu\text{-}S)(CO)_4(dppm)_2]$ (2)	1990(sh), 1953(st), 1868 (med), 1830(sh)	22.2 (dm, $^{1}J_{Rh\text{-}P}$ = 134 Hz), -3.6(m)[f]	2.6 (m,2H), 4.8(m,2H)[f]	215.8(m), 193.2(s), 193.5(dt, $^{1}J_{Rh\text{-}C}$ = 70Hz, $^{2}J_{P(Rh)\text{-}C}$ = 15 Hz), 193.8(b)[f]
$[RhRe(H_2S)(CO)_4(dppm)_2]$ (3)	h	11.6 (dm, $^{1}J_{Rh\text{-}P}$ = 146 Hz), -1.4(m)[i]	4.2 (m, 4H)[i]	204 (s, 4C)[i]
$[ReRh(CO)_4(\mu\text{-}H)(SH)(dppm)_2]$ (4)	h	30.8 (dm, $^{1}J_{Rh\text{-}P}$ = 126 Hz), 7.7(m)[j]	-0.85(t,1H, $^{3}J_{P(Rh)\text{-}H}$ = 15.3 Hz), -11.1(m, 1H, $^{1}J_{Rh\text{-}H}$ = 32 Hz, $^{2}J_{P(Rh)\text{-}H}$ = 13 Hz, $^{2}J_{P(Re)\text{-}H}$ = 7 Hz), 3.25(m, 2H), 3.7(m, 2H)[j]	248(s), 206(s), 196(s), 193(d, $^{1}J_{Rh\text{-}C}$ = 85 Hz)[j]
$[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SEt)(dppm)_2]$ (5)	1951(med), 1923(st), 1850(st)	29.8 (dm, $^{1}J_{Rh\text{-}P}$ = 123 Hz), 11.1(m)[g]	-10.5(m,1H, $^{1}J_{Rh\text{-}H}$ = 20.5 Hz, $^{2}J_{P(Rh)\text{-}H}$ = 10.0 Hz, $^{2}J_{P(Re)\text{-}H}$ = 10.0 Hz), 2.9(m, 2H), 4.6(m, 2H), 0.0(t,3H), 2.1(q, 2H)[g]	197.8(s,2C), 198.1 (dm, 1C, $^{1}J_{Rh\text{-}C}$ = 77 Hz, $^{2}J_{P(Rh)\text{-}C}$ = 14 Hz)[g]

Table 4.1 (continued)

Compound	IR, cm^{-1} [b]	NMR $\delta(^{31}P\{^{1}H\})$[c]	 $\delta(^{1}H)$[d,e]	 $\delta(^{13}C)$[d]
$[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SPh)(dppm)_2]$ (6)	1950(sh), 1922(st), 1841(med)	27.5 (dm, $^{1}J_{Rh\text{-}P}$ = 119 Hz), 6.3(m)[g]	-9.71(m,1H, $^{1}J_{Rh\text{-}H}$ = 22.3 Hz, $^{2}J_{P(Re)\text{-}H}$ = 9.0 Hz, $^{2}J_{P(Rh)\text{-}H}$ = 11.0 Hz), 3.6(m, 2H), 3.2(m, 2H)[g]	198.8(s), 197.1 (s), 189.1(dm, $^{1}J_{Rh\text{-}C}$ = 80 Hz)[g]
$[RhRe(HSEt)(CO)_4(dppm)_2]$ (7)	h	11.3 (dm, $^{1}J_{Rh\text{-}P}$ = 145Hz), -1.4(m)[i]	4.2(m,4H)[i]	203(s 4C)[i]
$[RhRe(CO)_4(\mu\text{-}H)(SEt)(dppm)_2]$ (8)	h	27.9 (dm, $^{1}J_{Rh\text{-}P}$ = 129 Hz), 8.5(m)[j]	-11.1(m,1H, $^{1}J_{Rh\text{-}H}$ = 26 Hz), 3.2(m,2H), 3.9(m,2H), 0.1(t,3H), 2.6(q,2H)[j]	246(s), 206 (s), 197(s), 193.7(dm, $^{1}J_{Rh\text{-}H}$ = 91Hz)[j]
$[RhRe(HSPh)(CO)_4(dppm)_2]$ (9)	h	11.7 (dm, $^{1}J_{Rh\text{-}P}$ = 145Hz), -1.3(m)[i]	4.2(m,4H)[i]	203(s 4C)[i]
$[RhRe(CO)_4(\mu\text{-}H)((SPh)(dppm)_2]$ (10)	h	27.0 (dm, $^{1}J_{Rh\text{-}P}$ = 127Hz), 8.1(m)[g]	-11.4(m,1H, $^{1}J_{Rh\text{-}H}$ = 28Hz) 3.4(m,2H), 3.7(m, 2H)[g]	246(s), 206(s), 196(s), 193.4(dm, $^{1}J_{Rh\text{-}C}$ = 88Hz)[g]
$[RhRe(CO)_4(H)(SPh)(dppm)_2]$ (11)	h	29.1 (dm, $^{1}J_{Rh\text{-}P}$ = 105Hz), -5.4(m)[j]	-10.65(m,1H, $^{2}J_{P(Re)\text{-}H}$ = 10.4Hz) 4.5(m,2H), 4.7(m, 2H)[j]	203(dm, $^{1}J_{Rh\text{-}C}$ = 78Hz), 201(s), 194(s,2C)[j]

[a] Abbreviations used: w = weak, med = medium, st = strong, sh = shoulder, m = multiplet, t = triplet, dm = doublet of multiplets, q = quartet, b = broad.

[b] CH_2Cl_2 solution in KCl cells. [c] Vs 85% H_3PO_4 in CD_2Cl_2. [d] Vs TMS in CD_2Cl_2. [e] Phenyl resonances are not given. [f] Ambient temperature. [g] -40°C. [h] IR not obtained for this labile intermediate. [i] -60°C. [j] -20°C.

Low Temperature NMR Studies

The solvent CD_2Cl_2 was vacuum distilled into an NMR tube containing 50mg (42.8 μmol) of compound 1 under argon at -196°C. Benzenethiol, ethanethiol or hydrogen sulfide were added by gas-tight syringe to the NMR tubes at -78°C. These tubes were flame sealed at -196°C, then transferred to the NMR probe at -80°C. The various NMR experiments were performed at this temperature, then the probe was warmed in 10° intervals with the appropriate spectra being obtained at the different temperatures. The spectroscopic results of these studies are reported in Table 4.1.

X-ray Data Collection

Red crystals of $[RhRe(CO)_3(\mu\text{-H})(\mu\text{-SEt})(dppm)_2]$ (5) were obtained by slow evaporation of a concentrated solution of the complex in 1:1 THF/Et_2O. Several suitable crystals were mounted and flame sealed under Ar in glass capillaries. Data were collected on an Enraf-Nonius CAD4 diffractometer with use of MoKα radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $20.0° \leq 2\theta \leq 24.0°$. A monoclinic crystal system was established by the usual peak search and reflection indexing programs, and systematic absences (h0l: l = odd, 0k0: k = odd) in the data were consistent with the space group $P2_1/c$.

Intensity data were collected at 22°C using the $\theta/2\theta$ scan technique to a maximum $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak width on either side of the peak. Three reflections were chosen as intensity standards and were remeasured at 120-min intervals of the X-ray exposure. There was no significant systematic decrease in the intensities of these standards so no correction was applied. A total of 9654 unique reflections were measured and processed in the usual way using a value of 0.04 for p[10]; of these 5011 were observed and were used in refinements.[11] Absorption corrections were applied to the data using the method of Walker and Stuart.[12] The details of the data collection are sumarized in Table 4.2.

Structure Solution and Refinement

The structure was solved in the space group $P2_1/c$ using standard Patterson techniques to locate the Rh and Re atoms and the normal sequence of least-squares and difference Fourier cycles to locate all other atoms. Atomic scattering factors[13,14] and anomalous dispersion terms[15] were taken from the usual tabulations. All hydrogen atoms, with the exception of the hydride ligand, were included as fixed contributions but not refined. Their idealized positions were calculated from the geometries about the attached carbon atoms, and they were assigned thermal parameters 20% greater than the equivalent isotropic B's of their attached C atoms. One THF molecule was located and, apart from the large thermal parameters of this group, suggesting some disorder, it refined acceptably. The hydride ligand was successfully refined with use of an isotropic thermal parameter. The methyl group of the bridging ethylthiolate group did not behave well, suggesting that it was slightly disordered. Although the electron density associated with this carbon was diffuse only one maximum was observed. The top ten peaks in the final difference Fourier map (0.68 - 1.03 e/Å^3) were in the vicinities of the Re atom, the disordered methyl group of the thiolato ligand and the THF molecule. The positional and thermal parameters are given in Table 4.3.

Table 4.2 Crystallographic Data for [$RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SEt)(dppm)_2$]·THF

formula	$C_{59}H_{58}O_4P_4SReRh$
fw	1276.2
space group	$P2_1/c$ (No. 14)
a, Å	12.216(3)
b,Å	19.845(7)
c,Å	23.316(7)
β, deg	103.19(2)
V, $Å^3$	5503
Z	4
d_{calcd}, g cm^{-3}	1.540
temp, °C	22
radiation, Å	MoKα, 0.71069
monochromator	graphite
μ, cm^{-1}	27.175
transmission coefft (min, max)	0.702, 1.338
unique data collected	9654
unique observed data (NO)	5011
no. of variables (NV)	370
R^a	0.049
R_w	0.056
error in obs. of unit wt. (GOF)	1.516

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[a] As defined in Table 2.2.

Table 4.3 Positional and Thermal Parameters for [RhRe(CO)$_3$(μ-H)(μ-SEt)-(dppm)$_2$]·THF [a,b]

Atom	x	y	z	B(Å^2)[c]
Re	0.18442(4)	0.11142(2)	-0.22341(2)	3.139(8)
Rh	0.35985(7)	0.21447(5)	-0.17965(4)	3.26(2)
S	0.3912(3)	0.0899(2)	-0.1899(2)	5.02(8)
P(1)	0.2938(2)	0.2333(2)	-0.0968(1)	3.46(7)
P(2)	0.1472(2)	0.1049(2)	-0.1272(1)	3.52(6)
P(3)	0.3747(2)	0.2457(2)	-0.2725(1)	3.40(7)
P(4)	0.2203(2)	0.1216(2)	-0.3204(1)	3.27(6)
O(1)	0.5812(7)	0.2771(5)	-0.1239(4)	6.6(3)
O(2)	0.0655(7)	-0.0230(4)	-0.2551(4)	7.0(2)
O(3)	-0.0382(7)	0.1830(5)	-0.2682(4)	7.1(3)
C(1)	0.4979(9)	0.2514(6)	-0.1446(5)	4.7(3)
C(2)	0.113(1)	0.0285(6)	-0.2428(5)	4.9(3)
C(3)	0.0445(9)	0.1538(6)	-0.2503(5)	4.3(3)
C(4)	0.2369(9)	0.1578(5)	-0.0699(5)	3.7(3)
C(5)	0.3411(8)	0.1760(5)	-0.3263(4)	3.3(2)
C(6)	0.454(1)	0.0566(9)	-0.1174(7)	9.6(5)
C(7)	0.533(2)	0.014(2)	-0.108(1)	26(1)
C(11)	0.4007(9)	0.2612(6)	-0.0319(5)	4.1(3)*
C(12)	0.456(1)	0.2187(7)	0.0116(6)	6.1(3)*
C(13)	0.542(1)	0.2447(8)	0.0581(6)	7.0(4)*
C(14)	0.563(1)	0.3099(8)	0.0588(6)	6.9(4)*
C(15)	0.515(1)	0.3539(8)	0.0200(6)	7.3(4)*
C(16)	0.430(1)	0.3295(7)	-0.0278(6)	6.0(3)*

Table 4.3 (continued)

C(21)	0.1808(8)	0.2938(5)	-0.0987(5)	3.5(2)*
C(22)	0.1053(9)	0.3072(6)	-0.1522(5)	4.6(3)*
C(23)	0.015(1)	0.3503(8)	-0.1535(6)	6.9(4)*
C(24)	-0.000(1)	0.3803(7)	-0.1022(6)	6.4(3)*
C(25)	0.071(1)	0.3662(7)	-0.0501(6)	6.5(4)*
C(26)	0.161(1)	0.3219(6)	-0.0474(5)	5.2(3)*
C(31)	0.1622(8)	0.0223(6)	-0.0898(5)	3.6(2)*
C(32)	0.1299(9)	0.0155(6)	-0.0356(5)	4.1(2)*
C(33)	0.148(1)	-0.0454(6)	-0.0049(5)	4.9(3)*
C(34)	0.197(1)	-0.0980(7)	-0.0271(6)	5.7(3)*
C(35)	0.226(1)	-0.0937(8)	-0.0794(6)	7.4(4)*
C(36)	0.209(1)	-0.0321(7)	-0.1107(6)	5.6(3)*
C(41)	0.0018(8)	0.1251(5)	-0.1248(5)	3.6(2)*
C(42)	-0.0309(9)	0.1801(6)	-0.0971(5)	4.5(3)*
C(43)	-0.148(1)	0.1934(7)	-0.1025(6)	5.6(3)*
C(44)	-0.225(1)	0.1514(7)	-0.1331(6)	5.6(3)*
C(45)	-0.196(1)	0.0955(7)	-0.1598(6)	6.1(3)*
C(46)	-0.081(1)	0.0823(7)	-0.1560(5)	5.4(3)*
C(51)	0.5166(8)	0.2680(5)	-0.2790(4)	3.4(2)*
C(52)	0.548(1)	0.3350(7)	-0.2832(5)	5.4(3)*
C(53)	0.661(1)	0.3495(7)	-0.2858(6)	6.2(3)*
C(54)	0.735(1)	0.2986(8)	-0.2826(6)	6.8(4)*
C(55)	0.705(1)	0.2325(8)	-0.2792(6)	7.0(4)*
C(56)	0.596(1)	0.2175(7)	-0.2766(5)	5.0(3)*
C(61)	0.2866(9)	0.3144(6)	-0.3122(5)	3.8(2)*

Table 4.3 (continued)

C(62)	0.202(1)	0.3391(7)	-0.2903(6)	6.0(3)*
C(63)	0.127(1)	0.3870(8)	-0.3225(6)	7.6(4)*
C(64)	0.143(1)	0.4060(7)	-0.3766(6)	6.8(4)*
C(65)	0.228(1)	0.3839(7)	-0.3978(5)	5.7(3)*
C(66)	0.301(1)	0.3373(6)	-0.3658(5)	4.9(3)*
C(71)	0.2565(9)	0.0465(5)	-0.3579(5)	3.8(2)*
C(72)	0.281(1)	-0.0145(6)	-0.3297(5)	4.9(3)*
C(73)	0.309(1)	-0.0721(7)	-0.3577(6)	5.7(3)*
C(74)	0.308(1)	-0.0684(7)	-0.4168(5)	5.4(3)*
C(75)	0.286(1)	-0.0076(7)	-0.4469(6)	6.0(3)*
C(76)	0.261(1)	0.0497(7)	-0.4173(6)	5.8(3)*
C(81)	0.0959(9)	0.1508(5)	-0.3749(5)	3.6(2)*
C(82)	0.008(1)	0.1051(7)	-0.3897(6)	6.1(3)*
C(83)	-0.095(1)	0.1271(8)	-0.4278(7)	7.5(4)*
C(84)	-0.106(1)	0.1921(8)	-0.4490(7)	7.3(4)*
C(85)	-0.017(1)	0.2355(8)	-0.4368(7)	7.6(4)*
C(86)	0.085(1)	0.2132(7)	-0.3973(6)	5.7(3)*
H(1)	0.251(9)	0.212(6)	-0.216(5)	5(1)*

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[a] Starred atoms were refined isotropically.

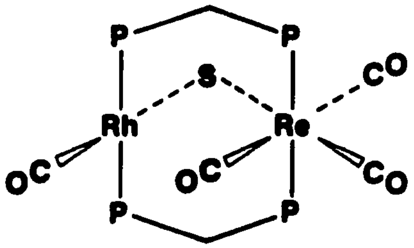
[b] THF molecule values given in the Supplementary Material.

[c] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Results and Discussion

The mixed-metal species, [RhRe(CO)$_4$(dppm)$_2$] (**1**), reacts readily with 1 equiv of H_2S yielding [RhRe(CO)$_4$(μ-S)(dppm)$_2$] (**2**) and H_2 quantitatively. This extremely facile reaction reconfirms the tendency of this low valent species to undergo binuclear oxidative addition-reactions as shown in Chapter 3, and also suggests that the coordinatively unsatured Rh center is of paramount importance to the reactivity of this species. By comparison, the coordinatively saturated dirhenium analogue, [Re$_2$(CO)$_6$(dppm)$_2$], required rather vigorous conditions before reactions with substrates were observed,[16] owing to the necessity for prior CO loss.

Formulation of **2** is based on its elemental analyses and its spectroscopic data. Its IR spectrum displays four carbonyl stretches (see Table 4.1) in a pattern very reminiscent of that observed (2046, 2001, 1937, 1908 cm^{-1}) for [RhRe(CO)$_4$(μ-H)(dppm)$_2$] [BF$_4$], the structure of which has been determined (see Chapter 3). The higher frequencies observed for the cationic species is consistent both with its positive charge and with the apparently excellent electron-donor capabilities of the bridging sulfide group in **1**; related sulfide-bridged complexes of Rh and Ir have also been observed to have low-carbonyl stretches.[17-19] The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a pattern consistent with an AA'BB'X spin system in which the diphosphine ligands bridge the metals in a trans arrangement, and the ^1H NMR spectrum shows no evidence of hydride species. The $^{13}C\{^1H\}$ NMR spectrum displays the expected four carbonyl resonances, with only the one at δ 193.5 showing obvious coupling to Rh($^1J_{Rh\text{-}C}$ = 70 Hz). Consequently the following structure is proposed in which the metals are bridged by the sulfide group, giving a square planar configuration typical of a Rh(I) center, as observed in $[M_2(CO)_2(\mu\text{-}S)(dppm)_2]$ (M = Rh. Ir),[17,18] and giving a coordinatively saturated octahedral geometry for Re(I). However, when the $^{13}C\{^1H\}$ NMR spectrum is also broadband ^{31}P-decoupled, the complex multiplet at low field (δ 215.8) resolves into an 8-line pattern in which coupling to two other carbonyl groups and to Rh becomes

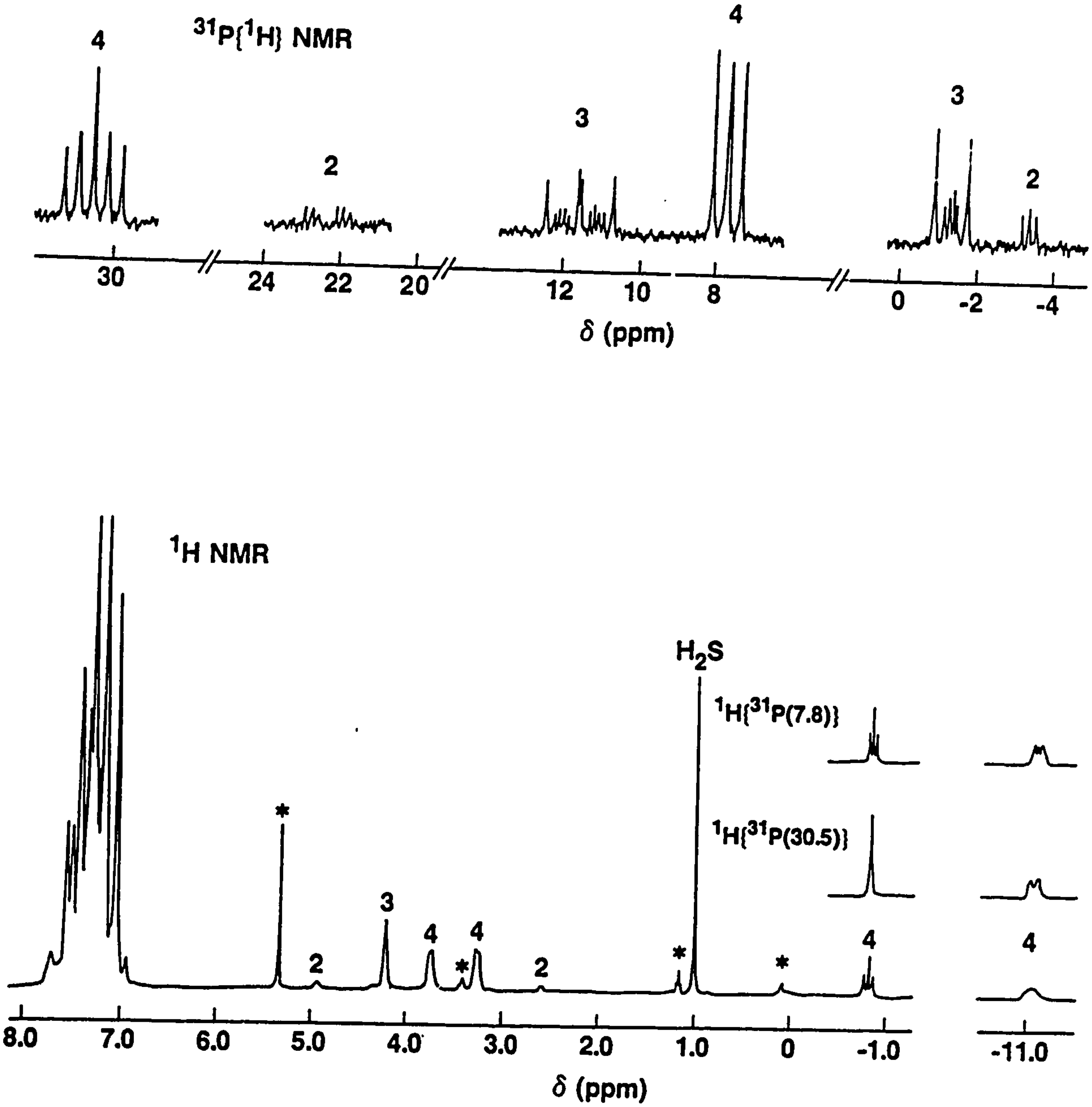


2

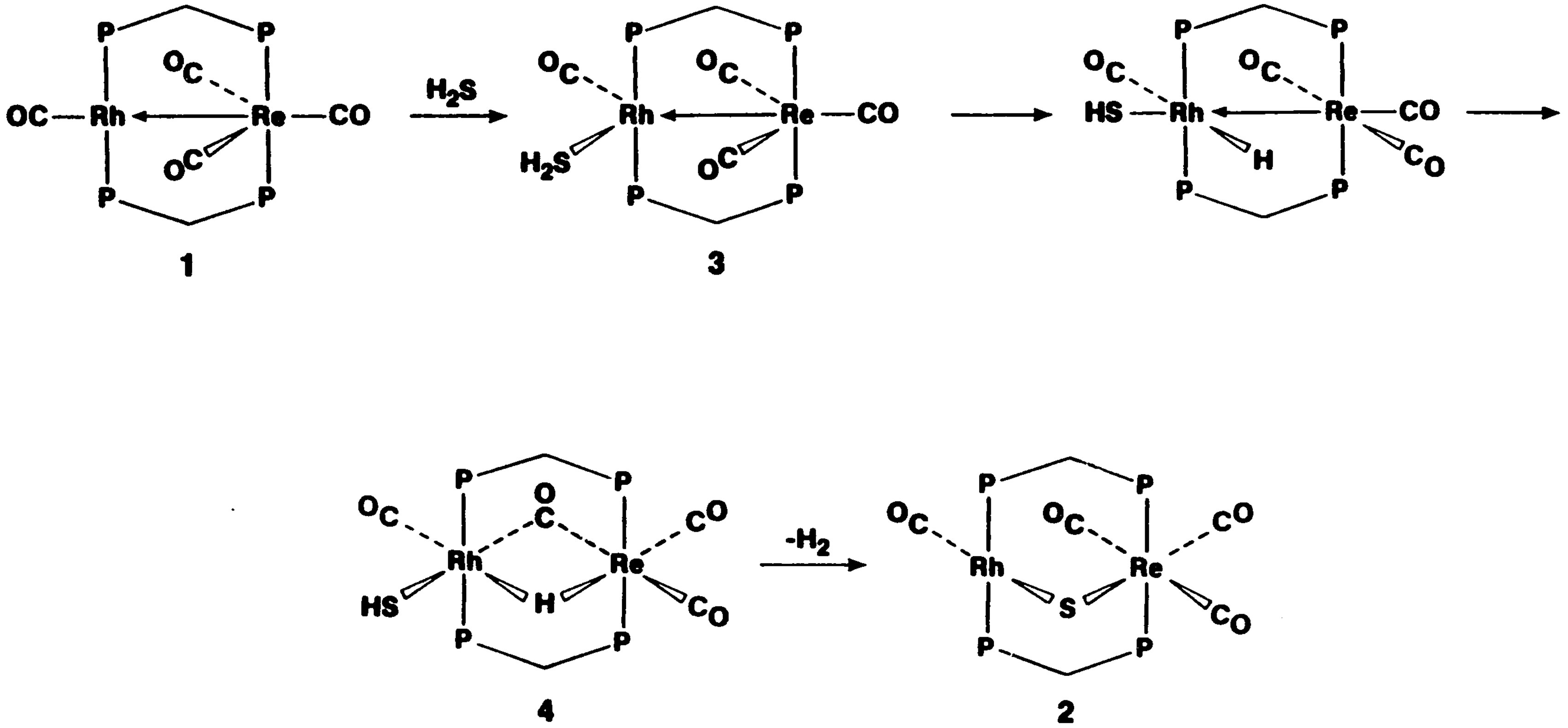
obvious ($^2J_{C\text{-}C}$ = 19 Hz, 4 Hz; $^1J_{Rh\text{-}C}$ = 9 Hz). This resonance corresponds to the carbonyl ligand on Re which is directed towards Rh; it displays a large coupling to the trans carbonyl and smaller coupling to the cis carbonyl group. The small value for the Rh coupling suggests that this ligand is best viewed as terminally bound to Re, as shown, but having a weak semi-bridging interaction with Rh. The coupling between the other two Re-bound carbonyls ($^2J_{C\text{-}C}$ = 4 Hz) is also consistent with these groups being mutually cis. Oxidative addition of H_2S to the related binuclear species, $[Pd_2Cl_2(dppm)_2]$[3] and $[Rh_2(CO)_3(dppm)_2]$,[2] yielded rather analogous sulfide-bridged species, whereas the same reaction with $[Ir_2(CO)_3(dppm)_2]$[2] instead yielded a sulfide-bridged dihydride, which under more forcing conditions also yielded the sulfide-bridged analogue through H_2 loss.

In order to gain information about intermediates in the formation of 2, which could then lead to a better understanding of how the two metals are involved, the above reaction was performed and monitored at low temperature, by using ^1H, ^{13}C and ^{31}P NMR spectroscopy. At -80°C the $^{31}P\{^1H\}$ NMR spectrum shows only two species (**3** and **4**), in roughly equal proportions. Each species has a spectrum which is characteristic of an AA'BB'X spin system, displaying a second-order multiplet for the Re-bound phosphorus nuclei and a doublet of multiplets for those bound to Rh. Figure 4.1 shows the $^{31}P\{^1H\}$, ^1H, and $^1H\{^{31}P\}$ NMR spectra at -60°C, on which appears the resonances for **3** and **4** as well as those of the final product (**2**)(*vide infra*). The corresponding ^1H NMR spectrum (at -80°C) shows two highfield resonances, at δ - 0.85 (triplet) and -11.10 (multiplet) having chemical shifts which are characteristic of a sulfhydryl group[3,5-7,20,21] and a metal hydride, respectively. Heteronuclear phosphorus decoupling experiments establish that both of these high-field resonances are associated with species **4** and also establish that the SH proton is coupled to the two phosphorus nuclei on Rh but displays no coupling to Rh, while the hydride ligand is coupled to Rh and to all four phosphorus nuclei. All resonances due to the dppm methylene groups can also be assigned based on the decoupling experiments. The $^{13}C\{^1H\}$ NMR spectrum of a sample, which was 70% enriched with ^{13}CO, shows five carbonyl resonances. Four of these (three singlets and a doublet), belonging to **4**, integrate equally as one carbonyl each, while the fifth (a 280 Hz-wide signal) integrates as four carbonyls, based on the proportions of **3** and **4**, established by the $^{31}P\{^1H\}$ and ^1H NMR spectra. It appears, therefore, that both **3** and **4** are tetracarbonyl species so are formulated as shown in Scheme 4.1. Compound **3** is shown as an H_2S adduct even though no resonance can be established as due to a coordinated H_2S group. Assuming that this species is fluxional, as suggested by the $^{13}C\{^1H\}$ NMR spectrum , the H_2S may be rapidly exchanging with free H_2S in solution and may also be exchanging over both metals, as suggested by the one broad carbonyl resonance. This is assumed to occur by

Figure 4.1 ^1H NMR, $^{31}P\{^1H\}$, and $^1H\{^{31}P\}$ NMR spectra (at 161.9 MHz) at -60°C for the reaction of [$RhRe(CO)_4(dppm)_2$] with H_2S.



Scheme 4.1



a "merry-go-round" exchange of the ligands (CO and H_2S) in the equatorial plane perpendicular to the metal-phosphine bonds, such that these ligands migrate around the $RhReP_4$ framework. These NMR results can also be rationalized by an alternate fluctional process in which the Rh and Re-bound carbonyl ligands in **3** exchange through an intermediate with two bridging carbonyls, while **3** is also in rapid equilibrium with H_2S and **1**. Either mechanism is possible, however we feel that the latter is more likely since the former is without precedent. In spite of our failure to observe a resonance for the coordinated H_2S group, we are confident of this formulation since the $^{31}P\{^1H\}$ NMR spectrum of the labile CO adduct of **1** discussed in Chapter 3 has a very similar appearance to that of **3** and again displays only one broad carbonyl resonance. Although this CO adduct also cannot be isolated, the isoelectronic species $[IrOs(CO)_5(dppm)_2][BF_4]$ has been structurally characterized[22] and shows the type of structure proposed for **3**.

Attempts to obtain a better model of the proposed H_2S adduct, **3**, through addition of Me_2S to **1**, were not successful since surprisingly no reaction was observed, even at -80°C.

Transformation of **3** to **4** is envisioned as occurring via oxidative addition at Rh to give the intermediate shown, in which an octahedral Rh(III) center is formulated, and rearrangement to **4** should then be quite facile, explaining our failure to observe this precursor to **4**. Compound **4** is formulated as having a bridging carbonyl ligand, based on the low-field resonance at δ 248 in the $^{13}C\{^1H\}$ NMR spectrum. However, this resonance displays no resolvable coupling to Rh, suggesting that its interaction with this metal is weak. Owing to the uncertainty involving the exact binding mode of this carbonyl ligand it is difficult to make unambiguous assignments of the metal oxidation states and electron counts in this intermediate, although 18e configurations at both metals result if the bridging carbonyl donates one electron to each metal and if the bridged hydride is viewed as a Rh-H bond acting as a 2e donor to Re, as suggested later for compound **5** (*vide infra*). It should be noted that although the hydride-bridged species are drawn in the schemes without Rh-Re bonds, 3-center Rh-H-Re interactions are implied.

Warming the solution to -60°C leads to a substantial reduction in the concentration of **3**, as shown by the ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra, and a corresponding increase in the concentration of **4**. The final product **2** also appears at this temperature as shown in Figure 4.1. No other species is observed over the temperature range between -80°C and 20°C, so clearly the presumed second oxidative addition step is followed by rapid elimination of H_2.

Although similar studies on the low temperature reaction of H_2S with the Os analogue of **1**, $[RhOs(CO)_4(dppm)_2]^+$,[23] have revealed an additional intermediate which immediately precedes the formation of the bridging-sulfido tetracarbonyl, this has not been observed in the Rh/Re system. This complex, $[RhOs(CO)_3(\mu\text{-}SH)(H)(dppm)_2]^+$, is formed by loss of CO from $[RhOs(CO)_4(\mu\text{-}H)(SH)(dppm)_2]^+$, movement of the SH into a bridging position and migration of the hydride into a terminal position on Os. This intermediate then picks up CO with loss of H_2 to form the tetracarbonyl μ-sulfido species.

In an attempt to obtain further information about the monohydride intermediates in this binuclear oxidative-addition reaction, we attempted to model the H_2S chemistry by following the analogous reactions with thiols. Although compound **1** also reacts readily with the thiols HSEt and HSPh by oxidative addition of the H-S bond, as was the case for H_2S, the final products are not totally analogous to any of the proposed intermediates in the H_2S

reaction. In particular, the reactions with these thiols result in CO loss to yield the tricarbonyl complexes, $[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SR)(dppm)_2]$ (R = Et (5), Ph (6)). Both species display three carbonyl bands in the IR spectra and also have $^{31}P\{^1H\}$ spectra as expected for an AA'BB'X spin system . The ^1H NMR spectrum displays a high-field multiplet for each species, at δ -10.5 (5) and -9.7 (6), and selective ^{31}P decoupling experiments clearly indicate that the hydride ligand in each compound bridges the metals, displaying coupling to Rh and to all phosphorus nuclei (see Table 4.1).

The X-ray structure determination of 5 confirms our formulation, and furthermore establishes that the thiolato group bridges the metals on the opposite face of the dimer from the hydride ligand. Although this may appear to be unusual, facile tunnelling of a hydride ligand from one face of a dimer to the other has been previously proposed[19,24] in similar systems (see also Chapters 2 and 3). Figure 4.2 shows a perspective view of compound 5, and relevant bond lengths and angles are given in Tables 4.4 and 4.5. If the Rh-Re interaction is ignored, the geometry about Rh is that of tetragonal pyramid in which S occupies the apical site and P(1), P(3), C(1) and H(1) occupy the basal sites. The P(1)-Rh-P(3) and C(1)-Rh-H(1) angles of 150.5(1)° and 158(4)°, respectively, and the angles between S and the four basal groups, of between 93(4)°and 109.3(1)°, are consistent with this description. About Re the geometry is a distorted octahedron in which H(1), or more appropriately, the Rh-H(1) bond can be considered as occupying the sixth site opposite C(2) (*vide infra*). The major distortions result from the strain imposed by the bridging thiolate group and the associated acute Rh-S-Re angle of 72.44(8)°. Consistent with the distorted octahedral geometry about Re, the P(2)-Re-P(4) angle (178.25(9)°) is close to linear, unlike the analogous phosphine arrangement about Rh, and all other angles, apart from those involving sulfur but

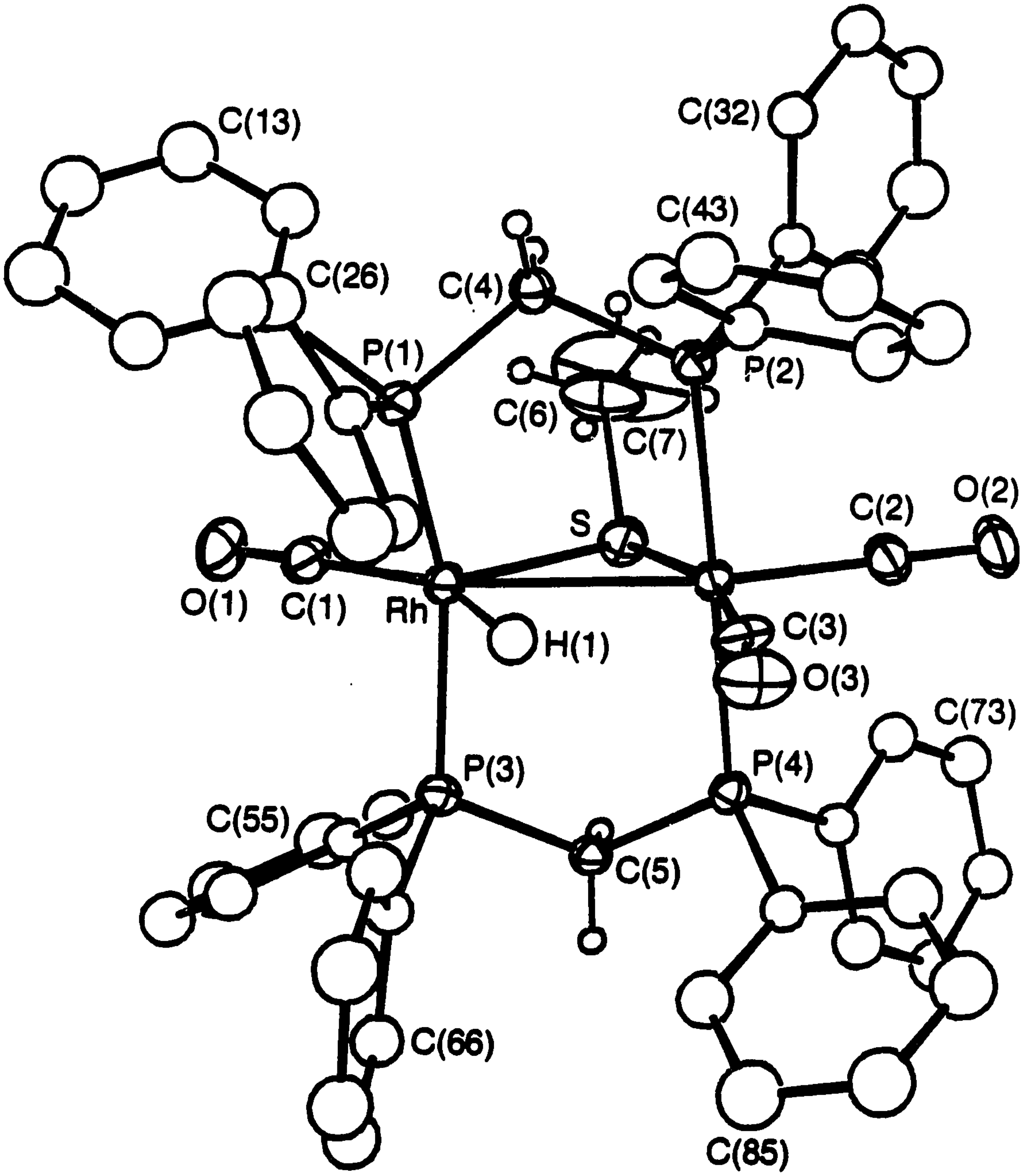


Figure 4.2 A perspective view of [RhRe(CO)$_3$(μ-H)(μ-SEt)(dppm)$_2$] (5) showing the numbering scheme. Thermal parameters are shown at the 20% level except for the methylene hydrogens on the dppm ligands and hydrogens on the ethylthiolate group, which are drawn arbitrarily small. Phenyl hydrogens are omitted.

Table 4.4 Selected Bond Lengths (Å) for [RhRe(CO)$_3$(μ-H)(μ-SEt)(dppm)$_2$] [a]

Re-Rh	2.9697(8)	P(1)-C(21)	1.823(9)
Re-S	2.505(3)	P(2)-C(4)	1.850(9)
Re-P(2)	2.392(2)	P(2)-C(31)	1.846(9)
Re-P(4)	2.408(2)	P(2)-C(41)	1.834(9)
Re-C(2)	1.87(1)	P(3)-C(5)	1.849(9)
Re-C(3)	1.88(1)	P(3)-C(51)	1.828(9)
Re-H(1)	2.1(1)	P(3)-C(61)	1.84(1)
Rh-S	2.521(3)	P(4)-C(5)	1.858(9)
Rh-P(1)	2.287(3)	P(4)-C(71)	1.831(9)
Rh-P(3)	2.299(3)	P(4)-C(81)	1.839(9)
Rh-C(1)	1.85(1)	O(1)-C(1)	1.14(1)
Rh-H(1)	1.4(1)	O(2)-C(2)	1.18(1)
S-C(6)	1.81(1)	O(3)-C(3)	1.16(1)
P(1)-C(4)	1.821(9)	C(6)-C(7)	1.27(2)
P(1)-C(11)	1.84(1)		

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[a] Parameters for the Phenyl rings and the THF molecule are given in the Supplementary Material.

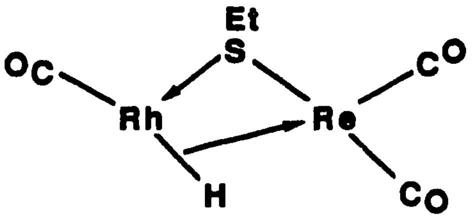
Table 4.5 Selected Angles (deg) for [RhRe(CO)$_3$(μ-H)(μ-SEt)(dppm)$_2$]

Rh-Re-S	54.04(6)	Re-Rh-C(1)	159.8(3)	C(4)-P(2)-C(31)	100.6(4)
Rh-Re-P(2)	89.53(6)	Re-Rh-H(1)	42(4)	C(4)-P(2)-C(41)	105.8(4)
Rh-Re-P(4)	89.62(6)	S-Rh-P(1)	109.3(1)	C(31)-P(2)-C(41)	99.9(4)
Rh-Re-C(2)	161.9(3)	S-Rh-P(3)	97.4(1)	Rh-P(3)-C(5)	112.6(3)
Rh-Re-C(3)	109.6(3)	S-Rh-C(1)	106.7(3)	Rh-P(3)-C(51)	115.0(3)
Rh-Re-H(1)	26(3)	S-Rh-H(1)	93(4)	Rh-P(3)-C(61)	121.0(3)
S-Re-P(2)	95.28(9)	P(1)-Rh-P(3)	150.5(1)	C(5)-P(3)-C(51)	101.2(4)
S-Re-P(4)	85.45(9)	P(1)-Rh-C(1)	91.4(3)	C(5)-P(3)-C(61)	101.6(4)
S-Re-C(2)	108.0(3)	P(1)-Rh-H(1)	93(4)	C(51)-P(3)-C(61)	102.9(4)
S-Re-C(3)	162.9(3)	P(3)-Rh-C(1)	92.9(3)	Re-P(4)-C(5)	115.9(3)
S-Re-H(1)	78(3)	P(3)-Rh-H(1)	73(4)	Re-P(4)-C(71)	119.7(3)
P(2)-Re-P(4)	178.25(9)	C(1)-Rh-H(1)	158(4)	Re-P(4)-C(81)	112.1(3)
P(2)-Re-C(2)	90.1(3)	Re-S-Rh	72.44(8)	C(5)-P(4)-C(71)	98.9(4)
P(2)-Re-C(3)	89.1(3)	Re-S-C(6)	122.3(5)	C(5)-P(4)-C(81)	108.1(4)
P(2)-Re-H(1)	97(3)	Rh-S-C(6)	108.1(5)	C(71)-P(4)-C(81)	100.3(4)
P(4)-Re-C(2)	91.2(3)	Rh-P(1)-C(4)	113.1(3)	Rh-C(1)-O(1)	177(1)
P(4)-Re-C(3)	89.8(3)	Rh-P(1)-C(11)	114.9(3)	Re-C(2)-O(2)	179(1)
P(4)-Re-H(1)	81(3)	Rh-P(1)-C(21)	119.9(3)	Re-C(3)-O(3)	175.8(9)
C(2)-Re-C(3)	88.5(5)	C(4)-P(1)-C(11)	102.7(4)	P(1)-C(4)-P(2)	115.4(5)
C(2)-Re-H(1)	170(2)	C(4)-P(1)-C(21)	101.7(4)	P(3)-C(5)-P(4)	116.2(4)
C(3)-Re-H(1)	85(3)	C(11)-P(1)-C(21)	102.2(4)	S-C(6)-C(7)	123(2)
Re-Rh-S	53.52(7)	Re-P(2)-C(4)	116.0(3)	Re-H(1)-Rh	112(5)
Re-Rh-P(1)	92.10(7)	Re-P(2)-C(31)	118.1(3)		
Re-Rh-P(3)	93.87(7)	Re-P(2)-C(41)	114.2(3)		

[a] Angles for the Phenyl rings and the THF molecule are given in the Supplementary Material.

including those involving H(1), are near to the idealized values. The Re-P distances (2.392(2), 2.408(2)Å) are longer than the Rh-P distances (2.287(3), 2.299(3)Å), consistent with the larger covalent radius of Re compared to Rh.[25] All other parameters within the diphosphine and carbonyl groups are as expected.

The unusual aspects of the structure involve the central core of the metals, the hydride and thiolate ligands. We suggest that the parameters involving these groups imply a bonding pattern as shown below. In spite of the larger metallic radius of Re, the Re-S distance (2.505(3)Å), is shorter than the Rh-S distance (2.521(3)Å), and suggests that the thiolate ligand functions as an anionic group towards Re, binding to Rh via a weaker dative bond, The Rh-S interaction appears to be substantially weaker than the comparable interactions in the sulfhydryl-bridged species, $[RhCl(H)(\mu\text{-}SH)(PPh_3)_2]_2$[4] and the sulfide-bridged species, $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$,[17] in which Rh-S distances of 2.384(1)Å and 2.367(3)Å, respectively, were observed, lending support to our proposal of a weaker dative interaction in **5**. The sixth coordination site on Re (opposite C(2)) is then occupied by the Rh-H bond which forms an agostic-like interaction with Re. This three-center Rh-H-Re interaction would be expected to result in a longer Rh-Re distance than in a two-electron, two-center interaction between the metals; consequently the Rh-Re distance (2.9697(8)Å) in **5** is much longer than in the precursor **1** (2.7919(6)Å).[8] Such a view of bridged hydrides has been considered previously,[26] and can be a useful way of considering the three-centered two-electron M-H-M' interaction. Also consistent with such a description, the Rh- H(1) bond (1.4(1)Å) is substantially shorter than the Re-H(1) distance (2.1(1)Å), although in reality these distances are not accurately determined owing to the dominant X-ray scattering by the



5

heavy metals. Therefore, the true hydride location is probably further from Rh and closer to Re by as much as 0.2-0.3Å.

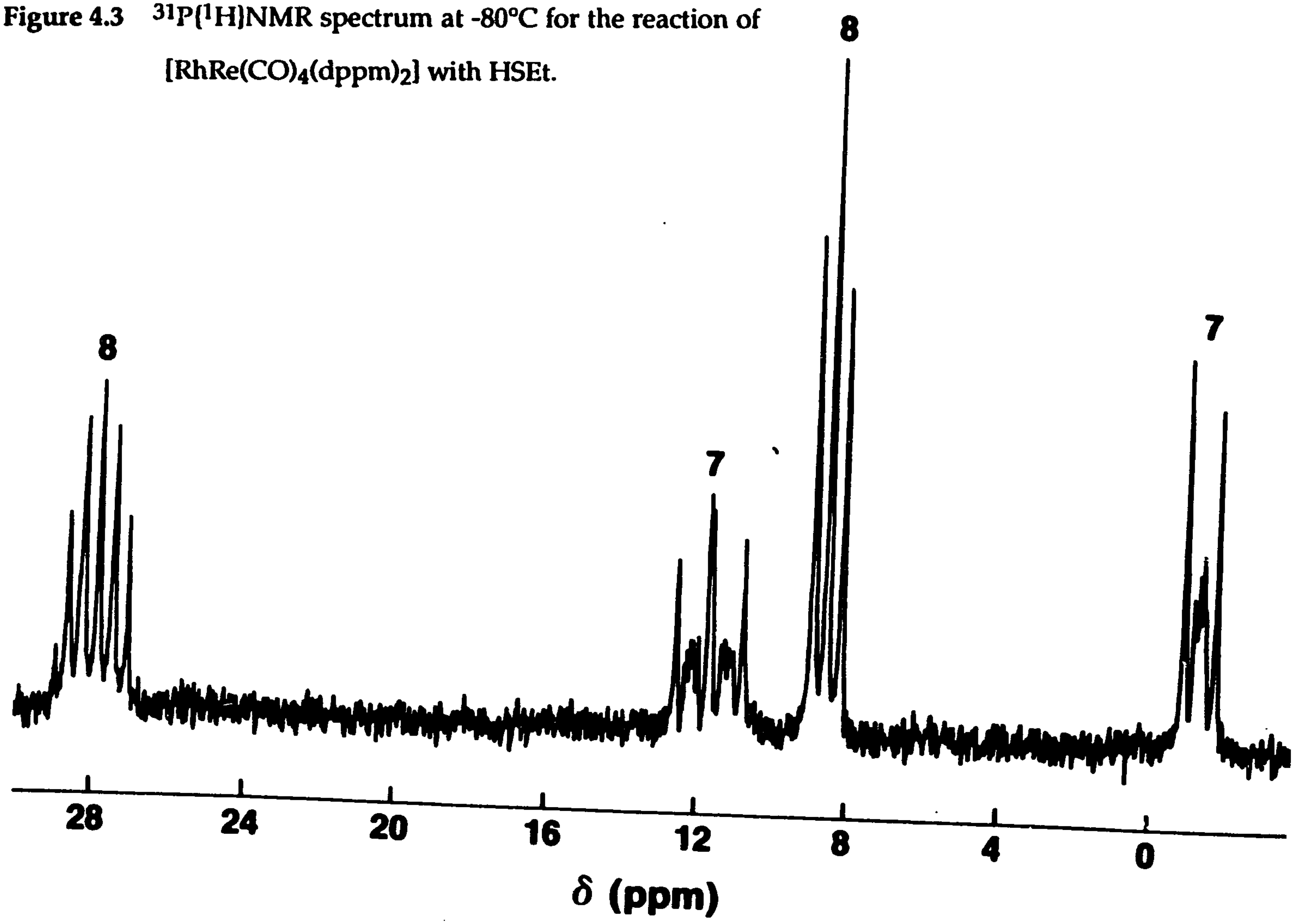
The geometry within the bridging thiolato group is normal, although there is clearly disorder of the methyl carbon about several closely spaced, unresolved positions.

In an attempt to again characterize intermediates in these transformations involving the thiols we monitored these reactions by NMR spectroscopy at low temperatures. In the reaction of **1** with HSEt at -80°C only two products are again observed in the $^{31}P\{^1H\}$ NMR spectrum as shown in Figure 4.3. It is significant that even at -80°C there is no evidence of starting material, indicating that **1** is clearly reactive. The two intermediates observed (**7** and **8**) have $^{31}P\{^1H\}$ NMR patterns almost superimposable on those observed in the H_2S reaction, so are given analogous formulations, as shown in Scheme 4.2. Compound **7** is proposed to be an EtSH adduct, although again we failed to detect the ^1H NMR signal for the coordinated thiol. Species **8** contains a hydrido ligand which bridges both metals as shown by the hydride resonance at δ -11.1, displaying coupling to Rh and the four phosphorus nuclei. The $^{13}C\{^1H\}$ NMR spectrum shows that both species are tetracarbonyls, and again the first adduct (**7**) displays only a broad resonance integrating as four carbonyl groups, while **8** shows four separate resonances integrating as one carbonyl each. The presence of only one broad carbonyl resonance in the $^{13}C\{^1H\}$ NMR spectrum of **7** again suggests a process which exchanges all carbonyls, possibly *via* the same mechanism as compound **3**. Significantly, in a related reaction of a Pt_3 cluster with thiols a fluxional HSR adduct was proposed and again no resonance due to the thiol was observed.[27] Monitoring this reaction as the temperature is increased shows a decrease in all NMR resonances due to **7** with a concomitant increase in those of **8**. Resonances due to **5** do not appear until approximately -20°C and by ambient temperature only this species remains. No additional resonances appear throughout the temperature range investigated.

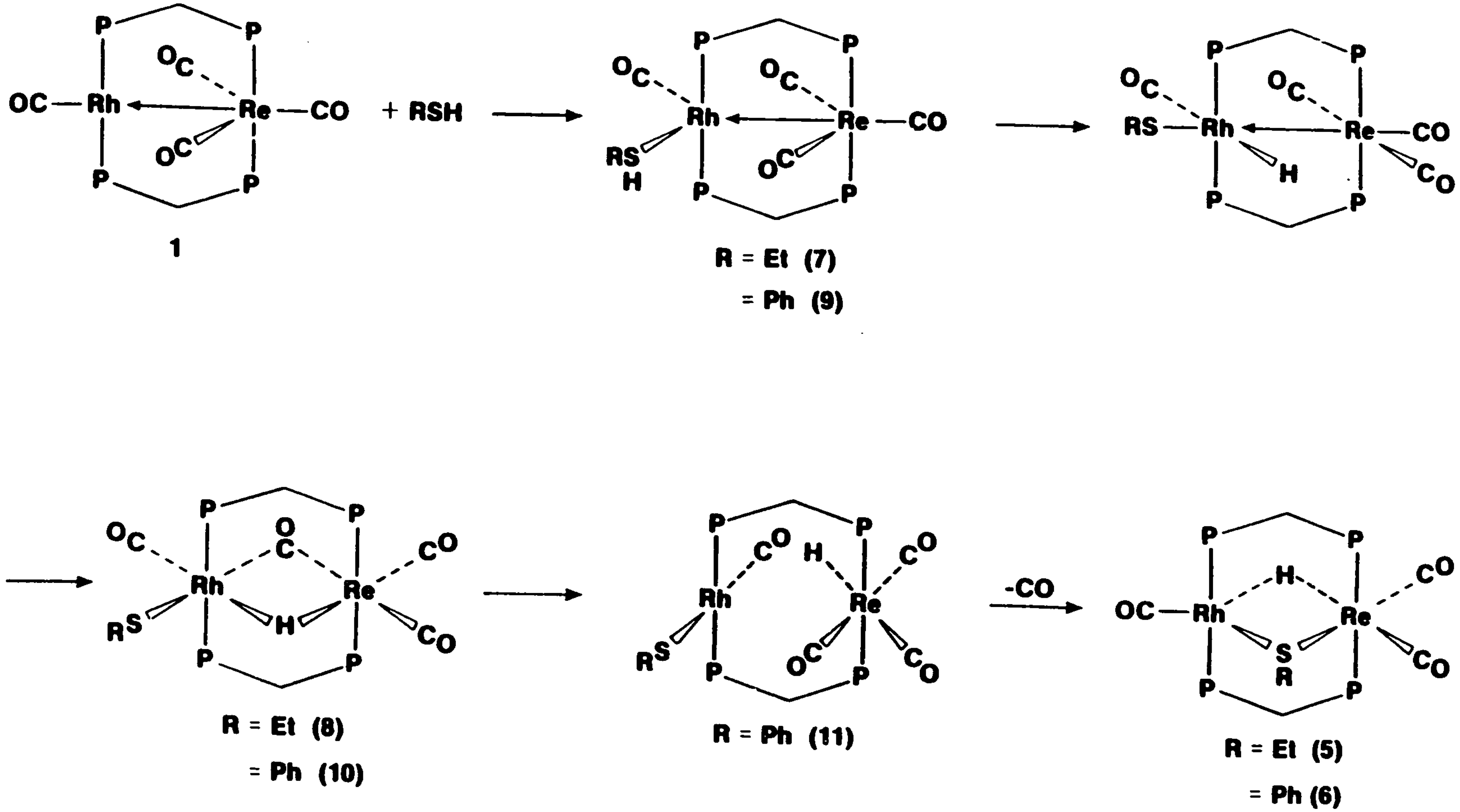
The reaction involving benzenethiol proceeds in much the same manner except that an additional species (**11**) appears at -80°C, together with **9** and **10** which appear exactly analogous to **7** and **8**, respectively. Compound **11** displays a hydride resonance, a broad singlet at δ -10.65, in the ^1H NMR spectrum, and selective ^{31}P decoupling shows that it is bound only to Re, since no effect is observed on irradiating the Rh-bound phosphous nuclei, whereas collapse to a narrower signal is observed on decoupling the Re-bound phosphorus nuclei. The $^{13}C\{^1H\}$ NMR spectrum also shows that this intermediate is a tetracarbonyl. We therefore propose the structure shown in Scheme 4.2 for **11**. Although we cannot unambiguously establish whether the thiolato group and the hydride ligand are on opposite faces of the dimer, as shown, this appears reasonable based on the structure determination of **5**.

It is apparent that the initial stages in the reactions of **1** with H_2S and thiols are analogous. We first observe the simple HSR (R = H, Et, Ph) adducts, in which these groups presumably coordinate at the unsaturated Rh center, followed by oxidative addition to yield a bridging hydride species. Not unexpectedly, the pathways involving H_2S and the thiols begin to diverge after this, since for H_2S, oxidative addition of the second H-S linkage can

Figure 4.3 $^{31}P\{^1H\}$NMR spectrum at -80°C for the reaction of $[RhRe(CO)_4(dppm)_2]$ with HSEt.



Scheme 4.2



occur, whereas the analogous process is much less facile for the R-S linkage of the thiolato group. An intermediate such as **11**, which was only observed for HSPh, may also be important in the second oxidative addition of H_2S since, as formulated, this yields a coordinatively unsaturated, Rh(I) center which can then oxidatively add to the coordinated S-H moiety giving a dihydride species which then reductively eliminates H_2 very readily. In the case of the thiols, for which the second oxidative-addition reaction does not occur, another pathway, in which the terminal thiolato group on Rh forms a dative bond to Re with expulsion of CO, becomes favorable.

Conclusions

Throughout these studies we find no evidence that the Re atom is directly involved in the oxidative-addition reactions. However it is clear that this atom plays a significant role. It appears that the Re can serve to generate coordinative unsaturation at Rh after the first oxidative-addition step, by both cleavage of the Re→Rh dative bond and possibly by accepting a hydrido ligand as shown in the HSPh reaction (species **11**). By contrast, the mononuclear complexes $[RhCl(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$ were also found to undergo the first oxidative addition step with H_2S,[4] but in neither case did oxidative addition of the second S-H bond occur, presumably since the products of the first oxidative additions were in the +3 oxidation states and were much less prone to further oxidative addition. Subsequent reaction of compound **4**, via transfer of the hydride ligand to Re yielding a species analogous to **11**, is akin to reductively eliminating the "$HRe(CO)_3P_2$" moiety to regenerate a Rh(I) center, which is again capable of oxidatively adding to the second S-H bond. The structure determination of **5** also lends support to the idea that facile electron and ligand reorganization over the central core can occur. Although the thiolato group in intermediate **11** is apparently bound to Rh with the hydride on Re, the reverse appears more appropriate in **5**, with the hydride ligand more closely associated with Rh and the thiolate more tightly bound to Re. Such reorganization is clearly important in promoting reactivity in these mixed-metal systems.

Although the studies reported herein do not suggest that the H_2S and thiol reactions procede by a common mechanism after the formation of $[RhRe(\mu\text{- }H)(SR)(CO)_4(dppm)_2]$ (R= Ph, Et, SH), unpublished results within our group have shown that these pathways may be more closely related than originally thought. These results have established that the reaction of H_2S with $[RhOs(CO)_4(dppm)_2]^+$ procedes through a tricarbonyl intermediate, before H_2 loss, with a terminally bound hydride on Os and a bridging SH, as mentioned earlier in this Chapter. This strongly suggests that in the reaction of **1** with H_2S, an analogous tricarbonyl intermediate, too short lived to detect, may be formed via CO loss from **4**. This complex may then lose H_2 and pick up CO to form **2**. This implies that Schemes 3.1 and 3.2 may not diverge, as originally thought, since both may lead to tricarbonyl species. However, in the case of the H_2S reaction, the postulated tricarbonyl complex is able to react further, by losing H_2 and scavenging CO, to form **2**. Conversely, **4** and **5** are not able to react in this fashion, because they cannot undergo dihydrogen loss. Currently we are attempting to obtain addition information on the intermediates in such reactions with aims of learning more about the involvement of the Re center in this chemistry.

Supplementary Material Available

Anisotropic thermal parameters, additional bond lengths and angles and hydrogen atom parameters, summary of crystallographic data, and positional parameters for all atoms (9 pages); listings of the observed and calculated structure factors (26 pages). These are available from M. Cowie upon request.

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Chapter 5

Unusual Mixed-Metal Carbonate-Bridged Complexes Via Oxidation of a Carbonyl Ligand in $[RhM(CO)_4(Ph_2PCH_2PPh_2)_2]$ (M = Mn, Re) and $[IrRe(CO)_5(Ph_2PCH_2PPh_2)_2]$.[†]

Introduction

The activation of molecular oxygen by transition metal complexes is an area of considerable interest, in a large part, owing to its relevance to the catalytic oxidation of organic substrates.[1-3] Complexes of the iron, cobalt and nickel triads have played a dominant role in dioxygen activation and a large number of species in which the dioxygen moiety is bound either terminally to one of these metals or bridging two metals, in either peroxo or superoxo formulations, have been characterized.[4-7] In many of these complexes the coordinated O_2 moiety has been shown to react with substrate molecules resulting in substrate oxidation by oxygen atom transfer.[8-14]

It has long been surprising to us that one well known class of binuclear complexes of the above metals, those bridged by dppm ligands (dppm = $Ph_2PCH_2PPh_2$), have been rather unreactive with dioxygen. To our knowledge $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ appears to be the only documented O_2 adduct of this class,[15] although a related dioxygen adduct of $[IrCl(CO)(dppp)]_2$ (dppp = $Ph_2P(CH_2)_3PPh_2$), in which the metals are widely separated, has been reported.[16]

[†] A version of this chapter has been accepted for publication. Antonelli, D.M. and Cowie, M. 1991. *Organometallics*..

During the investigations of the low-valent, mixed-metal complexes [$RhM(CO)_4(dppm)_2$] (M = Mn, Re) discussed in Chapters 3 and 4, it was noted that these species underwent facile oxidative-addition reactions; even exposure of the RhRe complex to chlorinated solvents yielded the chloro-bridged species [$RhRe(CO)_3(\mu\text{-}Cl)_2(dppm)_2$] as noted in Chapter 3 and elsewhere.[17] The reactions of these species with dioxygen were therefore carried out in attempts to obtain analogous oxidation products in which the coordinated dioxygen ligand could be viewed as a peroxo group, much as had been observed in [$Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2$]. The results of this study, in which we failed to observe simple O_2 adducts but instead observed the unusual, facile oxidation of a carbonyl ligand, are reported herein.

Experimental Section

General Experimental Conditions

All solvents were dried and deoxygenated before use and transferred directly to the reaction mixture by cannula. Reactions were conducted with use of standard Schlenk procedures. Prepurified argon was used without further drying or deoxygenating. Hydrated rhodium(III) chloride and iridium(III) chloride were obtained from Johnson Matthey Ltd. and $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were purchased from Strem and sublimed before use. Bis-diphenylphosphino-methane (dppm) was obtained from Aldrich. The 99% carbon-13-enriched carbon monoxide was obtained from Isotec Inc. while O_2 was purchased from Matheson. The compounds [$RhMn(CO)_4(dppm)_2$] (1), [RhRe(CO)4(dppm)2] (2)[18](see also Chapter 2), [$IrCl(dppm)_2$],[19] and [PPN][$Re(CO)_5$][20] were all prepared according to the literature methods.

The ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer, and infrared spectra were run on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr disks) or solutions (KCl windows, 0.5 mm path length). Elemental analyses were performed by the microanalytical service within the department.

Preparation of Compounds

(a) [IrRe(CO)$_5$(dppm)$_2$] (3).

The compound [IrCl(dppm)$_2$] (50 mg, 50.2 μmol) was dissolved in 5 mL of THF and 1 equiv (44 mg, 50.2 μmol) of [PPN][Re(CO)$_5$] in 5 mL of THF was added via cannula. The light orange solution was then stirred for 22 h, during which time a white precipitate of PPNCl appeared. Ten mL of Et_2O was then added by syringe and the solution was filtered to remove PPNCl. After the solvent was removed in vacuo, 2 mL of CH_2Cl_2 was added and CO was passed through the solution at a rate of *ca.* 1 mL sec^{-1} for 15 min with stirring. Twenty mL of Hexane was added and the solution was stirred while a yellow precipitate quickly formed. The solution was filtered and the product washed with 5 x 5 mL of Et_2O. Yield: 53 mg (81%) of a bright yellow powder. Anal. Calcd. for $C_{55}H_{44}IrO_5P_4Re$: C, 51.32; H, 3.44%. Found: C, 51.73; H, 4.01%. The spectroscopic data for all compounds is given in Table 5.1.

(b) [RhMn(CO)$_3$(μ-CO$_3$)(dppm)2] (4).

The compound [RhMn(CO)$_4$(dppm)$_2$] (1) (50 mg, 48.1 μmol) was dissolved in 10 mL of THF. Five mL (ca. 5 equiv) of O_2 was added by gastight syringe

Table 5.1. Spectral Data[a]

		NMR	
	IR, cm^{-1} [b]	$\delta(^{31}P\{^1H\})$ [c]	$\delta(^1H)$ [d]
$[IrRe(CO)_5(dppm)_2]$ (3)	2008 (w), 1965 (s), 1918 (s), 1905 (s), 1877 (m)	-10.1 (m), -2.8 (m)	4.71 (s, 4H)
$[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (4)	1977(m), 1922(m), 1843(s), 1649(m)	57.2 (m), 23.0 (dm, $^1J_{Rh\text{-}P}$ = 132 Hz)	3.38 (m, 2H), 3.53 (m, 2H)
$[RhRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (5)	1968 (s), 1905 (s), 1825 (vs), 1671 (m)	21.8 (dm, $^1J_{Rh\text{-}P}$ = 128 Hz), 16.3 (m)	3.42 (m, 2H), 3.68 (m, 2H)
$[IrRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (6)	1951 (s), 1906 (vs), 1824 (vs), 1670 (w)	14.3 (m), 14.9 (m)	4.26 (m, 2H), 3.32 (m, 2H)

[a] Abbreviations used: IR: w = weak, m = medium, s = strong, vs = very strong; NMR: m = multiplet, dm = doublet of multiplets, s = singlet. [b] CH_2Cl_2 cast on KBr disk. [c] vs 85% H_3PO_4, -40°C in CD_2Cl_2 solvent. [d] Vs TMS, 25°C in CD_2Cl_2 solvent.

and the yellow solution was stirred for 3 h, during which time the solution gradually turned light yellow-brown. The THF was removed in vacuo and the residue was recrystallized from CH_2Cl_2/Et_2O to yield 43 mg (83%) of a light yellow-brown powder. Anal. calcd. for $C_{54}H_{44}MnO_6P_4Rh$: C, 60.58; H, 4.14. Found: C, 60.07; H, 4.28.

(c) $[RhRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (5).

In a procedure identical with that of part (b), 50 mg (42.8 μmol) of $[RhRe(CO)_4(dppm)_2]$ (2) was reacted with O_2 (*ca.* 5 equiv) over 1 1/4 h to yield 41 mg (80%) of a fine yellow-orange powder. Anal. calcd. for $C_{54}H_{44}O_6P_4ReRh$: C, 53.96 ; H, 3.69. Found: C, 53.52; H, 3.95.

(d) $[IrRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (6).

Compound 3 (50 mg, 39 μmol) was dissolved in 5 mL of CH_2Cl_2 and 5 mL of O_2 (*ca.* 4 equiv) was added by syringe causing the yellow solution to darken slightly. After 30 min. of stirring the solvent was removed in vacuo and the residue was recrystallized from CH_2Cl_2/Et_2O to yield 43 mg (85%) of an orange powder. Anal. calcd. for $C_{54}H_{44}IrO_6P_4Re$: C, 50.24; H, 3.43%. Found: C, 50.88; H, 4.01%.

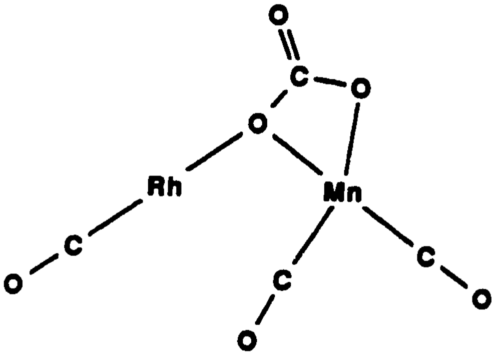
X-Ray Data Collection

Orange crystals of $[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (4) were obtained from CH_2Cl_2/Et_2O. Suitable crystals were mounted and flame-sealed in glass capillaries under argon to minimize decomposition. Unit cell parameters were obtained from least-squares refinements of 25 well-distributed reflections in the range $20.0° \leq 2\theta \leq 24.0°$. A monoclinic cell was established by the usual peak-search and reflection-indexing programs; the systematic absences established the space group as either Cc or C2/c. The centrosymmetric space group was established by successful refinement of the structure.

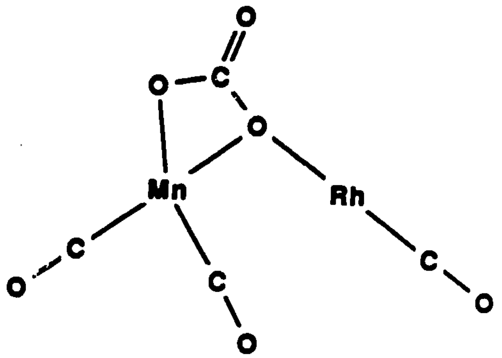
Intensity data were collected at 22°C with use of the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak widths on either side of the scans. Three reflections were chosen as intensity standards and remeasured at 120 min intervals of X-ray exposure. There was no systematic decrease in the intensities, so no correction was applied. Data were processed in the usual way with a value of 0.04 for p,[21] and absorption corrections were applied to the data by using the method of Walker and Stuart.[22,23]

Structure Solution and Refinement

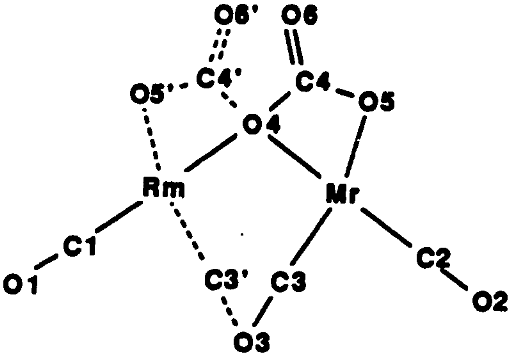
The structure was solved by conventional Patterson and Fourier techniques in space group C2/c. Although location of all atoms was straightforward, initial refinements resulted in unusually high thermal parameters for several of the atoms of the carbonate and carbonyl groups. In addition the isotropic thermal parameter for Rh was unusually high (*ca.* 4.5 $Å^2$) while that of Mn was unusually low (*ca.* 0.7 $Å^2$). A difference Fourier calculation at this stage showed the presence of additional peaks corresponding to atoms of superimposed carbonyl and carbonate groups. This together with the anomalous thermal parameters for the metals led to the model shown in which two complex molecules (A) and (B) are disordered in approximately a 70:30 ratio (determined from the relative peak intensities of the ordered and disordered atoms). The two disordered molecules (A and B) are superimposed such that they have several of the atom positions in common. This is shown in (C) in which Rm and Mr indicate the disordered Rh and Mn positions with Rm being 70% Rh and Mr being 70% Mn. The solid lines connect atoms of the major rotomer whereas the dashed lines show the minor one. The disordered atoms are either unprimed or primed, with the former having the higher occupancy. There was no apparent disorder involving the phosphine groups which appeared to be well behaved.



(A)



(B)



(C)

All non-hydrogen atoms were located. Atomic scattering factors[24,25] and anomalous dispersion terms[26] were taken from the usual sources. Hydrogen atoms were included as fixed contributions and were not refined. Their idealized positions were calculated from the geometries of the attached carbon atoms with a C-H distance of 0.95 Å being used. Hydrogens were assigned thermal parameters of 20% greater than the isotropic B's of the attached carbon atoms. A summary of the crystallographic data is given in Table 5.2. The positional and isotropic thermal parameters for the non-hydrogen atoms, except for those of the phenyl rings, are given in Table 5.3.

Table 5.2 Crystallographic Data for [RhMn(CO)$_3$(μ-CO$_3$)(dppm)$_2$]

formula	$C_{54}H_{44}O_6P_4MnRh$
fw	1043.69
space group	C2/c
a, Å	35.591 (6)
b, Å	12.556 (3)
c, Å	25.277 (5)
β, deg	116.46 (2)
V, Å^3	10112.7
Z	8
d_{calcd}, g cm^{-3}	1.371
temp, °C	22
radiation, Å	MoKα, 0.71069
monochromator	graphite
μ, (cm^{-1})	7.285
transmission coefft. (min, max)	0.901-1.113
unique data collected	9278
observed data (NO)	2942
no. of variables (NV)	366
R[a]	0.079
Rw	0.104
error in obs. of unit wt (GOF)	2.577

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[a] As defined in Table 2.2.

Table 5.3 Positional and Thermal Parameters for [RhMn(CO)$_3$(μ-CO$_3$)(dppm)$_2$]

Atom ^{a}	x	y	z	B, Å$^{2\ b}$
Rh	-0.11852(5)	0.1774(2)	0.04260(8)	3.27(4)
Mn	-0.18187(7)	0.0704(2)	-0.08672(9)	2.52(5)
P(1)	-0.1037(1)	0.0098(4)	0.0831(2)	2.7(1)
P(2)	-0.1582(1)	-0.0949(4)	-0.0409(2)	2.7(1)
P(3)	-0.1409(2)	0.3413(4)	-0.0038(2)	3.2(1)
P(4)	-0.2072(2)	0.2373(5)	-0.1213(2)	3.0(1)
O(1)	-0.0344(4)	0.253(1)	0.1155(6)	6.1(5)
O(2)	-0.1961(4)	0.003(1)	-0.2056(5)	5.4(4)
O(3)	-0.0899(4)	0.121(1)	-0.0644(6)	7.1(4)
O(4)	-0.1774(3)	0.123(1)	-0.0076(4)	2.9(3)
O(5)	-0.2316(4)	0.037(1)	-0.0701(6)	3.4(4)
O(5)'	-0.155(1)	0.202(3)	0.078(2)	1.2(9)*
O(6)	-0.2279(4)	0.085(2)	0.0199(6)	4.5(5)
O(6)'	-0.222(3)	0.178(8)	0.028(4)	14.0(3)*
C(1)	-0.0660(6)	0.224(2)	0.0893(9)	5.0(7)
C(2)	-0.1920(5)	0.027(2)	-0.1602(8)	3.3(5)
C(3)	-0.1273(8)	0.108(2)	-0.075(1)	5.2(8)*
C(3)'	-0.092(2)	0.147(6)	-0.008(3)	3.0(2)*
C(4)	-0.2154(8)	0.082(2)	-0.015(1)	4.6(9)

Table 5.3 (continued)

Atom	x	y	z	B, Å^2
C(4)'	-0.185(2)	0.158(6)	0.039(3)	3.0(2)*
C(5)	-0.1433(5)	-0.092(1)	0.0401(6)	2.4(5)
C(6)	-0.1952(5)	0.333(2)	-0.0598(7)	3.5(5)

---

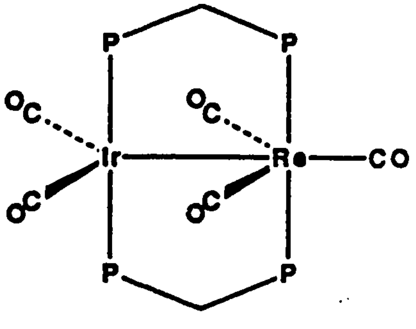
[a] Phenyl carbons are given as Supplementary Material. Primed atoms have 30% occupancy and are related to unprimed (70% occupancy) atoms by the rotational disorder.

[b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3\ [a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + a\beta(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$

Results and Discussion

The rhodium complexes of interest, $[RhM(CO)_4(dppm)_2]$ (M = Mn (**1**), Re (**2**)), are readily prepared, as previously reported[18] and described in Chapter 2, by reaction of $[RhCl(dppm)_2]$ with the sodium salts of the appropriate metal carbonylate anions, $M(CO)_5^-$. However, the IrRe analogue is not obtained by the analogous route utilizing $[IrCl(dppm)_2]$ and $NaRe(CO)_5$, even after 3 days in THF. On the assumption that ion pairing in the sodium salt was reducing the nucleophilicity of the $Re(CO)_5^-$ anion,[27] the PPN salt (PPN = $Ph_3PNPPh_2^+$) was used instead, resulting in the formation of two dppm-bridged IrRe products in an approximately 2:3 mole ratio within 22 h. Treatment of this solution with CO results in complete conversion of the minor product into the major one. It appears that the one equiv of CO released when the dppm groups unwind to bridge the two metals is readily scavenged by the resulting tetracarbonyl complex to yield the pentacarbonyl product $[IrRe(CO)_5(dppm)_2]$ (**3**). The tetracarbonyl species, $[IrRe(CO)_4(dppm)_2]$, which corresponds to the Rh complexes **1** and **2**, is not easily prepared from **3** via carbonyl loss, however it can be prepared by another route as reported[28] and as discussed in Chapter 6. In any case, compound **3** reacts with substrate molecules much as does the tetracarbonyl precursor and because it is more readily handled it has been used in the chemistry reported herein.

The $^{31}P\{^1H\}$ NMR spectrum of **3** displays two multiplets at δ -10.1 and -2.8. Based on a comparison with the spectrum of the Rh analogue,[18] which displays the Re-bound phosphorus resonance at δ -1.6, the low-field resonance in **3** is assigned to the Re-bound phosphorus nuclei and the high field resonance is assigned to those bound to Ir. The IR spectrum of **3** displays five carbonyl stretches at 2008, 1965, 1918, 1905 and 1877 cm^{-1}, again closely comparable to the Rh analogue. Based on these data the structure of 3 is proposed to be analogous to that of the isoelectronic species $[RhRe(CO)_5(dppm)_2]$,[17] discussed in Chapter 3, and $[IrOs(CO)_5(dppm)_2]^+$,[19]



3

the latter of which was characterized by an X-ray structure determination.

The reaction of compounds 1, 2 and 3 with O_2 in THF results in the formation of one product in each case, although at very different rates. With the RhMn compound (1) the reaction requires approximately 3 h, whereas the reactions with the RhRe (2) and IrRe (3) compounds are much faster requiring only 1/4 h and 1/2 h, respectively.

The $^{31}P\{^1H\}$ NMR spectrum of the RhMn product (4) displays two signals at δ 57.2 (multiplet) and 23.0 (doublet of multiplets, $^1J_{P\text{-}Rh}$ = 132 Hz) in a pattern typical of an AA'BB'X spin system, suggesting that the phosphines have remained mutually trans about each metal. The IR spectrum of 4 shows three carbonyl bands at 1977, 1922, and 1843 cm^{-1}, and a band at 1649 cm^{-1} which can be assigned as a carbonate stretch. This carbonate stretch is somewhat higher than those reported for the related carbonate-bridged dirhodium compounds, $[Rh_2(\mu\text{-}CO_3)(CO)_2(P(i\text{-}Pr)_3)_4]$[29] (1533 cm^{-1}), $[Rh_2(\mu\text{-}CO_3)(PPh_3)_5]$[30] (1485 cm^{-1}), and $[(COD)_2Rh_2(\mu\text{-}CO_3)]_3$[31] (1530 cm^{-1}), however it is still close to the expected region for bridging carbonate complexes.[32] The ^1H NMR spectrum of 4 displays two distinct resonances for the dppm methylene protons, indicating the two faces of the complex on either side of the $RhMnP_4$ plane have different environments. It was originally suspected that water might be involved in the reactions, however this was dismissed owing to the failure of compounds **1-3** to react with H_2O at ambient temperature. A search of the ^1H NMR spectra of all products produced no unidentified resonances; in particular, no evidence of a bicarbonate proton was observed.

On the basis of these spectroscopic data a complex containing a carbonato group and three terminal carbonyl ligands can be proposed. However, these data alone are not sufficient to establish the coordination mode of the carbonato group.

The X-ray structure determination of $[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (4) confirms that the species contains a carbonate group and establishes that this group bridges the metals as shown in Figure 5.1. Although as noted earlier the non-phosphine components of the molecule are disordered in a 70:30 ratio, only the molecule having the larger occupancy is shown. In Tables 5.4 and 5.5 the parameters involving both disordered molecules are shown, with the atoms of the minor species being primed, however in this discussion only the parameters of the major species are discussed since they are more reliable. In any case a comparison of the parameters in these tables shows excellent agreement between the two disordered molecules. Owing to this disorder there will be some uncertainty in the metal-ligand parameters.

Both diphosphine ligands bridge the metals in the usual trans configuration with P(1)-Rh-P(3) and P(2)-Mn-P(4) angles of 173.9(1)° and 172.3(1)°, respectively. The metal-phosphorus distances, ranging from 2.295(4) to 2.343(4) Å, are normal, and as noted, any difference expected based on covalent radii differences of Rh and Mn are masked by the disorder. Both metals have the geometries expected

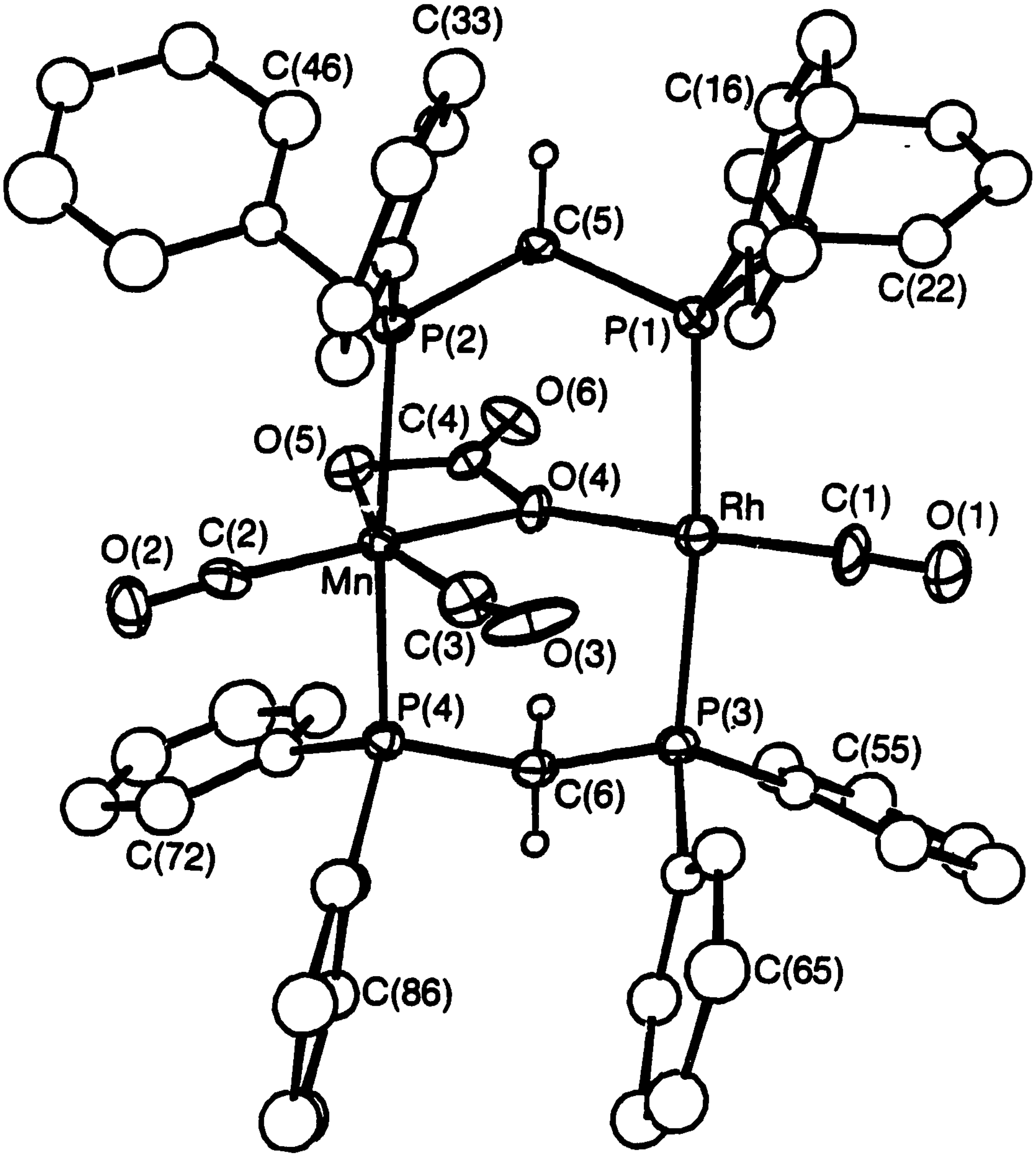


Figure 5.1 A perspective view of $[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (4). Thermal ellipsoids are shown at the 20% level except for methylene hydrogens which are shown arbitrarily small; phenyl hydrogens are omitted. Only one of the two disordered molecules (having the 70% occupancy) is shown.

Table 5.4 Selected Bond Lengths (Å) for $[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$[1]

Rh-P(1)[2]	2.296(4)	P(1)-C(5)	1.86(1)	C(1)-O(1)	1.09(1)
Rh-P(3)	2.327(4)	P(1)-C(11)	1.84(1)	C(2)-O(2)	1.13(1)
Rh-O(4)	2.025(8)	P(1)-C(21)	1.77(1)	C(3)-O(3)	1.24(2)
Rh-C(1)	1.81(1)	P(2)-C(5)	1.87(1)	C(3)'-O(3)	1.51(5)
Mn-P(2)	2.343(4)	[illegible]31)	1.86(1)	C(4)-O(4)	1.37(2)
Mn-P(4)	2.295(4)	[illegible]41	1.86(1)	C(4)-O(5)	1.37(2)
Mn-O(4)	2.046(8)	[illegible]C(6)	1.82(1)	C(4)-O(6)	1.16(2)
Mn-O(5)	2.04(1)	P(3)-C(51)	1.84(1)	C(4)'-O(4)	1.39(5)
Mn-C(2)	1.81(2)	P(3)-C(61)	1.79(1)	C(4)'-O(5)'	1.22(5)
Mn-C(3)	1.89(2)	P(4)-C(6)	1.86(1)	C(4)'-O(6)'	1.26(8)
Mn'-O(5)'	1.90(2)	P(4)-C(71)	1.86(1)		
Mn'-C(3)'	1.92(5)	P(4)-C(81)	1.83(1)		

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[1] Additional bond lengths involving the phosphine groups are given in the Supplementary Material.

[2] The atoms labelled Rh and Mn are actually a 70:30 mix of Rh:Mn and Mn:Rh, respectively, owing to disorder (see experimental section). Primed atoms have 30% occupancy and are related to the unprimed (70% occupancy) atoms by the rotational disorder.

Table 5.5 Selected Angles (deg) for [RhMn(CO)$_3$(μ-CO$_3$)(dppm)$_2$]

P(1)-Rh-P(3)[2]	173.9(1)	O(4)-Mn-C(3)	98.2(7)	Mn-O(4)-C(4)	95(1)
P(1)-Rh-O(4)	86.6(3)	O(5)-Mn-C(2)	110.8(5)	Mn-C(2)-O(2)	176(1)
P(1)-Rh-C(1)	92.2(5)	O(5)-Mn-C(3)	161.4(7)	Mn-C(3)-O(3)	172(1)
P(3)-Rh-O(4)	87.3(3)	C(2)-Mn-C(3)	87.4(7)	O(4)-C(4)-O(5)	104(2)
P(3)-Rh-C(1)	93.9(5)	P(1)-Mn'-O(5)'	90.3(8)	O(4)-C(4)-O(6)	125(2)
O(4)-Rh-C(1)	178.3(5)	P(1)-Mn'-C(3)'	92(2)	O(5)-C(4)-O(6)	131(2)
P(2)-Mn-P(4)	172.3(1)	P(3)-Mn'-O(5)'	86.9(8)	P(1)-C(5)-P(2)	115.4(6)
P(2)-Mn-O(4)	87.2(3)	P(3)-Mn'-C(3)'	90(2)	P(3)-C(6)-P(4)	117.1(7)
P(2)-Mn-O(5)	82.7(3)	O(4)-Mn'-O(5)'	67.6(8)	Mn'-O(4)-C(4)'	84(2)
P(2)-Mn-C(2)	95.8(4)	O(4)-Mn'C(3)'	101(1)	Rh'-O(4)-C(4)'	166(2)
P(2)-Mn-C(3)	91.7(6)	O(5)'-Mn'-C(1)	111(1)	Mn'-O(5)'-C(4)'	95(3)
P(4)-Mn-O(4)	85.5(3)	O(5)'-Mn'-C(3)'	168(2)	Mn'-C(3)'-O(3)	157(3)
P(4)-Mn-O(5)	91.9(3)	C(1)-Mn'-C(3)'	80(2)	O(4)-C(4)'-O(5)'	113(4)
P(4)-Mn-C(2)	91.3(4)	Rh-O(4)-Mn	109.2(4)	O(4)-C(4)'-O(6)'	117(6)
P(4)-Mn-C(3)	91.7(6)	Rh-O(4)-C(4)	153(1)	O(5)'-C(4)'-O(6)'	124(7)
O(4)-Mn-O(5)	64.0(4)	Mn-O(5)-C(4)	96(1)		
O(4)-Mn-C(2)	173.6(5)	Rh-C(1)-O(1)	177(1)		

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[1] Additional angles involving the phosphine groups are given in the Supplementary Material.

[2] Labelling as in footnote 2 of Table 5.4.

for Rh(I) and Mn(I) formulations; for Rh the geometry is almost exactly square planar whereas for Mn the slight distortion from octahedral results from the small bite of the chelating carbonate group, giving an O(4)-Mn-O(5) angle of 64.0(4)°.

As shown in Figure 5.1, the carbonate dianion bridges the metals in an unusual manner. One oxygen atom (O(4)) bridges the metals while another (O(5)) is bound solely to Mn. As such, the carbonate chelates the Mn center while simultaneously binding in a monodentate fashion to Rh. The third oxygen (O(6)) remains uncomplexed and directed away from the metals. In this binding mode the CO_3^{2-} group functions as a 6-electron donor giving Rh a 16e configuration and Mn its favored 18 valence-electron count. The carbonate coordination mode is reflected in the shorter C(4)-O(6) distance of 1.16(2) Å for this non-coordinated oxygen atom, compared with the values involving the coordinated oxygens, for which the C(4)-O(4) and C(4)-O(5) distances both equal 1.37(2) Å; both values are close to the values expected for double and single C-O bonds, respectively.[32] This observed bridging mode for the carbonate group in compound 4 is highly unusual. In other compounds containing bridging carbonate ligands either this group binds through all three oxygen atoms[30-32,34-38] or only two oxygens are bound, such that each oxygen binds to only one metal, functioning as a 2-electron donor to each.[39-43]. The observed mode is necessary in order to yield the appropriate electron counts at the metals; the mode in which all three oxygens are bound, which would also give the correct electron counts, appears not to be possible in this case since the large separation necessary is not permitted by the bridging dppm groups. As it is, the intraligand P-P separations of 3.146(5) and 3.137(5) Å, are large and the P-C-P angles at the methylene groups are also quite large (115.4(6)°, 117.1(7)°), showing the strain within the dppm groups.

All angles around C(4) are consistent with sp^2 hybridization of this atom, apart from the slight compression of O(4)-C(4)-O(5) to 104(2)°, resulting from chelation to Mn. For the same reason the Mn-O(4)-C(4) and Mn-O(5)-C(4) angles (95(1)° and 96(1)°) are also somewhat compressed. All parameters within this carbonate group are consistent with other determinations involving such groups.[29-32, 34-43]

The Rh-O(4), Mn-O(4) and Mn-O(5) distances (2.025(8), 2.046(8) and 2.04(1) Å, respectively) appear to be normal for such bonds, falling within the range (2.061(5) - 2.141(4) Å)[30,31] observed in related carbonate-bridged dirhodium complexes, and well within the rather wide range (1.88(5)-2.32(11) Å) noted in other carbonate-bridged species.[32] The wide Rh-O(4)-Mn angle of 109.2(4)° and the long Rh-Mn separation of 3.317(2) Å are consistent with the absence of a Rh-Mn bond, as expected for a Rh(I)/Mn(I) system. All atoms within the $Mn(CO_3)$ group are planar (the largest deviation being 0.03(2) Å) although the Rh atom is situated 0.295(2)Å out of this plane.

The spectroscopic data for compounds **5** and **6** compare closely to that of **4**. Each complex displays two resonances in the $^{31}P\{^1H\}$ NMR spectrum, and for **5** the resonance for the Rh-bound phosphorus nuclei appears close to that in **4**. However in compound **6** both sets of phosphorus resonances (Re- and Ir-bound) are at similiar chemical shifts so their differentiation is not possible, although both fall close to that for the Re-bound phosphorus nuclei in **5**. All three compounds also have similar ^1H NMR spectra and almost superimposable IR spectra, particularly in the carbonyl region. In addition all complexes show a carbonate stretch in the region between 1649 and 1671 cm^{-1}. For compound **5** the $^{13}C\{^1H\}$ NMR spectrum was obtained on a sample prepared from *ca.* 70% ^{13}CO-enriched starting material (**2**). This spectrum displays three carbonyl resonances at δ 203.3, 200.3 and 189.5. The first two are unresolved, however the third is a doublet of triplets, displaying coupling of 77 Hz to the Rh nucleus and of 16 Hz to the two Rh-bound phosphorus nuclei; all signals integrate equally indicating that the species is a tricarbonyl, having two carbonyls on Re and one on Rh. The carbonate carbon, a singlet at δ 163.0, also integrating as one carbon, compares closely to the resonances reported for $[Rh_2(COD)_2(\mu\text{-}CO_3)]_3$[31] at δ 167 and for $[WH_2(CO_3)(PMe_3)_4]$ at δ 163.5.[44] These data indicate that compounds **5** and **6** are also carbonate-bridged species having structures analogous to that of **4**.

Attempts to observe intermediate species in the above transformations of a carbonyl ligand to a carbonate group were unsuccessful. Over the temperature range between -60°C and 22°C, only the starting materials and final products were ever observed when the reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy. We had hoped to be able to observe the presumed O_2 adduct that precedes CO oxidation, but this was not possible. Although it appears that oxidation of a coordinated carbonyl is occurring, we cannot unambiguously rule out the possibility that CO dissociation follows O_2 coordination and that the coordinated peroxo group attacks the free CO; both mechanisms for carbon monoxide oxidation have been proposed.[45,46] It is also of interest to establish how the two metals are involved in the oxidation and to determine which carbonyl (bound to the group 9 (Rh,Ir) or the group 7 (Mn,Re) metal) is transformed. These questions also could not be addressed in this study owing to the extreme facility of the oxygen transfer reaction and due to the fact that selectively ^{13}CO-labelled precursors (**1**-**3**) could not be obtained owing to facile CO exchange over both metals.[17]

Protonation of the carbonate groups in compounds **4**, **5** and **6** was investigated in attempts to effect conversion to the corresponding bicarbonate-bridged complexes. It was felt that under a CO atmosphere such species might react further liberating CO_2 and yielding hydroxide-bridged species such as $[MM'(CO)_4(\mu\text{-}OH)(dppm)_2]^+$ (M = Rh, Ir; M' = Mn,Re). These attempts were unsuccessful in that in all cases the attempted protonation yielded a complex mixture of between 4 to 8 products, whether carried out in the presence or absence of CO. In the case of compound 4 these reactions always yielded paramagnetic species which precluded the acquisition of a high resolution NMR spectrum.

Conclusions

The low-valent, mixed-metal complexes, $[RhM(CO)_4(dppm)_2]$ (M = Mn, Re) and $[IrRe(CO)_5(dppm)_2]$, react readily with O_2 resulting in the unusual oxidation of a coordinated carbonyl ligand to a bridging carbonate group. The resulting binding mode of the carbonate group, in which one oxygen atom bridges the metals while a second oxygen is chelated to the group 7 metal, appears to be unprecedented. Although the functions of the two metals were not established in this study, it is clear that mixed-metal complexes such as 1-3 have a rich potential for substrate activation; previous reports of oxidation of a coordinated carbonyl ligand in related mononuclear complexes are few.[46-48]

<u>Supplementary Material Available:</u> Listings of the phenyl carbon parameters, hydrogen atom parameters, anisotropic thermal parameters, and additional bond lengths and angles (8 pages); listings of the observed and calculated structure factors (15 pages). All Supplementary Data are available from M. Cowie upon request.

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Chapter 6

Unusual, Coordinatively Unsaturated Rhodium/Rhenium and Iridium/Rhenium, Alkyl, Acyl and Hydrido Complexes. Structure of $[RhRe(CH_3)(CO)_4(Ph_2PCH_2PPh_2)_2][CF_3SO_3]\cdot 3CH_2Cl_2$ †

Introduction

Coordinatively unsaturated, square planar complexes of Rh(I) and Ir(I) have played an important role in advancing our understanding of homogeneous catalysts.[1-5] Two species that have been pivotal in this regard are $[RhCl(PPh_3)_3]$[6] and $[IrCl(CO)(PPh_3)_2]$.[7] Of the many phosphine-containing complexes of this type studied, surprisingly few have been reported[8,9] in which an alkyl or related group is the anionic ligand. Stable alkyl complexes of this type could serve as important models for unstable intermediates involved in a variety of metal-catalyzed transformations of organic substrates, such as hydrogenation, hydroformylation and carbon monoxide reduction.

Our interests in utilizing binuclear, dppm-bridged (dppm = $Ph_2PCH_2PPh_2$) complexes of Rh and Ir as models for transformations occurring at two or more adjacent metals[10] led us to investigate alkyl derivatives of such complexes. Binuclear alkyl complexes of Rh(I) and Ir(I) are, like the mononuclear analogues, extremely rare,[8] although related diplatinum complexes are well known.[11,12] In an attempt to stabilize binuclear alkyl complexes involving coordinatively unsaturated Rh and Ir

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centers we turned to a class of heterobinuclear complexes in which these metals are combined with Re,[13-15] since low-valent rhenium-alkyl species are well known.[16] We thus decided to investigate alkyl derivitives of the complexes $[RhRe(CO)_4(dppm)_2]$ and $[IrRe(CO)_5(dppm)_2]$, whose oxidative-addition chemistry has been thoroughly discussed in Chapters 3-5 of this thesis. It was of interest to establish whether the alkyl moiety in such species would be coordinated to Re or to the group-9 metal; both cases should give rise to interesting reactivity of the alkyl group. In the latter case the alkyl group would be bound to Rh or Ir, which have a strong tendency to be coordinatively unsaturated, whereas in the former case the Re-alkyl unit would be adjacent to the unsaturated Rh or Ir center. In either case such complexes, containing *both* a coordinatively unsaturated metal *and* an alkyl ligand, should serve as useful models for mixed-metal catalysts.

Experimental Section

General Experimental Conditions

All solvents were dried and distilled under argon before use. Tetrahydrofuran was dried and deoxygenated with Na/Ph_2CO, as were Et_2O, benzene, and hexane. Dichloromethane was dried over P_2O_5. Prepurified argon was used without further treatment. Carbon monoxide and dihydrogen were used as received from Matheson. The hydrated rhodium(III) and iridium(III) trichlorides were obtained from Johnson Matthey Ltd. and $Re_2(CO)_{10}$ was purchased from Aldrich and sublimed before use. Methyl triflate, $HBF_4{\cdot}Et_2O$, triflic acid, and $LiEt_3BH$ in THF (1.0 M) were also purchased from Aldrich. All other chemicals were used as received without further purification. The 99% carbon-13 enriched Carbon monoxide was obtained from Isotec Inc. The compounds, [RhRe(CO)$_4$(dppm)$_2$] (1)[13] and [IrRe(CO)$_5$(dppm)$_2$] (2)[15] were prepared as discussed in Chapters 2 and 5, respectively.

All NMR experiments were conducted on a Bruker AM-400 spectrometer operating at 161.9 MHz for ^{31}P. In all cases an internal deuterated solvent lock was used. In general, deuterated solvents were dried over P_2O_5, freeze-pump-thaw degassed and vacuum distilled into the 5 mm NMR tube containing the sample. These tubes were flame sealed with the contents at -196°C for the variable temperature NMR experiments.

Infrared spectra were recorded on either a Nicolet 7199 Fourier transform interferometer or a Perkin Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr discs), casts (CH_2Cl_2 on KBr discs), or solutions (KCl windows, 0.5 mm path length). Elemental analyses and mass spectrometry experiments were conducted by the respective departmental services.

Preparation of Compounds

a) [RhRe(CH$_3$)(CO)$_4$(dppm)$_2$][CF$_3$SO$_3$] (3).

The compound [RhRe(CO)$_4$(dppm)$_2$] (1) (100 mg, 85.5 µmol) was dissolved in 5 mL of benzene and $CF_3SO_3CH_3$ (9.7 µL, 85.5 µmol) was then added by syringe. The yellow solution was stirred for 3 h during which time a pale yellow precipitate had formed. The benzene was then removed in vacuo and the yellow solid recrystallized from CH_2Cl_2/Et_2O to yield 93 mg (82%) of a pale yellow powder (1). Anal. Calcd. for $C_{56}H_{47}F_3O_7P_4ReRhS$: C, 50.42; H, 3.55. Found: C, 49.85; H, 3.55. Spectral parameters for all the compounds prepared are found in Table 6.1.

Table 6.1 Spectral Data [a]

Compound	IR, cm^{-1}	NMR		
		δ(^{31}P{^{1}H}) [d]	δ(^{1}H) [e]	δ(^{13}C) [e]
[RhRe(CH$_3$)(CO)$_4$(dppm)$_2$]-[CF$_3$SO$_3$] (3)	2022 (vs), 1973 (s), 1828(m), 1808 (s) [b]	31.7 (dm, $^{1}J_{Rh\text{-}P}$ = 141 Hz), 3.4 (m)	0.78 (td, 3H, $^{3}J_{P\text{-}H}$ = 7 Hz, $^{2}J_{Rh\text{-}H}$ = 2 Hz), 3.11 (s, 4H)	226.2 (bm, 2C, $^{1}J_{Rh\text{-}C}$ = 19 Hz) 188.5 (bm, 2C)
[RhRe(C(O)CH$_3$)(CO)$_4$(dppm)$_2$]-[CF$_3$SO$_3$] (4)	2033 (s), 1969 (vs), 1842 (m), 1807 (m), 1642 (s) [b]	16.6 (dm, $^{1}J_{Rh\text{-}P}$ = 162 Hz), 2.5 (m)	0.86 (s, 3H), 3.27 (m, 4H)	229.0 (bm, 2C, $^{1}J_{Rh\text{-}C}$ = 21 Hz) 213.9 (bm, 2C), 256.2 (dm, 1C, $^{1}J_{Rh\text{-}C}$ = 32 Hz)
[RhRe(CH$_3$)(CO)$_3$(CH$_3$CN)-(dppm)$_2$][CF$_3$SO$_3$] (5)	1964 (m), 1919 (vs), 1782 (m) [b]	31.3 (dm, $^{1}J_{Rh\text{-}P}$ = 146 Hz), 13.2 (m)	1.11 (s, 3H), 0.26 (td, 3H, $^{3}J_{P\text{-}H}$ = 8 Hz, $^{2}J_{Rh\text{-}H}$ = 2 Hz), 2.98 (m, 2H), 3.56 (m, 2H)	241.2 (dm, $^{1}J_{Rh\text{-}C}$ = 32 Hz, 1C), 204.6 (bs, 1C), 194.0 (m, 1C)
[RhRe(CH$_3$)(CO)$_2$(CH$_3$CN)$_2$-(dppm)$_2$][CF$_3$SO$_3$] (6)	1731 (vs), 1769 (m), 1958 (w, ν-CN), 1912 (w, ν-CN) [b]	32.9 (dm, $^{1}J_{Rh\text{-}P}$ = 151 Hz), 13.7 (m)	2.98 (bs, 4H), 1.51 (s, 6H), -0.08 (td, 3H, $^{3}J_{P\text{-}H}$ = 6 Hz, $^{2}J_{Rh\text{-}H}$ = 2 Hz)	232.0 (bm, 2C, $^{1}J_{Rh\text{-}C}$ = 14 Hz)

Table 6.1 (continued)

		NMR		
Compound	IR,cm^{-1}	$\delta(^{31}P\{^1H\})$ ^{d}	$\delta(^1H)$ ^{e}	$\delta(^{13}C)^e$
[IrRe(CH$_3$)(CO)$_4$(dppm)$_2$]- [CF$_3$SO$_3$] (7)	2012 (vs), 1963 (s), 1792 (sh), 1779 (s) ^{b}	21.2 (m), 4.5 (m)	1.34 (t, 3H, $^3J_{H\text{-}P}$ = 8 Hz), 3.06 (m, 4H)	224.6 (bs, 2C), 189.4 (bs, 2C)
[IrRe(CH$_3$)(CO)$_5$(dppm)$_2$]- [CF$_3$SO$_3$] (8)	2011 (m), 1991 (vs), 1952 (m), 1927 (m) ^{b}	0.5 (m), -11.7 (m)	0.69 (t, 3H, $^3J_{H\text{-}P}$ = 4 Hz), 4.33 (m, 4H)	199.6 (m, 2C), 192.1 (bs, 1C), 189.8 (t, 2C)
[IrRe(C(O)CH$_3$)(CO)$_5$(dppm)$_2$]- [CF$_3$SO$_3$] (9)		-2.5 (m), -16.6 (m)	2.18 (s, 3H), 4.45 (bs, 4H)	224.0 (bs, 1C), 198.8 (t, 2C), 192.2 (bs, 1C), 191.1 (bs, 1C)
[IrRe(m-H)(CO)$_4$(dppm)$_2$]- [CF$_3$SO$_3$] (10)	2038 (w), 1991 (vs), 1954 (s), 1912 (m) ^{b} 1993 (vs), 1948 (m) ^{c}	14.5 (m), 7.1 (m)	3.98 (s, 4H), -9.51 (m, 1H, $^2J_{PH}$ = 8 Hz, $^2J_{PH}$ = 5 Hz)	198.8 (bs, 2C), 189.6 (bs, 1C) 175.2 (t, 1C)
[IrRe(CO)$_4$(dppm)$_2$] (11)	1964 (m), 1908 (m), 1823 (s), 1801 (s) ^{b}	20.1 (m), 2.9 (m)	4.7 (m, 4H)	

Table 6.1 (continued)

Compound	IR, cm^{-1}	NMR $\delta(^{31}P\{^1H\})$ [d]	 $\delta(^1H)$ [e]	 $\delta(^{13}C)$ [e]
$[IrRe(CH_3)(\mu-H)(CO)_4(dppm)_2]$-$[CF_3SO_3]$ (12)		4.2 (m), 2.4 (m)	-0.32 (t, $^2J_{P-H}$ = 4 Hz), -10.21 (m)	214.8 (bm, 1C), 210.4 (bm, 1C), 198.8 (bs, 1C), 191.9 (bs, 1C)
$[IrRe(H)_2(CO)_4(dppm)_2]$-$[CF_3SO_3]_2$ (13)	2069 (m), 2043 (w) 1975 (s), 1948 (m) [b]	-0.3 (m), -3.3 (m)	5.62 (m, 2H), 5.23 (m, 2H), -22.13 (td, $^2J_{H-H}$ = 6 Hz, $^2J_{P-H}$ = 12 Hz), -14.72 (bm, $^2J_{P-H}$ = 10.1 Hz, $^2J_{P-H}$ = 7.3 Hz)	192.4 (bs, 1C), 192.2 (bs, 1C), 187.9 (bs, 1C), 184.0 (bs, 1C)
$[IrRe(H)_3(CO)_4(dppm)_2]$-$[CF_3SO_3]$ (14)	2123 (w), 2049 (m), 2018 (m), 1952 (s), 1927 (s) [b]. 2133 (w), 2042 (w), 2030 (w), 1955 (s), 1922 (s) [c]	-1.2 (m), -6.3 (m)	4.56 (bs, 4H), -10.60 (t, 1H, $^2J_{P-H}$ = 16 Hz), -13.91 (bs, 2H)	189.5 (bs, 2C), 189.3 (bm, 1C), 171.4 (bm, 1C)
$[IrRe(H)_2(CO)_4(dppm)_2]$ (15)	2008 (w), 1965 (s), 1924 (s), 1885 (s), 1860 (s) [b]	3.6 (m), 2.3 (m)	4.98 (m, 2H), 4.05 (m, 2H), -10.54 (m, $^2J_{P-H}$ = 12 Hz, $^2J_{P-H}$ = 4 Hz, $^2J_{H-H}$ = 4 Hz), -11.18 (dt, $^2J_{P-H}$ = 18 Hz)	213.3 (bs, 1C), 210.5 (bs, 1C) 198.5 (bs, 1C), 189.1 (bs, 1C)

Notes: [a] Abbreviations used: IR; w = weak, m = medium, s = strong, vs = very strong: NMR; m = multiplet, dm = doublet of multiplets, s = singlet, t = triplet, td = triplet of doublets, bs = broad singlet, bm = broad multiplet. [b] Nujol mull on KBr plates. [c] CH_2Cl_2 casts on kBr plates. [d] VS 85% H_3PO_4, -40°C in CD_2Cl_2 solvent. [e] VS TMS -40°C in CD_2Cl_2 solvent; resonances for the dppm phenyl hydrogens are not given. [f] $J_{P(M)-H}$ is the coupling constant between the phosphorus nucle[illegible] to M and hydrogen.

b) [RhRe(C(O)CH$_3$)(CO)$_4$(dppm)$_2$][CF$_3$SO$_3$] (4).

Compound 3 (100 mg, 75.0 µmol) was dissolved in 5 mL of CH$_2$Cl$_2$. The yellow solution was left under an atmosphere of CO for 27 h with stirring. Removal of the solvent in vacuo yielded a yellow residue. Recrystallization from CH$_2$Cl$_2$/Et$_2$O gave 106 mg (98%) of a deep yellow solid which analyzed as [RhRe(C(O)CH$_3$)(CO)$_4$(dppm)$_2$][CF$_3$SO$_3$]·CH$_2$Cl$_2$. Anal. Calcd. for C$_{58}$H$_{49}$Cl$_2$F$_3$O$_8$P$_4$ReRhS: C, 48.14; H, 3.41. Found: C, 47.94; H, 3.32.

c) [RhRe(CH$_3$)(CO)$_3$(CH$_3$CN)(dppm)$_2$][CF$_3$SO$_3$] (5).

Compound 3 (100 mg, 75.0 µmol) was dissolved in 5 mL of CH$_2$Cl$_2$. To this yellow solution was added a solution of Me$_3$NO·2 H$_2$O (8.3 mg, 75.0 µmol) in 2 mL of CH$_3$CN. The yellow solution was stirred for 1 h with no obvious color change. The solvents were then removed in vacuo and the resulting residue was recrystallized from CH$_2$Cl$_2$/Et$_2$O to give a yellow powder (5) in 83% yield (84 mg). Anal. Calcd. for C$_{57}$H$_{50}$F$_3$NO$_6$P$_4$ReRhS: C, 50.85; H, 3.74. Found: C, 50.22; H, 3.99.

d) [RhRe(CH$_3$)(CO)$_2$(CH$_3$CN)$_2$(dppm)$_2$][CF$_3$SO$_3$] (6).

In a procedure identical to that for the preparation of 5, 100 mg (75.0 µmol) of 3 was reacted with 2 equivalents of Me$_3$NO·2 H$_2$O (16.6 mg, 150.0 µmol) in CH$_3$CN/CH$_2$Cl$_2$. A yellow powder, 6, was isolated in 91% yield (93 mg). Anal. Calcd. for C$_{58}$H$_{53}$F$_3$N$_2$O$_5$P$_4$ReRhS: C, 51.22; H, 3.89. Found: C, 50.86; H, 4.21.

e) [IrRe(CH$_3$)(CO)$_4$(dppm)$_2$][CF$_3$SO$_3$] (7).

The compound, [IrRe(CO)$_5$(dppm)$_2$] (2) (100 mg, 77.8 µmol), was dissolved in 5 mL of benzene and CF$_3$SO$_3$CH$_3$ (8.8 µL, 77.8 µmol) was added by syringe. The orange solution was then stirred under a slow argon purge for 3 h, during which time an orange-tan precipitate formed. Removal of solvent in vacuo and recrystallization of the residue yielded 91 mg (83%) of a light orange-brown powder. Anal. Calcd. for $C_{56}H_{47}F_3IrO_7P_4RhS$: C, 47.26; H, 3.33. Found: C, 47.49; H, 3.71.

f) [IrRe(CH$_3$)(CO)$_5$(dppm)$_2$][CF$_3$SO$_3$] (8).

Compound 7 (100 mg, 70.3 μmol) was dissolved in 5 mL of CH_2Cl_2. Carbon monoxide was bubbled through the solution at a rate of ca. 5 mL/sec for 5 min. The resulting solution went from orange to yellow over 20 min after which the CH_2Cl_2 was allowed to evaporate under a stream of CO to yield a yellow residue which was recrystallized from CH_2Cl_2/Et_2O to give 96 mg (94%) of a pale yellow powder (8). Anal. Calcd. for $C_{57}H_{47}F_3IrO_8P_4ReS$: C, 47.17; H, 3.26. Found: C, 47.02, H, 3.56.

g) [IrRe(H)(CO)$_4$(dppm)$_2$][CF$_3$SO$_3$] (10).

Compound 7 (100 mg, 70.3 μmol) was dissolved in CH_2Cl_2 (5 mL). Dihydrogen was bubbled rapidly through the solution for 5 min and then the system was closed and stirred for 3 h, during which time the original orange color had faded to faint yellow. The solution was then stirred under a purge of Ar for 1 h causing it to turn dark red in color. The solvent was then removed in vacuo and the orange-red residue recrystallized from CH_2Cl_2/Et_2O to yield 84 mg (85%) of an orange-red powder (10). Anal. Calcd. for $C_{55}H_{45}F_3IrO_7P_4ReS$: C, 46.87; H, 3.22. Found: C, 46.47; H, 3.68.

h) [IrRe(CO)$_4$(dppm)$_2$] (11).

Compound 10 (100 mg, 7.1 μmol) was slurried in 5 mL of THF. To this mixture was added 71 μL of a 1.0 M solution of potassium tert-butoxide in

THF. The solid quickly dissolved to give a yellow-orange solution. Evaporation of the THF gave a yellow solid which was recrystallized from CH_2Cl_2 to give 71 mg (80%) of an air sensitive powder. Anal. Calcd. for $C_{54}H_{44}IrO_4P_4Re$: C, 51.56; H, 3.53. Found: C, 51.83; H, 4.06.

i) $[IrRe(H)_2(CO)_4(dppm)_2][CF_3SO_3]_2$ (13).

Compound 10 (100 mg, 70.9 μmol) was dissolved in 5 mL of CH_2Cl_2. Triflic acid (6.3 μL, 70.9 μmol) was then added by syringe. The reddish solution instantly turned faint yellow and the solution was stirred for an additional 10 min. The solvent was then removed in vacuo and the yellow residue recrystallized from CH_2Cl_2/Et_2O to afford 101 mg (91%) of a yellow powder. Anal. Calcd. for $C_{56}H_{46}F_6IrO_{10}P_4ReS_2$: C, 43.13; H, 2.97. Found: C, 43.31; H, 3.48.

j) $[IrRe(H)_3(CO)_4(dppm)_2][CF_3SO_3]$ (14).

Compound 10 (100 mg, 70.9 μmol) was dissolved in 5 mL of CH_2Cl_2. The reddish solution was stirred under an H_2 purge (ca. 1/2 mL sec^{-1}) for 1 h, over which time is assumed a faint yellow color. The rate of the purge was increased to 2 mL sec^{-1} in order to evaporate the solvent. The pale yellow solid remaining was left under vacuum for 2 h and then collected. Yield: 97 mg (96%). Anal. Calcd. for $C_{55}H_{47}F_3IrO_7P_4RhS$: C, 46.81; H, 3.36. Found: C, 46.99; H, 3.71.

k) $[IrRe(H)_2(CO)_4(dppm)_2]$ (15).

The compound, $[IrRe(CO)_5(dppm)_2]$ (2) (100 mg, 77.8 μmol) was dissolved in 5 mL THF. Dihydrogen was passed over the orange solution with stirring at a rate of 1/2 mL sec^{-1} for 1 h. The flow of H_2 was stopped and the yellow solution was stirred for an additional hour. The THF was removed in vacuo and the yellow solid was recrystallized from CH_2Cl_2/Et_2O to yield 86 mg (85%) of a yellow powder. Anal. Calcd. for $C_{55}H_{46}IrO_4P_4Re$: C, 52.38; H, 3.67. Found: C; 52.54; H, 3.58.

Reaction of [IrRe(CO)$_5$(dppm)$_2$] with CH_2O.

A solution of [IrRe(CO)$_5$(dppm)$_2$] (100 mg, 77.8 μmol) in 5 mL of THF was saturated with an excess of CH_2O generated by the thermal decomposition of paraformaldehyde in a separate flask. The solution was stirred for 17 h and the solvent was evaporated in vacuo to yield a yellow solid which was identified as **15** by IR, $^{31}P\{^1H\}$ NMR and ^1H NMR spectroscopy

Reaction of 3 with H_2.

A solution of **3** (100 mg, 75.0 μmol) was stirred under H_2 for 31 [illegible] Removal of the solvent gave a yellow powder which was identified as [RhRe(H)(CO)$_4$(dppm)$_2$][CF_3SO_3][14] by IR $^{31}P\{^1H\}$ NMR, and ^1H NMR spectroscopy.

Reaction of 3 with $LiHBEt_3$.

To a solution of **3** (100 mg, 75.0 μmol) was added 75.0 μL (*ca.* 1 eqiv) of 1.0 M $LiHBEt_3$ in THF. The reaction proceeded slowly over 2 days to give a quantitative yield of [RhRe(CO)$_4$(dppm)$_2$] (**1**) as determined by $^{31}P\{^1H\}$ and ^1H NMR spectroscopies.

Reaction of 4 with $LiHBEt_3$.

A solution of **4** (100 mg, 73.4 μmol) was reacted with *ca.* 1 equiv (74 μL) of 1.0 M $LiHBEt_3$ in THF. After 1 h the solvent was removed and the yellow residue was identified by $^{31}P\{^1H\}$ and ^1H NMR spectroscopies as $[RhRe(CO)_4(dppm)_2]$.

Reaction of 7 with $LiHBEt_3$.

To an orange solution of 7 (100 mg, 70.3 μmol) in 5 mL of THF was added *ca.* 1 equiv (71 μL) of 1.0 M $LiHBEt_3$ in THF. The solution instantly turned light yellow. After 1 h of additional stirring the THF was removed in vacuo and the solid was identified as $[IrRe(CO)_4(dppm)_2]$ by IR, $^{31}P\{^1H\}$ NMR and ^1H NMR spectroscopies.

X-Ray Data Collection

Yellow crystals of $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]\cdot 3CH_2Cl_2$ were obtained by slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution of the complex. Several suitable crystals were mounted and flame-sealed under argon in glass capillaries to minimize decomposition. Data were collected on an Enraf-Nonius CAD 4 diffractometer with use of MoKα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 well-distributed reflections in the range $20.0 \leq 2\theta \leq 24.0$. A triclinic cell was established by the usual peak-search and reflexion-indexing programs; the lack of systematic absences established the space group as either $P1$ or $P\bar{1}$. A cell reduction failed to locate a higher symmetry cell.[17] The centrosymmetric space group was established as the more probable one on the basis of the successful refinement of the structure.

Intensity data were collected at 22° C by using the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak widths on either side of the scans. Three reflections were chosen as intensity standards and were remeasured at 120 min intervals of X-ray exposure. There was no significant systematic decrease in the intensities of these standards so no correction was applied. A total of 10,643 unique reflections were measured and processed in the usual way, by using a value of 0.04 for p;[18] of these, 8106 were observed and used in subsequent calculations.[19] Absorption corrections were applied to the data by using the method of Walker and Stuart.[20] The crystallographic data are summarized in Table 6.2.

Structure Solution and Refinement

The structure was solved by conventional Patterson techniques to obtain the Rh and Re positions, while all other atoms were located by the usual sequence of full-matrix, least-squares and difference Fourier techniques. All atoms of the complex cation and anion were located. In addition, three molecules of CH_2Cl_2 per formula unit of complex were also located. The hydrogen atoms on the Rh-bound methyl group were located and together with the hydrogen atoms of the dppm ligands were included as fixed contributions in their idealized positions at 0.95 Å from the attached carbon atoms having the appropriate hybridization. The thermal parameters of all hydrogens were fixed at 1.2 times the isotropic B of the attached carbon atom.

Atomic scattering factors[21,22] and the anomalous dispersion terms[23] were taken from the usual tabulations. Positional and isotropic thermal parameters, except for those of the solvent molecules, the phenyl carbons and the hydrogen atoms are given in Table 6.3; the others appear as supplementary material.

Table 6.2 Crystallographic Data for $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]\cdot 3CH_2Cl_2$ (3)

formula	$C_{59}Cl_6F_3H_{53}O_7P_4ReRhS$
fw	1588.84
space group	$P\bar{1}$ (No. 2)
a, Å	15.055 (1)
b, Å	21.239 (3)
c, Å	10.662 (1)
α, deg	97.83 (1)
β, deg	105.647 (7)
γ, deg	100.195 (9)
V, Å^3	3169.7
Z	2
d calcd, g cm^{-3}	1.66
temp, °C	22
radiation, Å	MoKα, 0.71069
monochromator	graphite
μ, cm^{-1}	2.71
transmission coefft. (min, max)	0.901-1.113
unique data collected	10643
observed data (NO)	8106
no. of variables (NV)	494
R[a]	0.039
Rw	0.049
error in obs. of unit wt (GOF)	1.508

[a] As defined in Table 2.2

Table 6.3 Positional and Thermal Parameters for $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]\cdot 3CH_2Cl_2$ ^{a}

Atom	x	y	z	B (Å^2) ^{b}
Re	0.24860(2)	0.32069(1)	0.08438(2)	2.454(5)
Rh	0.23922(3)	0.19557(2)	-0.06168(4)	2.71(1)
S ^{c}	0.7092(2)	0.2306(1)	0.5109(3)	7.23(7)
P(1)	0.3865(1)	0.18579(8)	0.0697(2)	3.02(4)
P(2)	0.4019(1)	0.31939(8)	0.2338(2)	2.74(3)
P(3)	0.0864(1)	0.18[illegible](8)	-0.2051(2)	2.89(3)
P(4)	0.0918(1)	0.31946(8)	-0.0571(2)	2.78(3)
F(1) ^{c}	0.7731(4)	0.1285(3)	0.5450(9)	13.2(3)
F(2) ^{c}	0.6595(5)	0.1356(4)	0.6228(7)	12.8(2)
F(3) ^{c}	0.6286(7)	0.1183(5)	0.407(1)	20.7(5)
O(1)	0.3266(3)	0.3014(2)	-0.1620(4)	4.1(1)
O(2)	0.1636(3)	0.1876(2)	0.1585(4)	4.3(1)
O(3)	0.1854(3)	0.3690(3)	0.3277(4)	5.1(1)
O(4)	0.3179(4)	0.4650(2)	0.0775(5)	5.7(1)
O(5) ^{c}	0.6226(4)	0.2473(4)	0.5041(9)	10.8(3)
O(6) ^{c}	0.7494(6)	0.2400(5)	0.4129(9)	13.0(3)
O(7) ^{c}	0.7827(6)	0.2568(5)	0.646(1)	16.9(4)
C(1)	0.2922(4)	0.2920(3)	-0.0791(6)	3.1(1)
C(2)	0.1989(4)	0.2236(3)	0.1023(6)	3.2(1)

Table 6.3 (continued)

Atom	x	y	z	B (Å^2)[b]
C(3)	0.2087(4)	0.3509(3)	0.2390(6)	3.3(1)
C(4)	0.2923(4)	0.4112(3)	0.0808(6)	3.4(1)
C(5)	0.2341(5)	0.1059(3)	-0.1768(7)	4.5(2)
C(6)	0.4198(4)	0.2365(3)	0.2374(6)	3.0(1)
C(7)	0.0206(4)	0.2364(3)	-0.1290(6)	3.1(1)
C(8)[c]	0.6990(8)	0.1509(6)	0.534(1)	11.9(4)

---

[a] See Supplementary Data for Phenyl Carbon and Solvent Parameters.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}$ [$a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)$].

[c] $CF_3SO_3^-$ Anion.

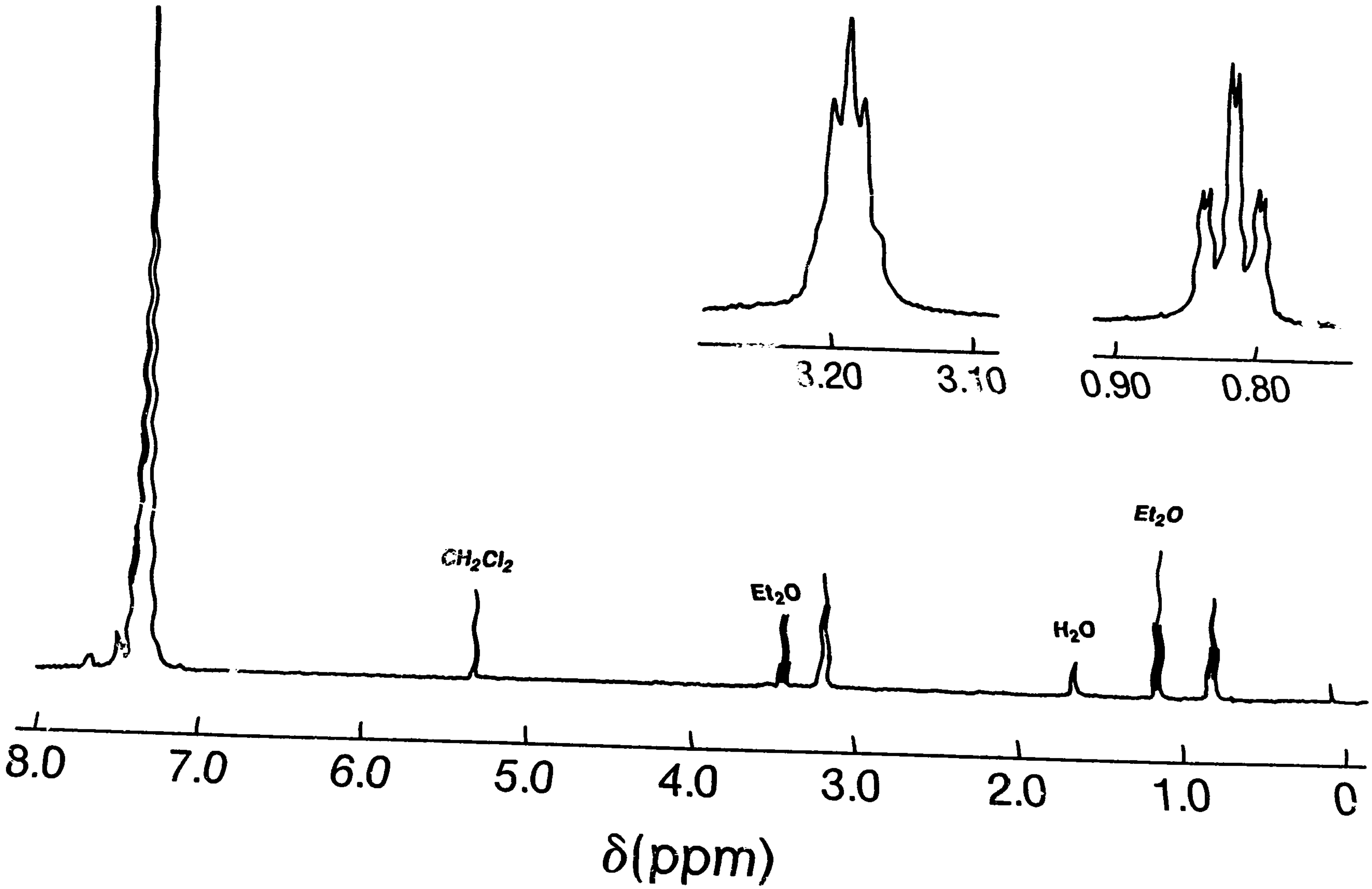
Results and Discussion

(a) Rhodium Complexes

Our initial attempts to prepare mixed-metal Rh/Re species having alkyl or acyl ligands failed. For example, neither of the hydride complexes discussed in Chapter 3, $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ or $[RhRe(CO)_3(\mu\text{-}H)_2(dppm)_2]$,[14] reacted with dimethylmercury or with diazomethane, even after 24-48 h. Similarly, $[RhRe(CO)_3(\mu\text{-}Cl)_2(dppm)_2]$,[14] also discussed in Chapter 3, was to be unreactive towards MeMgBr after 72 h at 22° C. Although $Re(CO)_4(dppm)_2]$ (1) did react with CH_3I, CH_2I_2 and CH_2Br_2, a complex mixture of products resulted in each case and these reactions were not pursued further. Furthermore, attempts to prepare an acyl complex through reaction of 1 with $CH_3C(O)Cl$ also failed, giving no reaction after 48 h.

However, our previous protonation of compound 1, to yield the hydrido-bridged species $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$,[14] suggested that an analogous route might be employed to generate an alkyl species via reaction of 1 with an appropriate carbonium ion. Consistent with this suggestion, compound 1 reacts readily with 1 equiv of methyl triflate to yield $[RhRe(CH_3)(CO)_4\cdot(dppm)_2][CF_3SO_3]$ (3). The $^{31}P\{^1H\}$ NMR spectrum of 3 displays two resonances at δ 3.4 and 31.7, consistent with an AA'BB'X spin system, as previously observed in related species.[13,14] In the ^1H NMR spectrum, only one dppm methylene resonance, integrating as four protons, is observed at δ 3.11, and the resonance (3 H) for the methyl ligand is observed as a triplet of doublets ($^3J_{P\text{-}H} = 7$ Hz; $^2J_{Rh\text{-}H} = 2$ Hz) at δ 0.82. This spectrum is shown with expansions of the methylene and methyl resonances in Figure 6.1. Selective

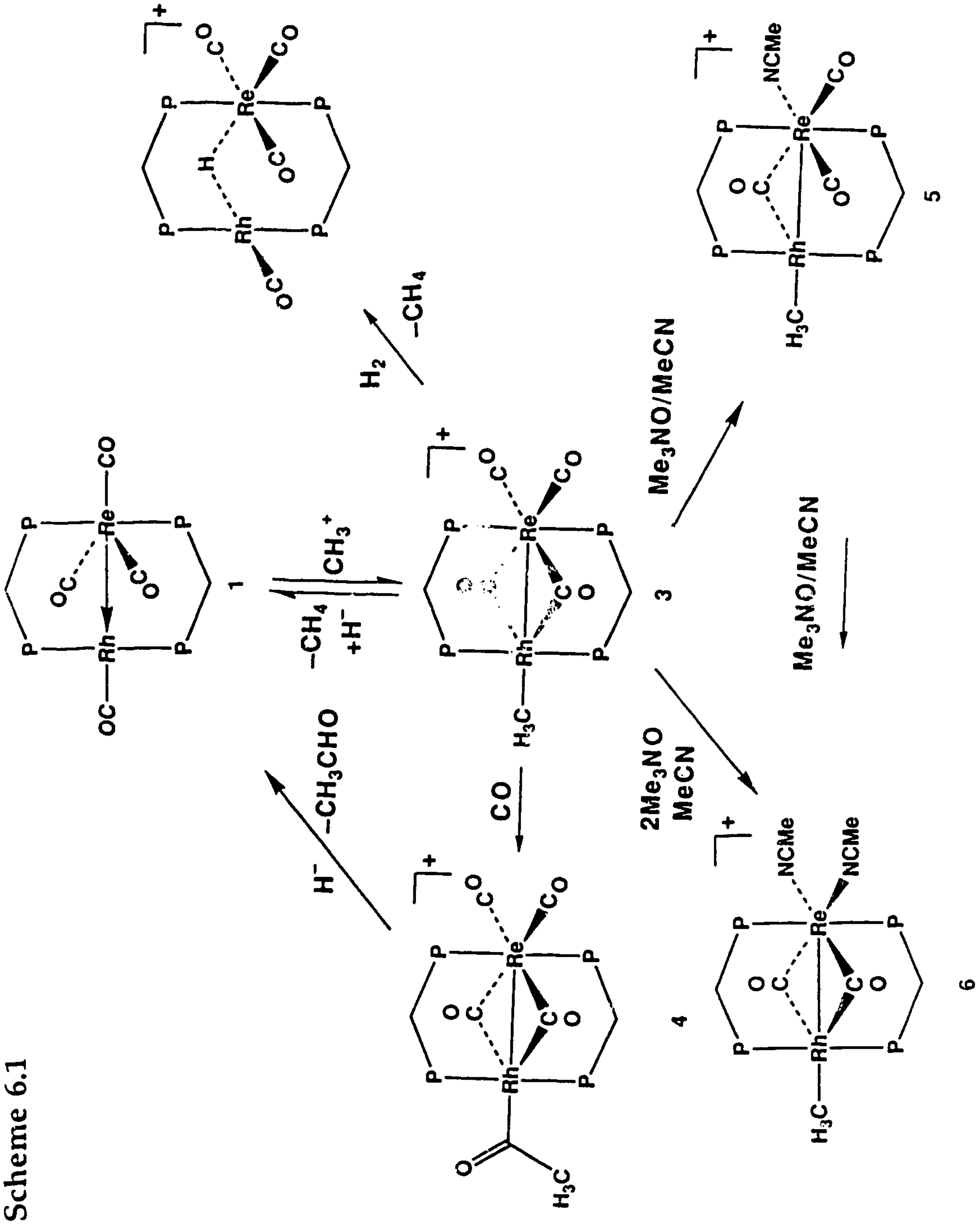
Figure 6.1 The 1H NMR Spectrum of [RhRe(CH_3)$(CO)_4$ $(dppm)_2$][CF_3SO_3]



phosphorus decoupling experiments indicate that the methyl group is bound only to Rh, since irradiating the low-field phosphorus signal causes the methyl resonance to collapse to a doublet, while irradiating the high-field ^{31}P signal causes no change in the methyl resonance. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched (*ca.* 30%) sample displays two broad multiplets in a 1:1 ratio at δ 226.2 and 188.5; the former resonance is shown by broadband ^{31}P decoupling to have a 19 Hz coupling to Rh. The IR spectrum of the unenriched sample has four carbonyl stretches at 2022 (vs) 1973 (s), 1828 (m) and 1808 (s) cm^{-1}. The two low-frequency carbonyl stretches in the IR spectrum and the low-field $^{13}C\{^1H\}$ carbonyl resonance suggest that two carbonyl groups bridge the metals, and the single resonance for the dppm methylene protons is indicative that both faces of the complex are identical, allowing exchange of the axial and equatorial positions for these protons. On this basis the structure shown in Scheme 6.1 is proposed.

The proposed structure has been confirmed by an X-ray structure determination of **3**, which is shown in Figure 6.2, while relevant bond lengths and angles are given in Tables 6.4 and 6.5. The CH_2Cl_2 solvent molecules and the triflate anion are well behaved and unexceptional. In the cation of compound **3** the diphosphine ligands bridge the metals in a trans arrangement as is often observed. If the semi-bridging carbonyl ligands are ignored, the coordination about Rh is square planar in which the two phosphorus atoms are mutually trans, as are the methyl group and the bond to Re. About Re the geometry is best described, by ignoring the Rh-Re interaction, as octahedral in which the phosphorus atoms are trans in the axial sites and the four carbonyls occupy the equatorial positions. The Re-P distances (2.432(1), 2.428(1) Å) are longer than the Rh-P bonds (2.348(1), 2.344(1) Å), consistent with the larger covalent radius of Re[24] and with the

Scheme 6.1


1
3
4
5
6
P
Re
Rh
CO
OC
H$_3$C
NCMe
H
+
CH_3^+
$-CH_4$
$+H^-$
H_2
$-CH_4$
$-CH_3CHO$
H^-
CO
$Me_3NO/MeCN$
$Me_3NO/MeCN$
$2Me_3NO$
MeCN

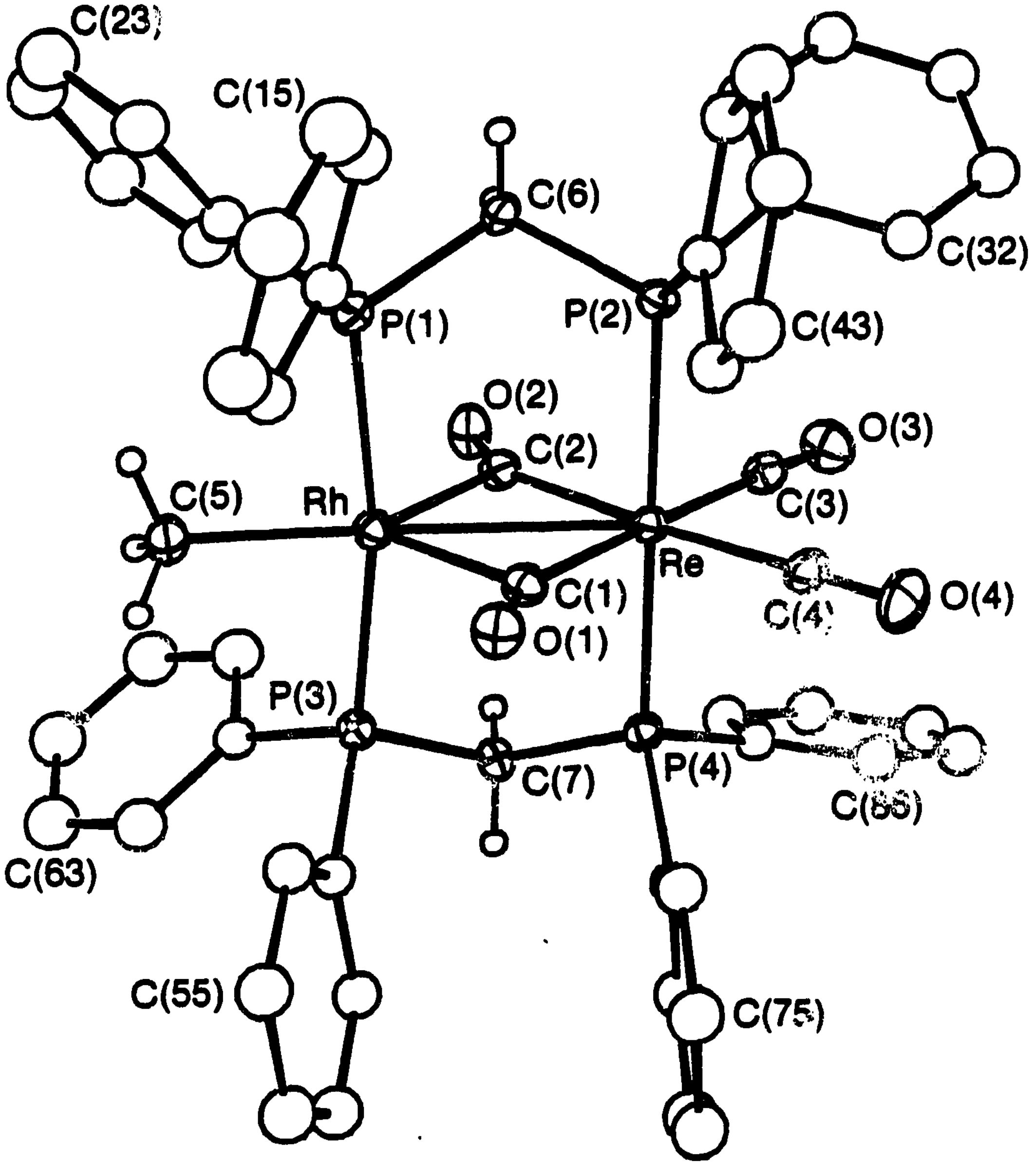


Figure 6.2 Perspective drawing of [RhRe(CH$_3$)(CO)$_4$(dppm)$_2$]$^+$ cation showing numbering scheme. Thermal ellipsoids are shown at the 20% level except for methylene hydrogens which are shown arbitrarily small. Phenyl hydrogens are omitted.

greater crowding about this center. As expected, the Re-CO distances involving the two terminal carbonyls are shorter (1.969(6), 1.928(6) Å) than those involving the semi-bridging carbonyls (2.076(5), 2.119(5) Å). These semi-bridging carbonyl ligands do interact significantly with Rh to give Rh-C contacts (2.114(5), 2.048(6) Å) that are actually shorter than those involving Re. Also noteworthy is the fact that these carbonyls appear to be bound in a compensating fashion, with a long Rh-C(1) distance being matched by a short Re-C(1) distance and the opposite being true for C(2). Although this might suggest that C(1) is primarily bound to Re and C(2) to Rh, the carbonyl angles suggest that this is not the case.[25] Both semi-bridging carbonyls are significantly more linear with respect to Re (Re-C(1)-O(1) = 153.9(5)°, Re-C(2)-O(2) = 148.9(4)°, Rh-C(1)-O(1) = 120.3(4)°, Rh-C(2)-O(2) = 124.8(4)°) suggesting a stronger involvement with this metal for both carbonyl groups. The Rh-C-Re angles at both semi-bridging carbonyls (85.8(2)°, 86.3(2)°) are acute, as expected when there is an accompanying metal-metal bond, and this is substantiated by the Rh-Re distance of 2.8510(5) Å, which is clearly consistent with there being a Rh-Re bond. This distance compares well with that determined (2.7919(6) Å)[13] in the precursor [RhRe(CO)$_4$(dppm)$_2$] (1) and is much shorter than that (3.0036(7) Å)[14] which resulted upon protonation of the Rh-Re bond in 1. The Rh-C(5) distance of 2.097(6) Å is consistent with other determinations involving Rh-carbon sigma bonds.[26]

The bonding in compound 3 can be viewed in either of two extremes. The first, maybe more conventional view, would involve a normal covalent Rh-Re bond with two bridging carbonyl groups. This would result in a Rh(II)-Re(0) formulation, with the positive charge localized on Rh. In the second view the positive charge is localized on Re to give a Rh(I)/Re(I) formulation and a dative Re → Rh bond. A molecular orbital description of this bond

Table 6.4 Selected Bond Lengths (Å) for $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]\cdot 3CH_2Cl_2$ [a]

Re-Rh	2.8510(5)	S-O(5)	1.396(6)	P(3)-C(61)	1.816(5)
Re-P(2)	2.432(1)	S-O(6)	1.362(8)	P(4)-C(7)	1.834(5)
Re-P(4)	2.428(1)	S-O(7)	1.525(9)	P(4)-C(71)	1.832(5)
Re-C(1)	2.076(5)	S-C(8)	1.73(1)	P(4)-C(81)	1.822(5)
Re-C(2)	2.119(5)	P(1)-C(6)	1.847(5)	F(1)-C(8)	1.27(1)
Re-C(3)	1.969([illegible])	P(1)-C(11)	1.831(6)	F(2)-C(8)	1.30(1)
Re-C(4)	1.928(6)	P(1)-C(21)	1.825(6)	F(3)-C(8)	1.46(2)
Rh-P(1)	2.344(1)	P(2)-C(6)	1.832(5)	O(1)-C(1)	1.162(6)
Rh-P(3)	2.348(1)	P(2)-C(31)	1.824(5)	O(2)-C(2)	1.173(6)
Rh-C(1)	2.114(5)	P(2)-C(41)	1.831(5)	O(3)-C(3)	1.136(6)
Rh-C(2)	2.048(6)	P(3)-C(7)	1.841(5)	O(4)-C(4)	1.148(6)
Rh-C(5)	2.097(6)	P(3)-C(51)	1.818(5)		

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 6.5 Selected Angles (deg) for $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]\cdot 3CH_2Cl_2$ [a]

Rh-Re-P(2)	90.40(3)	Re-Rh-C(5)	177.0(2)	Re-P(2)-C(41)	119.4(2)
Rh-Re-P(4)	89.67(3)	P(1)-Rh-P(3)	169.91(5)	C(6)-P(2)-C(31)	103.6(2)
Rh-Re-C(1)	47.7(1)	P(1)-Rh-C(1)	93.2(1)	C(6)-P(2)-C(41)	103.7(2)
Rh-Re-C(2)	45.9(2)	P(1)-Rh-C(2)	91.9(2)	C(31)-P(2)-C(41)	101.9(2)
Rh-Re-C(3)	134.3(2)	P(1)-Rh-C(5)	86.0(2)	Rh-P(3)-C(7)	111.0(2)
Rh-Re-C(4)	138.5(2)	P(3)-Rh-C(1)	95.7(1)	Rh-P(3)-C(51)	117.4(2)
P(2)-Re-P(4)	177.06(5)	P(3)-Rh-C(2)	92.1(2)	Rh-P(3)-C(61)	115.0(2)
P(2)-Re-C(1)	90.7(1)	P(3)-Rh-C(5)	84.7(2)	C(7)-P(3)-C(51)	105.3(2)
P(2)-Re-C(2)	88.6(1)	C(1)-Rh-C(2)	94.4(2)	C(7)-P(3)-C(61)	102.5(2)
P(2)-Re-C(3)	89.3(2)	C(1)-Rh-C(5)	130.6(2)	C(51)-P(3)-C(61)	104.1(2)
P(2)-Re-C(4)	90.7(2)	C(2)-Rh-C(5)	135.0(2)	Re-P(4)-C(7)	112.4(2)
P(4)-Re-C(1)	91.5(1)	O(5)-S-O(6)	119.5(5)	Re-P(4)-C(71)	120.5(2)
P(4)-Re-C(2)	89.4(1)	O(5)-S-O(7)	112.9(5)	Re-P(4)-C(81)	111.5(2)
P(4)-Re-C(3)	88.6(2)	O(5)-S-C(8)	108.0(5)	C(7)-P(4)-C(71)	103.5(2)
P(4)-Re-C(4)	91.2(2)	O(6)-S-O(7)	110.0(6)	C(7)-P(4)-C(81)	104.8(2)
C(1)-Re-C(2)	93.5(2)	O(6)-S-C(8)	110.6(7)	C(71)-P(4)-C(81)	102.7(2)
C(1)-Re-C(3)	178.1(2)	O(7)-S-C(8)	92.4(7)	Re-C(1)-Rh	85.8 (2)
C(1)-Re-C(4)	90.8(2)	Rh-P(1)-C(6)	111.3(2)	Re-C(1)-O(1)	153.9(5)
C(2)-Re-C(3)	88.4(2)	Rh-P(1)-C(11)	116.4(2)	Rh-C(1)-O(1)	120.3(4)
C(2)-Re-C(4)	175.7(2)	Rh-P(1)-C(21)	114.6(2)	Re-C(2)-Rh	86.3(2)
C(3)-Re-C(4)	87.3(2)	C(6)-P(1)-C(11)	105.7(2)	Re-C(2)-O(2)	148.9(4)
Re-Rh-P(1)	94.66(4)	C(6)-P(1)-C(21)	101.4(2)	Rh-C(2)-O(2)	124.8(4)
Re-Rh-P(3)	94.88(4)	C(11)-P(1)-C(21)	106.1(3)	Re-C(3)-O(3)	179.2(5)
Re-Rh-C(1)	46.6(1)	Re-P(2)-C(6)	112.4(2)	Re-C(4)-O(4)	179.5(6)
Re-Rh-C(2)	47.9(2)	Re-P(2)-C(31)	114.1(2)	P(1)-C(6)-P(2)	112.7(3)

Table 6.5 (Continued)

P(3)-C(7)-P(4)	111.5(3)	S-C(8)-F(3)	100(1)	F(2)-C(8)-F(3)	105(1)
S-C(8)-F(1)	115.9(9)	F(1)-C(8)-F(2)	111(1)		
S-C(8)-F(2)	116(1)	F(1)-C(8)-F(3)	109(1)		

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

shows two electrons donated from the d_{xy} orbital on the Re into the empty Rh orbital. In this formulation all four carbonyls are considered as primarily bound to Re but with the two of those between the metals also accepting electron density from Rh resulting in the semi-bridging modes observed. A complete discussion of this type of bonding interaction is given in Chapter 1. Previous studies by Atwood and coworkers have shown that a methyl group results in a build-up of electron density on the metal.[9a] This together with the Re → Rh dative bond in **3** results in an electron rich Rh center which necessitates the semi-bridging carbonyls for removal of some of the excess electron density. It is this latter view that we favor.

Although, based on the much lower tendency of CH_3^+ than H^+ to bridge transition metals,[27] it was not unexpected that the structure of **3** would differ from that of the protonated analogue, $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$, it is unusual to obtain a species like **3** in which a coordinatively unsaturated Rh(I)-alkyl is stable. It seems clear that the semi-bridging carbonyls are largely responsible for this stability, being able, as noted, to remove the excess electron density on Rh and to bind to the open coordination sites above and below the square planar Rh center. The resulting incipient coordinative unsaturation at Rh (by movement of these carbonyls to terminal positions on Re) may suggest interesting subsequent chemistry of this species.

Attempts to protonate **3** to yield a dicationic hydrido methyl species failed as did attempts to deprotonate this species with methyl lithium or diisopropyl amide to give a methylene-bridged species. Similarly, compound **3** was unreactive towards trityl cation and to ethylene. This species is surprisingly robust, being stable in air for weeks. Compound **3** does, however, react slowly with $LiHBEt_3$ (superhydride) in THF to regenerate compound **1**, with loss of methane, as detected by mass spectrometry. Although the reaction was slow, taking *ca*. 3 days for completion, we were unable to detect the hydrido methyl intermediate; in fact no intermediate was detected by NMR spectroscopy, even when the reaction was monitored at -60° C.

Compound 3 also reacts with H_2 over 3 days in CH_2Cl_2 to generate $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$. Attempts to monitor this reaction at low temperature (-60° C) by ^1H NMR also failed to reveal any intermediates, as only starting material and product were observed. Presumably, this reaction occurs via oxidative addition of H_2 to Rh followed by reductive elimination of methane as has been reported for a mononuclear Rh(I) methyl complex[28] and for a related mononuclear Ir(I) methyl species.[9a]

Compound 3 reacts with carbon monoxide over 24 h to yield the acyl species $[RhRe(C(O)CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (4) as shown in Scheme 6.1. The ^1H NMR spectrum of 4 displays a multiplet at δ 3.27 for the four methylene protons and a singlet at δ 0.86 for the three methyl protons. The presence of only one methylene resonance over the temperature range 22° to -80° C again suggests that the acyl group occupies the site opposite the Rh-Re bond, as shown for the methyl precursor (3). This is further supported by the almost identical IR spectrum of these species in the carbonyl region. Compound 4 displays two carbonyl bands that are clearly terminal (2033, 1969 cm^{-1}) and two that can be considered as semi-bridging (1842, 1807 cm^{-1}) by comparison with 3. In addition, the CO stretch for the acyl group, at 1642 cm^{-1}, is as expected for Rh acyls.[29-33] The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of 4 displays three carbonyl resonances in a 2:2:1 intensity ratio; the broad multiplets at δ 229.0 and 213.9 can be assigned as the semi-bridging and terminal carbonyls, respectively, by selective ^{31}P decoupling of the ^{13}C NMR spectrum which shows that the low-field signal displays coupling to Rh of 21 Hz. This is also consistent with the trend for terminal carbonyls resonating at a higher field than bridging carbonyls. The third resonance, integrating as only one carbon, at δ 256.2, appears as a doublet of multiplets ($^1J_{Rh\text{-}C}$ = 31 Hz) and is assigned to the acyl carbonyl group by comparison with the ^{13}C chemical shifts involving other metal acyls.[34]

In an attemt to identify whether the acyl carbonyl group in 4 originated from added carbon monoxide or from one of the broad carbonyls a ^{13}CO-enriched sample of compound 3 was reacted with ^{12}CO. Unfortunately this experiment failed since the slow rate of formation of 4 is comparable to the rate of carbonyl scrambling over all positions in the product.

Although the closely related species $[Ru_2(CO)_5(C(O)CH_3)(dmpm)_2]^+$ (dmpm = $Me_2PCH_2PMe_2$) was found to lose CO at ambient temperature to yield an acyl-bridged species,[35] this was not observed with compound 4 which is stable for days under argon. The reaction of 4 with one equiv of Me_3NO yielded a mixture of compounds 4 and 3, together with two unidentified products in a 4:2:1:1 ratio, respectively. These unknown products were not identified.

Compound 4 does not react with excess H_2, even after 5 days at ambient temperature, neither does it react with $HBF_4{\cdot}Et_2O$ nor $CF_3SO_3CH_3$. It was assumed that reaction with H_2 would yield acetaldehyde and $[RhRe(CO)_4(\mu\text{-}H)(dmpm)_2]^+$, whereas protonation and methylation could give reactions either at the acyl oxygen to give the corresponding alkylidene species or at the metals to yield dicationic hydrido acyl or methyl acyl complexes which would be precursors to acetaldehyde or acetone upon reductive elimination. However, compound 4 does react with $LiBEt_3H$ to yield 1 together with acetaldehyde, which was detected by mass spectrometry in the vapor above the reaction mixture. A sample of 4, ^{13}CO-enriched at all carbonyl and acyl positions, undergoes exchange with ^{12}CO at all positions over 2 days.

The reaction of 3 with Me_3NO in CH_2Cl_2 leads to a mixture of five products which were not identified. However, in acetonitrile this reaction yields [RhRe(CH_3)$(CO)_3$(NCMe)$(dppm)_2$][CF_3SO_3] (5). This complex has three carbonyl bands in the IR spectrum, at 1964, 1919 and 1782 cm^{-1}, but no evidence for the N-C stretch of the acetonitrile ligand is obvious. The ^1H NMR spectrum displays two resonances for the dppm methylene protons, indicating that there is no plane of symmetry through the $RhReP_4$ atoms and displays a triplet of doublets at δ 0.26 ($^3J_{P\text{-}H}$ = 8 Hz, $^2J_{Rh\text{-}H}$ = 2 Hz) for the Rh-bound methyl group and a singlet at δ 1.11 for the acetonitrile protons. Selective ^{31}P decoupling experiments cause the signal at δ 0.26 to collapse into a doublet upon irradiation of the Rh-bound phosphorus resonance, whereas no effect is observed on irradiating the Re-bound phosphorus resonance, confirming that the methyl group is bound only to Rh. A $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of 5 shows three equal intensity signals at δ 241.2, 204.6, and 194.0. With broad-band ^{31}P and ^1H decoupling, together with resolution enhancement, the low-field resonance appears as a doublet of doublets with coupling to Rh of 32 Hz and to the high-field carbonyl in the trans position of 14 Hz. The large coupling to Rh indicates that this carbonyl is strongly bound to Rh and compares to the Rh-C coupling values due to the semi-bridging carbonyls in 3 and 4 of 19 Hz and 21 Hz, respectively. The very low-field resonance for this carbonyl is a further indication that this group is a more conventional symmetrically bridging carbonyl group. The structure shown in Sceme 6.1 is proposed based on the above data and the subsequent data for compound 6 (*vide infra*). Although we would have expected 5 to have two bridging carbonyls, as was observed for 3, this is clearly not the case as shown by the spectroscopic data. Another possibility, in which the positions of the acetonitrile and the trans carbonyl are interchanged, is also consistent with the data but appears less likely since it would be difficult to explain the transformation to compound **6**.

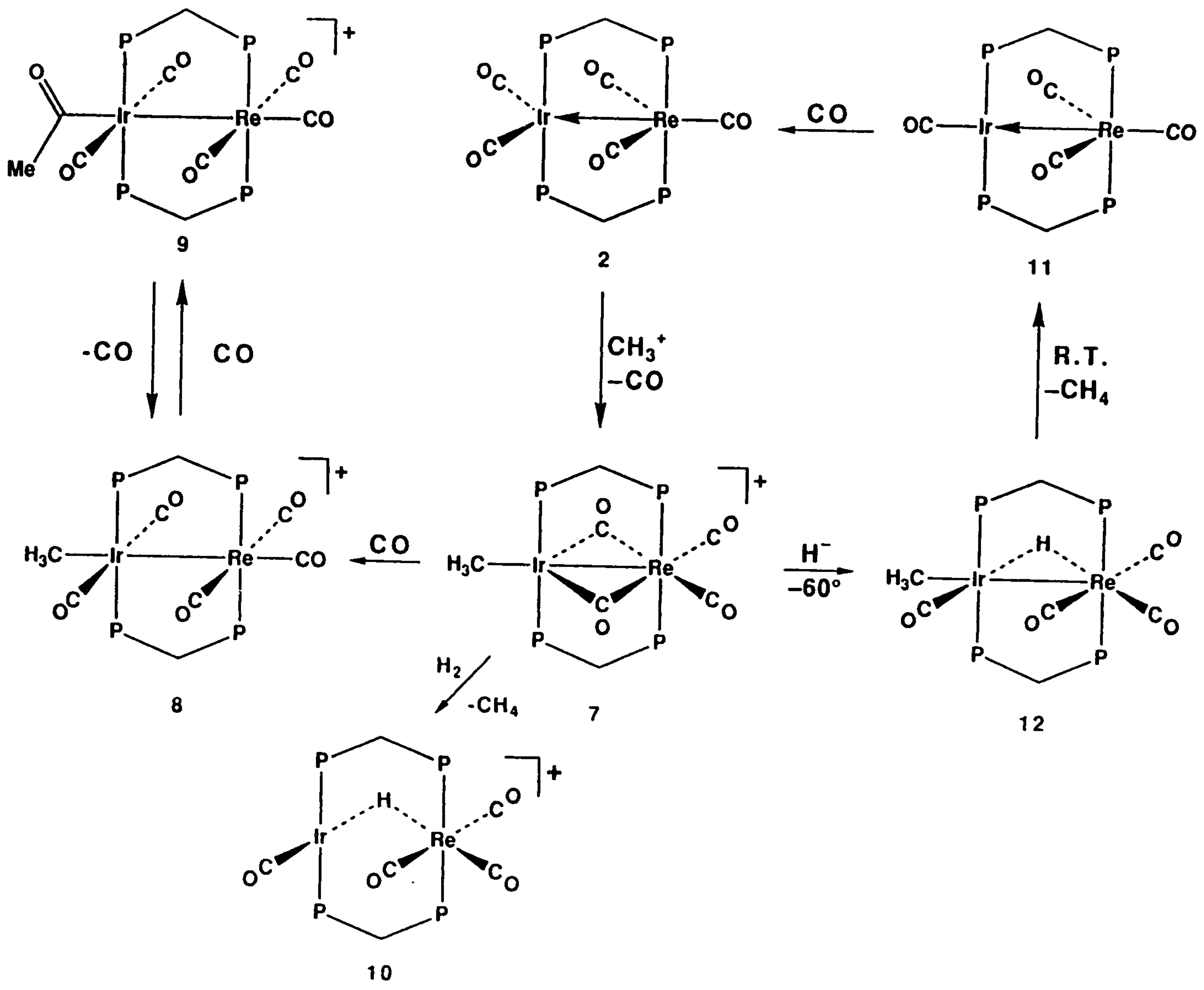
Compound **3** also reacts with 2 equivalents of Me_3NO in acetonitrile/ CH_2Cl_2 to give the bis (acetonitrile) adduct $[RhRe(CH_3)(CO)_2(CH_3CN)_2(dppm)_2][CF_3SO_3]$ (**6**) in quantitative yield. The same compound is also obtained in the reaction of **5** with 1 equivalent of Me_3NO in CH_3CN/CH_2Cl_2. Compound **6** displays 2 bands in the IR spectrum due to the carbonyl stretches, at 1731 and 1769 cm^{-1}, as well as two CN stretches at 1958, and 1912 cm^{-1}. The low values of the carbonyl stretching frequencies is suggestive of bridging carbonyl ligands. The ^1H NMR spectrum of **6** exhibits a signal for the dppm methylene protons at δ 2.98 (broad singlet, 4H) and one at δ -0.08 (triplet of doublets, 3H) for the Rh-bound methyl group. Selective $^1H\{^{31}P\}$ decoupling experiments establish unequivocally that this methyl group is still on Rh, with a value of $^1J_{Rh\text{-}H}$ of 2 Hz. The fact that only one signal is observed for the dppm CH_2 protons indicates that the two faces of the dimer are chemically equivalent. This is further supported by the appearance of only one proton resonance for the coordinated acetonitrile ligands at δ 1.51 ppm (6H) and one resonance for the carbonyls, at δ 232.0, in the $^{13}C\{^1H\}$ NMR spectrum. This latter resonance appears as a multiplet and broadband ^{31}P decoupling reveals a value of 14 Hz for $^1J_{Rh\text{-}C}$. This value compares to that for compound **3** of 19 Hz and therefore implies that these carbonyls are again semi-bridging as suspected on the basis of IR data. On the basis of these data we propose the structure shown for **6**. Substitution of the acetonitrile ligands in compounds **5** and **6**, by other unsaturated substrates is under investigation.

(b) Iridium Compounds

Methyl triflate also reacts with $[IrRe(CO)_5(dppm)_2]$ (2) to yield the alkyl species $[IrRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (7) as shown in Scheme 6.2. Although the lack of an NMR active metal nucleus in this IrRe compound leads to some ambiguity in identifying the two $^{31}P\{^1H\}$ resonances, the high-field resonance at δ 4.5 can be confidently assigned as due to the Re-bound phosphorus nuclei, based on a comparison with the equivalent resonance at δ 3.4 in the RhRe analogue 3. The IR spectrum of 7 is closely comparable to that of 3 and the ^1H NMR spectrum is also similar, displaying a single resonance at δ 3.06 for the dppm methylene protons and a triplet for the methyl protons at δ 1.34. Selective decoupling of the low-field ^{31}P resonance causes the methyl resonance to collapse to a triplet. Two carbonyl resonances, of equal intensity, are located at δ 224.6 and 189.4 in the $^{13}C\{^1H\}$ NMR spectrum. All data strongly support a structure for 7 exactly analogous to that of 3.

Compound 7 also reacts with carbon monoxide, but under a CO purge the product is not an acyl complex but rather is the pentacarbonyl methyl species, $[IrRe(CH_3)(CO)_5(dppm)_2][CF_3SO_3]$ (8). All carbonyl bands in the IR spectrum are above 1920 cm^{-1}, indicating that 7 has normal, terminal carbonyl groups and no semi-bridging groups as in 7. The ^1H NMR spectrum shows a triplet at δ 0.69 ($^3J_{P\text{-}H}$ = 4 Hz) and a single resonance for the dppm methylene protons. Selective phosphorus decoupling experiments indicate that the methyl hydrogens are coupled only to the phosphorus nuclei resonating at δ -11.7. Unless the methyl group has migrated to Re, which appears unlikely, the high-field ^{31}P resonance can be assigned to the Ir-bound phosphorus nuclei, based on their coupling to the methyl protons. The $^{31}C\{^1H\}$ NMR spectrum of a 90% ^{13}CO enriched sample of 8 shows three signals in a 2:1:2

Scheme 6.2



intensity ratio at δ 199.6 (multiplet), δ 192.1 (broad singlet) and δ 189.8 (triplet), respectively. Irradiation of the low-field ^{31}P resonance causes the low-field ^{13}C signal to collapse to a singlet, and the resonance at δ 192.1 to sharpen. Irradiation of the high-field ^{31}P resonance, on the other hand, causes the high-field triplet to collapse into a singlet. These data are consistent with the structure shown in Scheme 6.2. It may be that compound **8** models the intermediate species in the transformation of the rhodium-methyl species **3** to the acyl compound **4**, and if so indicates that carbonyl attack on **3** precedes methyl migration. The failure of the iridium-methyl species to yield an acyl product under conditions that successfully yielded the Rh-acyl product **4** reflects the decreasing tendency towards carbonyl insertion upon descending a triad.[36]

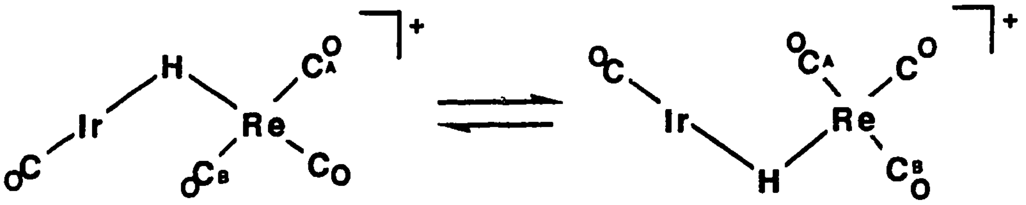
When compound **8** is placed in solution under approximately 1.5 atm of CO a new species (**9**) is formed in *ca.* 1:1 ratio compared to **8**. Complex **9** rapidly reconverts to **8** under an Argon purge in less than 5 min. The IR spectrum of this mixture of **8** and **9** shows a strong new band at 1626 cm^{-1} which is strongly suggestive of a metal-acyl CO stretch as seen for **4**. No additional carbonyl bands can be clearly resolved owing to the broad envelope which results from overlap of the bands due to both **8** and **9**. Complex **9** displays ^{31}P NMR multiplet resonances at δ -2.5 and -16.6, as expected for such a compound, and the ^{1}H NMR spectrum shows signals at δ 4.45 (broad singlet, 4H) and 2.18 (singlet, 3H) for the dppm methylene protons and the methyl protons, respectively. The presence of only one methylene signal suggests that **9** has mirror symmetry about the P_2ReIrP_2 plane. The lack of phosphorus coupling to the methyl group further suggests that an insertion has occurred, as supported by the IR evidence above. When a sample of **8** which is *ca.* 90% enriched with ^{13}CO is placed under 1.5 atm of ^{13}CO, the

$^{13}C\{^1H\}$ NMR spectrum shows four new peaks in addition to those due to **8**. These resonances appear at δ 224.0 (broad singlet, 1C), 198.8 (triplet, 2C), 192.2 (broad singlet, 1C) and 191.1 (broad singlet, 2C). Selective phosphorus decoupling experiments indicate that the lowest and highest-field resonances are bound to one metal while the three carbonyls associated with the middle two resonances are bound to the other. Although identification of the $^{31}P\{^1H\}$ resonances is equivocal, a comparison with the spectrum of **8** suggests that the higher-field resonance corresponds to the phosphorus nuclei bound to Ir, and therefore places the carbonyls associated with the ^{13}C resonances at δ 224.1 and 192.1 on this metal. It appears that the low-field ^{13}C resonance is that corresponding to the acyl group.[34] These data are consistent with the structure shown for **9** in Scheme 6.2. Carbonyl loss from **9** occurs readily under an argon purge to regenerate **8**.

Attempts to synthesize a stable acyl derivative involving the IrRe system through reaction of **2** with acetyl chloride and benzoyl chloride failed. These reactions proceeded slowly over several days to yield complex mixtures of products, which were not subsequently pursued.

As was the case for the RhRe-alkyl complex **3**, the IrRe analogue **7** also did not react further with methyl triflate or with $HBF_4{\cdot}OEt_2$ to give the corresponding dicationic dialkyl or alkyl hydrido species. Similarly we were unable to deprotonate the methyl group of **7** by using methyllithium or lithium diisopropyl amide in attempts to obtain a methylene-bridged species. Possibly not surprisingly, attempts to obtain a dicationic, methylene-bridged species by reaction of **7** with trityl cation also led to no reaction. Although the RhRe analogue **3** reacted with Me_3NO in acetonitrile to yield the acetonitrile species **5** and **6**, no reaction between Me_3NO and **7** was observed under the same conditions.

Compound 7 does react immediately with H_2 however, to yield the hydrido species $[IrRe(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (10) together with methane. The IR spectrum of **10** shows four terminal carbonyl stretches, very similar to those of $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$ discussed in Chapter 3, for which the structure was determined by X-ray methods.[14] The ^1H NMR spectrum of **10** shows only one resonance for the methylene protons at δ 3.98 and one for the hydride at δ -9.51, integrating in a 4:1 ratio, respectively. Selective ^{31}P decoupling experiments show that the hydride is coupled to both sets of phosphorus nuclei so is clearly bridging the metals. The $^{13}C\{^1H\}$ NMR spectrum displays three carbonyl resonances at δ 198.8, 189.6 and 175.2 in a 2:1:1 intensity ratio and selective ^{31}P decoupling clearly establishes that the high-field carbonyl is coupled to one set of phosphorus nuclei whereas the others are coupled to the alternate set. The structure shown in Scheme 6.2 is not consistent with these NMR data since two methylene resonances in the ^1H NMR and four separate carbonyl resonances in the ^{13}C NMR spectrum should be observed. However, it has previously been shown[14] that the analogous RhRe complex is fluxional such that the hydrido ligand passes between the metals, equilibrating both faces of the dimer and resulting in one average signal for two of the carbonyls. It is assumed that the same process is



10

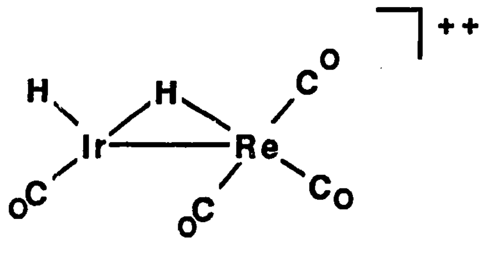
occurring in **10**, although decoalescence in the $^{13}C\{^1H\}$ NMR spectrum was not observed down to -60° C. Such a process has also been observed for the related species, $[RhFe(CO)_3(\mu\text{-}H)(dppm)_2]$[13] (see Chapter 2), $[RhCo(CO)_3\text{-}(\mu\text{-}H)(dppm)_2]^+$[37] and $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2]^+$.[10d] In this fluxional process the carbonyls labelled CO_A and CO_B are interchanging, yielding one average signal.

Attempts to observe a hydrido methyl intermediate in the reaction of 7 with H_2 at -78° C failed; only starting material and product were observed. The reaction of **10** with $CF_3SO_3CH_3$, in an attempt to synthesize a methyl hydrido species, also failed as no reaction occurred after 2 days.

Addition of $LiBEt_3H$ to compound 7 at ambient temperature results in the evolution of methane, as detected by mass spectrometry, with generation of $[IrRe(CO)_4(dppm)_2]$ (**11**), which has been previously observed in other studies.[15] This complex can be more conveniently obtained by the deprotonation of **10** with potassium tert-butoxide. Compound **11** has IR, $^{31}P\{^1H\}$ NMR, and ^1H NMR (see Table 6.1) spectra which are very similar to those of 1, $[RhMn(CO)_4(dppm)_2]$,[13] $[RhRe(CO)_4(dppm)_2]$[13](see Chapter 2) and $[IrOs(CO)_4(dppm)_2]^+$,[38] strongly suggesting that it has an analogous structure. Although no hydrido methyl compound could be observed under these conditions, reaction at -60° C did yield the hydrido methyl complex $[IrRe(CH_3)(CO)_4(\mu\text{-}H)(dppm)_2]$ (**12**), which was characterized by its NMR spectra at this temperature. The ^1H NMR spectrum of **12** shows a methyl resonance at δ -0.32 (triplet, $^2J_{P\text{-}H}$ = 4 Hz, 3H) and a high-field hydride resonance at δ -10.21 (multiplet, 1H). Although the selective ^{31}P decoupling experiments could not be performed, owing to the closeness of the phosphorus resonances, the multiplicity of the hydride resonance strongly suggests that this hydride is bridging the metals. The appearance of the methyl resonance as a triplet, on the other hand, suggests that it is terminally bound, probably to Ir. A ^{13}CO-enriched sample of **12** displays the four broad carbonyl resonances, in a 1:1:1:1 ratio, at δ 214.8, 210.4, 198.8 and 191.9. Warming the solution results in the transformation of **12** to **11**, accompanied by methane evolution.

Protonation of compound **10** by triflic acid yields the dicationic dihydride $[IrReH(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]_2$ (**13**). The two hydride signals show up clearly in the ^1H NMR spectra at δ -14.72 (multiplet) and -22.13 (triplet of doublets). Selective ^{31}P decoupling indicates that the low-field resonance is coupled to all phosphorus nuclei whereas the high-field one is coupled only to the phosphorus resonance at δ -0.3. Broadband phosphorus decoupling shows a coupling of 6 Hz between the two hydride ligands. The IR spectrum has four terminal carbonyl bands at 2069, 2043, 1975 and 1948 cm^{-1} and the $^{13}C\{^1H\}$ NMR spectrum has four equal intensity resonances at δ 192.4, 192.2, 187.9 and 184.0, corresponding to these carbonyls. Unfortunately the appropriate phosphorus decoupling experiments could not be carried out in the $^{13}C\{^1H\}$ NMR spectrum so we cannot unambiguously establish the structure. However the structure shown is consistent with the data and also is consistent with the previous complexes in which the Re atom frequently has 3 or 4 carbonyls.

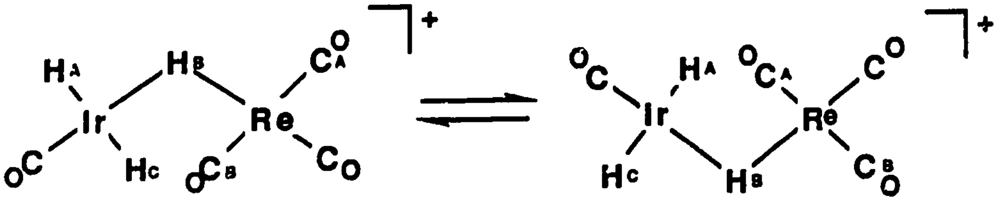
A trihydride species, $[IrRe(H)_2(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**14**), is obtained upon reaction of **10** with H_2. Its IR spectrum (Table 6.1) shows four terminal



13

carbonyl bands as well as one metal-hydride stretch (2123; Nujol), which is identified by its absence in the corresponding trideuteride species. In addition to phenyl resonances, the ^1H NMR spectrum of **14** at ambient temperature shows three resonances at δ 4.56, -10.60 and -13.91 in a 4:1:2 intensity ratio, corresponding to the dppm methylene hydrogens and the hydride ligands. Identification of the hydride bonding modes is not unambiguous since the ^{31}P resonances are too close for clear selective decoupling experiments to be carried out. The $^{13}C\{^1H\}$ NMR spectrum at this temperature has three carbonyl resonances at δ 189.5, 189.3 and 171.4 in a 2:1:1 ratio. No change was observed in any of the NMR spectra down to -80° C. In order to probe the nature of compound **14** further, the partially deuterated species $[IrRe(H)_2D(CO)_4(dppm)_2]^+$ and $[IrReH(D)_2(CO)_4(dppm)_2]^+$ were prepared from the treatment of $[IrReD(CO)_4(dppm)_2]^+$ and $[IrReH(CO)_4(dppm)_2]^+$ with H_2 and D_2, respectively. In both cases a statistical mix of H and D was observed over all hydride positions. In addition, flushing a sample of **14** with D_2 results in the complete disappearance of both hydride resonances in the ^1H NMR spectrum within minutes, and conversely purging the resulting trideuteride species with H_2 causes a rapid reappearance of these resonances. Furthermore, the addition of $DBF_4{\cdot}OEt_2$ to the dihydride **15** (*vide infra*) also results in rapid scrambling of deuterium over all three hydride sites.

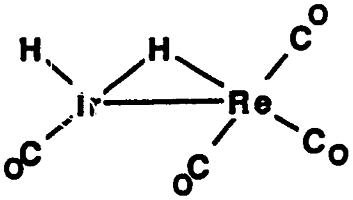
Based on the above data, the structure of **14** is not obvious, nor is the nature of the fluxionality involved. Although it is clear, based on both protonation and H_2 addition, that all hydrides exchange, coalescence of the two hydride resonances is never observed. We tentatively assume a structure for **14** which is related to that shown, in which a fluxional process, like that proposed for **10**, interchanges H_A and H_C and also CO_A and CO_B. This would



14

also explain the scrambling under H_2 or D_2 since either H_AH_B or H_BH_C can be lost when these respective pairs are mutually cis.

In an attempt to synthesize a formyl species related to the acyl complexes described, the reaction of **2** with formaldehyde was investigated. The reaction yielded $[IrRe(H)_2(CO)_4(dppm)_2]$ (**15**) as the only product. This species could also be obtained by reaction of **2** with H_2. The IR spectrum of **15** shows one terminal M-H stretch at 2008 cm^{-1} (identified by its absence in the corresponding deuteride) and four carbonyl stretches between 1965 and 1860 cm^{-1}. In the ^{1}H NMR spectrum two sets of methylene resonances and two hydride resonances (δ -10.54 and -11.18) are observed, and selective phosphorus decoupling shows that the high-field hydride is terminally bound whereas the other is bridging, although displaying stronger coupling (12 Hz) to one set of phosphorus nuclei than to the other (4 Hz). The $^{13}C\{^1H\}$



15

NMR spectrum displays four carbonyl resonances at δ 213.3, 210.5, 198.5 and

189.1, confirming that **15** is a tetracarbonyl. These data are consistent with the structure shown, which is related to that proposed for [IrRh(H)(μ-H)(CO)$_3$(dppm)$_2$],[10d] and is also closely related to the structure proposed for **14**.

Conclusions

The unusual alkyl complexes, [MRe(CH$_3$)(CO)$_4$(dppm)$_2$][CF$_3$SO$_3$] (M = Rh, Ir), result from the reactions of the neutral carbonyl precursors with methyl triflate. Although it is equivocal, one interpretation of the bonding in these compounds has the methyl group bound to a square-planar Rh(I) or Ir(I) center, with an accompanying Re→M dative bond trans to the methyl group. This dative bond results from donation of the pair of d_{xy} electrons of the octahedral d^6 Re(I) center. Two carbonyl groups on Re then accept electron density from these electron-rich group-9 metals, resulting in a semi-bridging arrangement for these groups. It is proposed that the stability of these unusual species results from the ability of the semi-bridging carbonyls to accept the excess electron density from Rh or Ir. The proposed coordinative unsaturation at Rh or Ir is manifest in the reactions of the methyl species with H$_2$, in which methane and the hydride-bridged species [MRe(CO)$_4$(μ-H)(dppm)$_2$][CF$_3$SO$_3$] (M = Rh, Ir) are produced, and in their reactions with CO. Although the iridium methyl complex does not yield the acyl species analogous to that of rhodium upon reaction with CO, the iridium pentacarbonyl methyl product obtained probably models a key intermediate in the Rh reaction. This is important since it implies that in these two binuclear complexes the coordination of carbon monoxide *precedes* methyl migration, supporting our arguments that the carbonyl groups in the starting methyl complexes are primarily associated with Re. The ability of the Ir complex to model related chemistry of Rh is also seen in the reaction of $[IrRe(CH_3)(CO)_4(dppm)_2]^+$ with $LiBEt_3H$ at -60°, in which the key hydrido methyl intermediate leading to methane formation was characterized.

The replacement of either one or two carbonyls in $[RhRe(CH_3)(CO)_4\text{-}(dppm)_2]^+$ with acetonitrile to give $[RhRe(CH_3)(CO)_3(CH_3CN)(dppm)_2]^+$ or $[RhRe(CH_3)(CO)_2(CH_3CN)_2(dppm)_2]^+$, respectively, suggests the possibility of replacement of these acetonitrile groups by carbanions or olefins, allowing the possibility of C-C bond formation in these systems, and also suggests that other interesting chemistry might be accessible through these species.

This work has shown that the chemistry described occurs primarily at the Rh or Ir centers. However, the rhenium carbonyl moieties clearly have an important influence on the stability of the products through their interactions with the group-9 metals. Future studies will attempt to extend our understanding of the involvment of the adjacent metals in the chemistry of these and related complexes and to expand the role the coordinatively saturated Re center in the chemistry.

Supplementary Material Available. Tables of thermal parameters for the anisotropic atoms, idealized hydrogen parameters, and bond distances and angles within the phenyl rings, along with a summary of crystal data and details of intensity collection (11 pages); a listing of observed and calculated structure amplitudes (34 pages). All Suplementary Data is available upon request from Dr. M. Cowie.

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Chapter 7

Conclusion

The object of these studies was to first find a rational route to bis-dppm bridged, mixed-metal dimers containing Rh, and then to investigate the chemistry of one of these systems in detail, in order to determine how the two metals cooperate with one another during subsequent reactions. It was hoped that the presence of two adjacent metals with distinctly different properties would lead to chemistry which was not observed in the respective homobimetallic systems. Rhodium was chosen as one of the metals because of its tendency to adopt a 16-electron coordinatively unsaturated configuration, while Re was selected as the other metal because of its rich alkyl and oxo chemistry. In some cases, the analogous Rh/Mn or Ir/Re systems were also investigated in order to determine the effect of exchanging one metal for another in the same group on the reactivity of the bimetallic system. For the most part, these studies were successful in demonstrating that the heterometals in these systems are capable of cooperating with each other in several ways.

The complex $[RhRe(CO)_4(dppm)_2]$(1) was synthesized by the reaction of $[Re(CO)_5]^-$ with $[RhCl(dppm)_2]$. This method of reacting a metalate anion with the above rhodium chloro complex was extended to a variety of monoanions of the form $[M(CO)_xH_n]^-$ (M= Co; x=4; n=0: M= Fe, Ru, Os; x=4, n=1: M= Mn, Re; x=5; n=0: M= Cr, W; x=5; n=1). The cyclopentadienyl-containing anions $[Fe(CO)_2Cp]^-$and $[Mo(CO)_3Cp]^-$ also yielded dimers on reaction with $[RhCl(dppm)_2]$. However, in these Cp-containing systems only one dppm ligand moved into a bridging orientation, presumably due to the steric effect of the cyclopentadienyl unit which apparently blocks the migration of one end of the second phosphine onto the adjacent metal. In spite of this limitation, this method proved successful as a general route to bis-dppm heterobimetallic carbonyl and carbonyl-hydride complexes containing Rh.

These complexes are best formulated as mixed-valent species containing a $[Rh(P)_2(CO)]^+$ unit and a mononegative heterometallic unit which donates two electrons to the Rh to complete its preferred 16-electron configuration. As discussed in Chapter 1, such a dative bond is labile and can act as a source of incipient coordinative unsaturation in subsequent reactions.

As mentioned above, the remainder of these studies focused on the reactivity of $[RhRe(CO)_4(dppm)_2]$. It was found, not at all unexpectedly, that the presence of the unsaturated Rh center greatly enhances the reactivity of the Rh/Re system as compared to its dirhenium analogue by allowing facile coordination of incoming substrates without prior dissociation of a ligand. While $[Re_2(CO)_6(dppm)_2]$ must be heated to 172 °C in order to react with dihydrogen, the analogous reaction with $[RhRe(CO)_4(dppm)_2]$ is rapid, even at -80 °C. In the case of the dirhenium analogue, thermally induced dissociation of a carbonyl is required in order to generate such a vacant coordination site at which oxidative addition can occur. Since the reaction with dihydrogen was facile, several other oxidative-addition reactions were attempted. These included reactions with H^+, HCl, Cl_2, and alkynes (Chpt. 3), H_2S and thiols (Chpt. 4), and O_2 (Chpt. 5). In all cases Rh(I)/Re(I) systems were formed as the only products. In the reactions with dihydrogen, hydrogen chloride, chlorine, ethanethiol and benzenelthiol, the products were invariably tricarbonyls, with two carbonyls on Re and one on Rh, and the two halves of the substrate molecule bridging opposite faces of the dimer. The reactions with H^+ and H_2S, on the other hand, gave closely analogous tetracarbonyl species with bridging hydrido and sulfido ligands, respectively. The reactions with alkynes yielded first tetracarbonyl species with a bridging alkyne parallel to the Rh-Re axis and no metal-metal bond. These complexes are unstable and readily lose CO to form a tricarbonyl species with a Rh-to-Re dative bond. As a further indication of the reactivity of these mixed metal species, the reactions of $[RhM(CO)_4(dppm)_2]$ (M=Mn, Re) and $[IrRe(CO)_5(dppm)_2]$ with dioxygen gave the interesting bridging carbonato complexes in which the carbonate ligand is η^2 with respect to the group-7 metal and η^1 with regards to the Rh or Ir. Although the majority of dppm-bridged bimetallics containing Rh or Ir are unreactive towards O_2, the above metal carbonyls react at ambient temperature to form the carbonates via a rare oxidation of a coordinated CO ligand. This reaction demonstrates the ability of a bimetallic system to coordinate ligands in modes which are not observed in monometallic complexes.

It was of interest to study some of these reactions at low temperature in order to gain information about intermediates in the formation of the final products alluded to above. Especially interesting was the mechanism resulting in the formation of $[RhRe(\mu\text{-}S)(CO)_4(dppm)_2]$, from compound **1** and H_2S. Although this reaction was facile at ambient temperature, yielding the sulfide-bridged product, low temperature NMR studies on this reaction, and on the reactions with ethanethiol and benzenethiol, were instrumental in elucidating several of the intermediates in these transformations. The presence in this system of the ^{31}P nuclei of the dppm ligands, ^{13}C nuclei of the carbonyl groups, and ^{103}Rh, all of which are NMR active, made the unequivocal location of the carbonyl and hydride ligands in these intermediates possible through heteronuclear $^1H\{^{31}P\}$ and $^{13}C\{^{31}P\}$ decoupling experiments and also through the observation of large one-bond Rh-coupling in the NMR spectra of these complexes.

These studies revealed that each of the three reactions follow identical pathways up to the formation of $[RhRe(SR)(CO)_4(\mu\text{-}H)(dppm)_2]$ (R=Et,Ph,H) which occurs after the initial oxidative addition. In the case of the thiols, this species rearranged to form a tricarbonyl with bridging hydrido and thiolato ligands on opposite faces of the dimer. An additional intermediate was detected immediately before the formation of the final product in the phenylthiol system in which a terminal hydride was bound to a $[Re(CO)_3(P)_2]$ unit. Although the analogous intermediate was not detected in either of the other two systems, it gave important clues concerning the rearrangement and loss of dihydrogen from $[RhRe(SH)(CO)_4(\mu\text{-}H)(dppm)_2]$. Since this loss requires a second oxidative addition of the S-H bond to a vacant coordination site on an adjacent metal it was important to establish that ligand migration, which is capable of regenerating this coordinative unsaturation, is facile in these systems. Although we did not isolate a dihydrido sulfide complex or one in which a vacant coordination site is adjacent to an S-H moiety, it is concluded, on the basis of these findings and similar studies of the analogous Rh/Ir and Rh/Os systems, that the loss of dihydrogen most likely occurs via migration of the SH group to Re followed by a second oxidative addition of the S-H bond to a 16-electron Rh center. The resulting dihydrido complex could then rearrange such that the two hydrides are cis on the Rh. At this stage reductive elimination could readily occur. Although it appears that CO loss only occurs in the two thiol reactions, but not in the H_2S reaction, unpublished results show that the Os analogue of **1**, $[RhOs(CO)_4(dppm)_2]^+$, forms a tricarbonyl intermediate upon reaction with H_2S. This intermediate loses H_2 and picks up CO to form the cationic Os analogue of the Rh/Re bridging-sulfide complex discussed above. This strongly suggests that the analogous process is occurring in the Rh/Re system, but that the tricarbonyl intermediate is too short lived to detect. If this is the case, then the thiol and H_2S reactions occur by the same mechanism. However, the thiol reactions stop at the tricarbonyl stage, because these tricarbonyl species cannot undergo H_2 loss and subsequent CO gain, as can the analogous species in the H_2S reaction. Although these studies did not unequivocally establish the mechanism of rearrangement and H_2 loss, they have shown that facile ligand migrations accompanied by reallocation of electron density between the two metals are facile in this system.

There are many other examples of metal-metal cooperativity throughout the studies in this thesis. For example, even though $[RhRe(CO)_4(dppm)_2]$ is coordinatively unsaturated, its reactivity towards dihydrogen is somewhat surprising, since monomeric Rh(I) complexes of the type $[Rh(CO)(P)_2X]$ (P=phosphine, X=halide) rarely yield isolable products in their reactions with H_2 unless the phosphines are strong sigma donors. This suggests that the $[Re(CO)_3P_2]$ unit in $[RhRe(CO)_4(dppm)_2]$ acts as a sufficiently strong electron donor to the Rh center to enhance its reactivity by increasing the electron richness of this center. This example clearly shows that the Re unit influences the reactivity of the Rh metal. Furthermore, the initial oxidative addition of a substrate molecule to the Rh(I) center in $[RhRe(CO)_4(dppm)_2]$ must first generate a Rh(III)/Re(-I) species which then must undergo a subsequent rearrangement to give the final Rh(I)/Re(I) system. Thus, the Re is ultimately oxidized from the -1 to the +1 configuration while the Rh center regains its monovalent configuration. Since the substrate initially oxidizes the Rh center, an electron reallocation between the two metals must occur at some stage of the reaction. This reallocation of electrons is a another clear example of metal-metal cooperativity.

The reactions with alkynes showed that the nature of the Rh-Re interaction could be changed by the facile loss of a carbonyl ligand from the alkyne-bridged tetracarbonyl. This initial tetracarbonyl complex has no Rh-Re bond, however loss of CO leads to a tricarbonyl with concomitant formation of a Rh→Re dative bond to compensate for the loss of the two electrons provided by the exiting CO. Here, the Rh metal labilizes the CO ligand on the adjacent Re center, thereby facilitating CO loss. This is an example of one metal acting as an electron sink in donating or accepting electron density from a neighboring metal to accommodate changes of the ligand environment in the system. The mechanism of this CO loss is not clear, however, studies on the analogous Rh/Os cationic complex have shown that the CO ligand first migrates to Rh and then dissociates, rather than dissociating from Os.

The result of this reaction was unexpected since the complexes, $[M_2(CO)_3(dppm)_2]$ (M=Rh, Ir) react with acetylenes to form species with parallel bridging alkynes which easily lose CO with a concomitant reorientation of this alkyne ligand into a perpendicular configuration in which it can act as a 4-electron pi-donor. The failure of the alkyne ligand to undergo this reorientation in the Rh/Re system is not understood, but may be due to a stronger Re-C σ–bond in the isolated product as compared to the Re-alkyne π–bond in the unobserved product with a perpendicularly bound alkyne. Steric crowding may also be a factor, since Re requires one more carbonyl ligand than Ir or Rh in these tricarbonyl bridging-alkyne complexes.

As discussed above, the reaction with dioxygen leads to the formation of the rare heterobimetallic carbonate-bridged complexes through the oxidation of a coordinated CO. Presumably the coordination of O_2 occurs on the group-9 metal while the more oxophilic Re or Mn center is able to bind to one or more oxygen atoms at some stage of the reaction. Since monometallic complexes of Rh(I) and Ir(I) often form η^2-O_2 adducts, as opposed to carbonates, upon reaction with dioxygen, these reactions show how the presence of an adjacent metal can open reactivity pathways which are unavailable in monometallic systems.

In these studies, the preparation of alkyl derivatives of the Rh/Re and Ir/Re systems were also investigated. The complexes $[MRe(CH_3)(CO)_4$-$(dppm)_2]^+$ (M=Rh, Ir), formed by the reaction of the parent metal carbonyl with methyltriflate, are rare examples of Rh(I) and Ir(I) alkyl complexes. These complexes are best formulated as containing a dative bond from the d^6 $[Re(P)_2(CO)_4]^+$ fragment to the group-9 metal. In this bond, two electrons are donated from the the Re d_{xy} orbital into the vacant Rh orbital directed along the metal-metal axis. The Rh and Ir interactions with the strongly sigma donating methyl group are presumably stabilized by the adjacent $[Re(CO)_4(P)_2]^+$ unit. This group can relieve the build-up of electron density on the Rh or Ir centers by back donation from the metal orbitals into the antibonding orbitals of the semibridging carbonyls. Therefore, the Re unit cooperates with the adjacent group-9 alkyl fragment by withdrawing excess electron density which would otherwise lead to the destabilization of the metal-alkyl bond, while at the same time donating two electrons to the group-9 metal center.

While the Rh methyl species readily inserts CO, the Ir analogue only does so under a surpressure (ca. 1.5 atm) of CO. Removal of the CO leads to rapid deinsertion in the Ir complex. The reason for this instability of the Ir-acyl complex is not understood. The first deinsertion product in this sequence is

$[IrRe(CH_3)(CO)_5(dppm)_2]^+$, the Rh analogue of which is presumably too unstable to observe. This complex further loses another molecule of CO to form the original tetracarbonyl methyl species. A comparison of the reactivities of the Rh and Ir methyl systems illustrates the greater tendency of Ir as opposed to Rh to hold on to CO in order to attain an 18-electron configuration. This is also reflected in the stability of $[IrRe(CO)_5(dppm)_2]$ and $[IrRe(H)(\mu\text{-}H)(CO)_4(dppm)_2]$ whose Rh analogues are only stable under CO, or not observed at all in the case of the dihydride. This is as expected in view of the well precedented increase in metal-carbonyl bond strengths in going from a second to a third-row metal. The Ir/Re system also shows a marked tendency to achieve higher oxidation states than the Rh/Re analogue. This is clearly exemplified by the fact that $[IrRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$ reacts with H^+ and H_2, while the rhodium analogue is inert towards these reagents. This is consistent with the trend down a triad of third-row metals stabilizing higher oxidation states more effectively than their second-row counterparts.

In all of the above cases the heterometals have been shown to act as either donors or acceptors of electron density with respect to each other while also allowing for facile ligand rearrangement about the metal framework and in some cases, unusual coordination modes of ligands. The only reactive center in these systems is, however, always the group-9 metal. This is because of its tendency, although this is not as strong in the case of Ir, to adopt a coordinatively unsaturated configuration which allows for facile coordination of incoming substrate molecules.

In spite of this limitation, we were successful in generating an incipient site of coordinative unsaturation at Re via the introduction of more labile acetonitrile ligands in place of carbonyls at this center. Hence, $[RhRe(CH_3)(CO)_4(dppm)_2]^+$ reacts with one or two equivalents of $(CH_3)_3NO$

in the presence of CH_3CN to yield the mono and di-acetonitrile adducts, respectively. These complexes show tremendous promise in expanding the chemistry of this system by offering one or two, in the case of the diacetonitrile adduct, additional sites of reactivity. Replacement of these ligands by a variety of carbanions, alkynes or olefins may lead to interesting carbon-carbon coupling reactions similar to those which occur in diruthenium complexes. Such reactions could deepen the understanding of metal-metal cooperativity and the surface chemistry of organic fragments in relation to catalysis.

In summary, we have seen a number of instances where unique chemistry has arisen as a result of the interaction of of two heterometals in a bimetallic complex. The manner and degree of this interaction has led to reactions which, in some cases, have not been observed in the respective homobimetallic analogues. The study of this area is by no means complete as the chemistry of several bimetallic species discussed in Chapter 2 have yet to be explored. Furthermore, the breadth of this chemistry has been expanded even more by the generation of the alkyl complexes discussed in Chapter 6 with labile acetonitrile ligands on Re which show potential to coordinate substrate molecules at either metal. Future studies of this chemistry promise to expand our knowledge of metal-metal interactions and, ultimately, the understanding of hetero and homogeneous catalysis.