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Oxidative Addition Reactions and Methylene-Bridged Diiridium Complexes

By

John Waititu Muritu ©

A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

Department of Chemistry

Edmonton, Alberta
Fall, 2000

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John Waititu Muritu
P.C.E.A. Kangaita Church
P. O. Box 879
Nyeri, Kenya.

Date Sept 28, 2000.

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Oxidative Addition Reactions and Methylene-Bridged Diiridium Complexes** submitted by John Waititu Muritu in partial fulfillment of the requirements for the degree of Master of Science

Martin Cowie
M. Cowie (Supervisor)

RGCavell
R. G. Cavell

KTChuang
K. T. Chuang

Date Sept 28, 2000

Abstract

When $[Ir_2(CO)_3(dppm)_2]$ **(1)** is reacted with CH_3I and CH_3OCH_2I the targeted oxidative addition products $[Ir_2(I)(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ **(3)** and $[Ir_2(CH_3OCH_2)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(2)** respectively are obtained. Addition of methyl triflate to compound **3** results in iodide abstraction and formation of $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ while addition of methyl triflate to compound **2** results in double C-H activation of the methylene group forming a methoxy-carbyne bridged product $[Ir_2(H)_2(CO)_2(COCH_3)(dppm)_2][CF_3SO_3]$. This demonstrates the ease of C-H activation when an electron withdrawing group is a substituent. Addition of I^- to $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ regenerates compound **3** in contrast to the methyl C-H activation that is observed by the addition of CO, ^tBuNC, PR_3, SO_2.

When $[Ir_2(CO)_3(dppm)_2]$ **(1)** is reacted with CH_2I_2 or ICH_2CN, the expected oxidative addition products are not formed. Instead a hydrogen atom is abstracted from one dppm and an iodine atom added to the metals to form $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ and methyl iodide or acetonitrile. Carrying out the reaction with $PhCH_2Br$, $CH_2{=}CHCH_2Br$, and $BrCH_2CN$, does not change the reaction except resulting in formation of the bromide analogue $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ **(4)**. These reactions proceed by free radical mechanisms.

Attempts to synthesize a chloro substituted methyl compound by reacting the methoxymethyl compound $[Ir_2(CH_3OCH_2)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(2)** with HCl instead produces the methylene-bridged compound $[Ir_2(I)(Cl)(CO)_2(\mu\text{-}CH_2)\text{-}(dppm)_2]$ **(6)**. Reaction of compound **2** with acetylene gives the alkyne-bridged product $[Ir_2(CH_2OCH_3)(I)(CO)_2(\mu\text{-}HC{\equiv}CH)(dppm)_2]$ **[7]**.

The methylene-bridged complex $[Ir_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CO)(dppm)_2][BF_4]_2$ **(10)** was synthesized by reacting $[Ir_2(I)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ **(9)** with $AgBF_4$ under CO. Reacting compound **10** with two equivalent Me_3NO in CH_3CN results in formation of $[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ **(11)**.

Attempts to form longer-chain hydrocarbon fragments by reacting compounds **8** and **11** with diazomethane, substituted alkynes, and Grignard reagents were not successful. However, the compounds showed reactivity with H_2, HC≡CH ^{t}BuNC, SO_2, CS_2, vinylmagnesuim bromide and PR_3. Compound **11** reacts with excess H_2 to form mainly the tetrahydride $[Ir_2(CO)_2(\mu\text{-}H)_2(H)_2(dppm)_2][BF_4]_2$ **(14)**, and methane. Reaction with HC≡CH gives the alkyne-bridged $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}HC{\equiv}CH)(dppm)_2][BF_4]_2$ **(16)** and the vinylidene-bridged $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}C{=}CH_2)(dppm)_2][BF_4]_2$ **(17)**. Reaction with SO_2 gives the SO_2 bridged adduct $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}SO_2)(dppm)_2][BF_4]_2$ **(18)** and the reaction with CS_2 gives the CS_2 adduct $[Ir_2(CO)_2(CS_2)(\mu\text{-}CH_2)\ dppm)_2][BF_4]_2$ **(19)**. Reaction of $[Ir(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CO)(dppm)_2][BF_4]_2$ **(10)** with vinyl magnesium bromide does not give the targeted vinyl-containing product but instead gives the dibromo methylene-bridged compound $[Ir_2(Br)_2(\mu\text{-}CH_2)(CO)_2(dppm)_2$ **(20)**.

$[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ **(8)** reacts with excess H_2 to give the iodo-bridged dihydride $[Ir_2(H)_2(CO)_2(\mu\text{-}I)(dppm)_2][CF_3SO_3]$ and methane, reaction with ^{t}BuNC forms $[Ir_2(I)(CO)_2(^tBuNC)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ **[22]** and reaction with PR_2R' produces the adduct $[Ir_2(I)(CO)_2(PR_2R')(\mu\text{-}CH_2)(dppm)_2]$ $[CF_3SO_3]$ (R=R'=Me=**23**; R=Me, R'=Ph= **24**)

To my wife Veronica
and children
Francis, James, Kenneth and Ruth

Acknowledgements

I wish to thank my supervisor, Dr. Martin Cowie for his support, guidance, encouragement, understanding and expert advice throughout my studies from coursework to the completion of this thesis.

The Cowie research group: Past and present are thanked a lot for their support in all aspects. I especially thank Darren George for introducing me to the chemistry and the techniques when I joined the group. Okemona Oke deserves a nod for very helpful discussions, friendship and keen interest in the initial stages of my work. Jeffrey Torkelson is thanked for starting the bridging methylene chemistry and very smart techniques. Todd Graham is thanked for everything. The present members are all great guys and a word of thanks to you all: Rob Hilts, Steve Trepanier, Dusan Ristic-Petrovic, Amjad Hussain, Bryan Rowsell, John Lo, and Jason Anderson.

I am also indebted to the department of chemistry for financial support and everybody in the department who directly or indirectly contributed to the successful completion of my studies. In particular all the staff at the NMR lab: Glen Bigham, Gerdy Aarts, and Lai Kong for the many hours spent and assistance in many different ways. I also thank Jeanette and Ilona for all their assistance.

Then I cannot forget my friends James Kariuki, Patrick Kamau, Okwado Akotsi, Grant Wangila, Gregory Kiilu, and Japhet Irangu. Your help from the courses to research was invaluable to the completion of this work.

Very special thanks to my wife Veronica and children for their patience and tireless understanding whenever they heard it again “I have to go to the lab”.

Finally, I express my gratitude to my father and mother for their daily prayers and confidence in me. Above all very special thanks to God.

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List of Abbreviations and Symbols

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

Crystallographic Abbreviations and Symbols

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

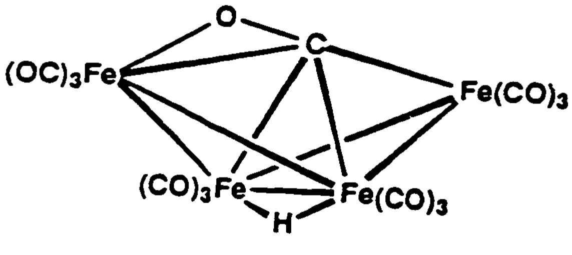
CHAPTER ONE

Introduction

In coordination compounds the metal atom or ion is surrounded by and bonded to a set of ligands (neutral molecules or anions) arranged in a distinct geometry. The physical and chemical properties of these compounds are determined by the metal, the ligands, the resulting metal-ligand bonds and the geometry of the compound.[1] Compounds containing associated metal centers are called clusters and are of great interest to synthetic and theoretical inorganic chemists, not only for the challenges of synthesis of the many forms thus far observed but also in development of explanations of the bonding between metals. Metal cluster compounds can be defined as: "those containing a group of two or more metal atoms that are held together to a significant extent by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the cluster".[2] In the past few years, studies on metal clusters have undergone a rapid expansion within inorganic and organometallic chemistry due in part to their relevance to catalysis.[3] A thorough understanding of how catalytic transformations of simple organic molecules into more complex useful end products occur is a continuing challenge to chemists. A large number of these transformations are catalyzed by transition metals. An understanding of the dynamics of metal-substrate interactions is therefore central to the rational design of highly efficient catalytic systems.

Industrial catalytic processes can be divided into two classes: homogeneous[4] and heterogeneous,[5] depending on the physical states of the catalysts and substrates under reaction conditions. A homogeneous catalyst is normally a transition-metal complex dissolved in the reaction solution. Such catalysts offer the advantages of being more readily understood due to the ease by which the discrete reaction steps can be monitored by spectroscopic techniques. In addition, since a single, well-defined catalyst or catalyst precursor is used, it is capable of high selectivity toward specific functional groups in substrates. Heterogeneous catalysts, in which the catalyst is in a different phase from the reactants are normally metals, metal oxides or metal sulfides, and the catalytic processes occur on the catalyst surfaces. These catalysts are generally preferred for industrial use because the catalyst can be easily recovered for re-use and generally possesses much higher thermal stability than complexes used in homogeneous processes. For heterogeneous catalysts, it is often difficult to identify the active component or reaction intermediates, and mechanistic information on the surface processes is rare.[3b, 4a, 4b] This is because there are potentially many different active sites and the severe conditions make studies of the interaction between the catalyst and substrate very difficult.[3c,6] One approach to obtaining valuable information about intermediates in heterogeneous systems is through the use of well-behaved model compounds which are usually studied under more amenable homogeneous conditions. Although a wealth of methods have been employed to study heterogeneous catalytic processes, including surface spectroscopy, probe-molecule studies and chemical trapping experiments, the exact modes of metal-substrate interactions are difficult to directly observe and models are important in elucidating mechanisms of action of these catalysts.[6a, 7]

Currently, most homogeneous processes occurring at a single metal center are rather well understood particularly for stoichiometric reactions and what has been learned about these systems has been adapted as models for heterogeneous processes.[3b,8] However, one common view is that polymetallic clusters[3c,9] are probably better representations of metal surfaces in heterogeneous catalysis than their mononuclear counterparts, due to the fact that the adjacent metals mimic to some degree the multi-metal environments of metal surfaces.[6c,10,11] The ability of clusters to utilize adjacent metals in the activation of substrate molecules as proposed for surfaces is uniquely demonstrated by the tetrairon complex [Me_3NCH_2Ph][$Fe_4(CO)_{13}H$] **(A)** in which a carbonyl is bound to four metals; three metals are bound to the carbonyl carbon, while the fourth is bound in a side-on fashion through the C-O bond as shown in the following diagram.[12]

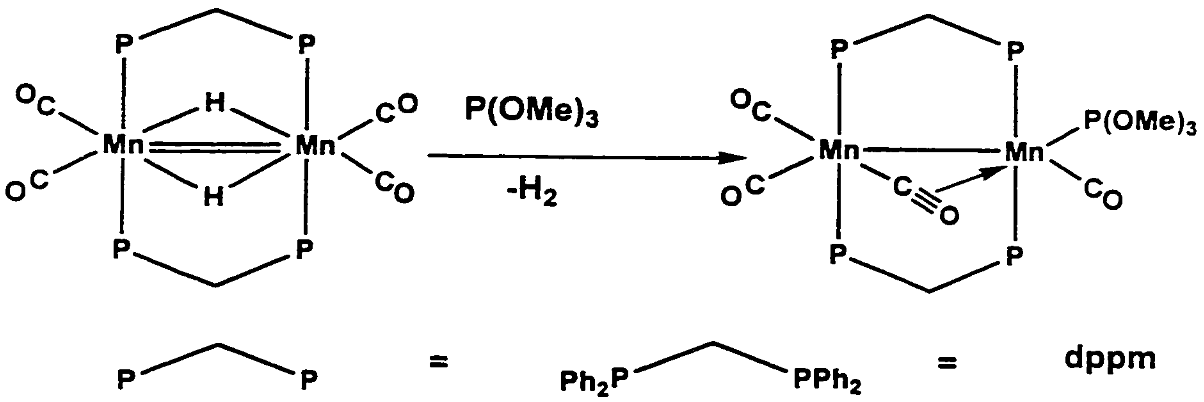


A

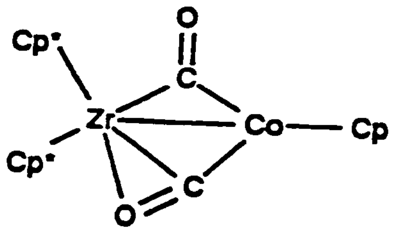
This structure demonstrates one of the attractive features of metal clusters in allowing the activation of multiple bonds in molecules such as carbon monoxide and nitrogen.[3,6c] The dissociative chemisorption of CO or N_2 on a metal surface occurs under reasonably mild conditions and it is proposed that this occurs by binding of these molecules to surface metal atoms in a side-on fashion. Although such binding modes are difficult to confirm on a surface,[13] complex **A** serves as a model for such a process. Simple bonding arguments allow a rationalization of the bond-order reduction through donation of electron density from the occupied π orbitals of the substrate and concomitant back donation from the metals into the π^* antibonding orbitals. In contrast, the triple bonds of such substrates are not readily cleaved at a single metal center of mononuclear complexes.

Binuclear complexes can be viewed as prototypical clusters containing two metals and represent the simplest multi-metal system in which the involvement of adjacent metals in the chemistry can be studied. Although a binuclear system is a poorer model of a metal surface or other heterogeneous systems than a multi-metal cluster of higher nuclearity, it does offer the advantage of ease of study. It is anticipated that the chemistry of bimetallic compounds in which the two metal atoms are held in close proximity, may show differences from that of mononuclear compounds owing to the possibilities of interactions between the metals and/or between bridging ligands and the metals –features that are absent in mononuclear compounds.[14] The structures and some reactivity patterns of these bimetallic compounds are expected to be unique as a result of cooperative involvement of the two adjacent metals.[15]

Metal-metal cooperativity effects can manifest themselves in a number of ways. Ligands can adopt coordination modes that are not possible for mononuclear complexes (such as the bridging of the two metal centers) giving rise to increased reactivity in the binuclear complexes.[16] For example, the movement of a ligand from a bridging to a terminal position could serve as a means of creating a vacant coordination site at one of the metals for attack by an incoming substrate. Also, the reverse, in which movement of a ligand from a terminal to a bridging position, could be a means of creating coordinative saturation at the adjacent metal, thus stabilizing the resulting complex. Another scenario would involve binding of a ligand by one metal center while the adjacent metal acts as a sink or source of additional electron density or molecular fragments as dictated by the requirements of the neighbouring metal. In the example below[17] the terminal CO group on one of the Mn centers, acts as an electron source by simultaneously binding in a π fashion to the adjacent Mn atom thereby compensating for the electronic unsaturation at this metal, which would have an unfavourable 16e configuration in its absence. There is also the possibility that a substrate molecule may be coordinated at one metal center and then induced to react with molecules or fragments that are coordinated to the adjacent metal.[16a]

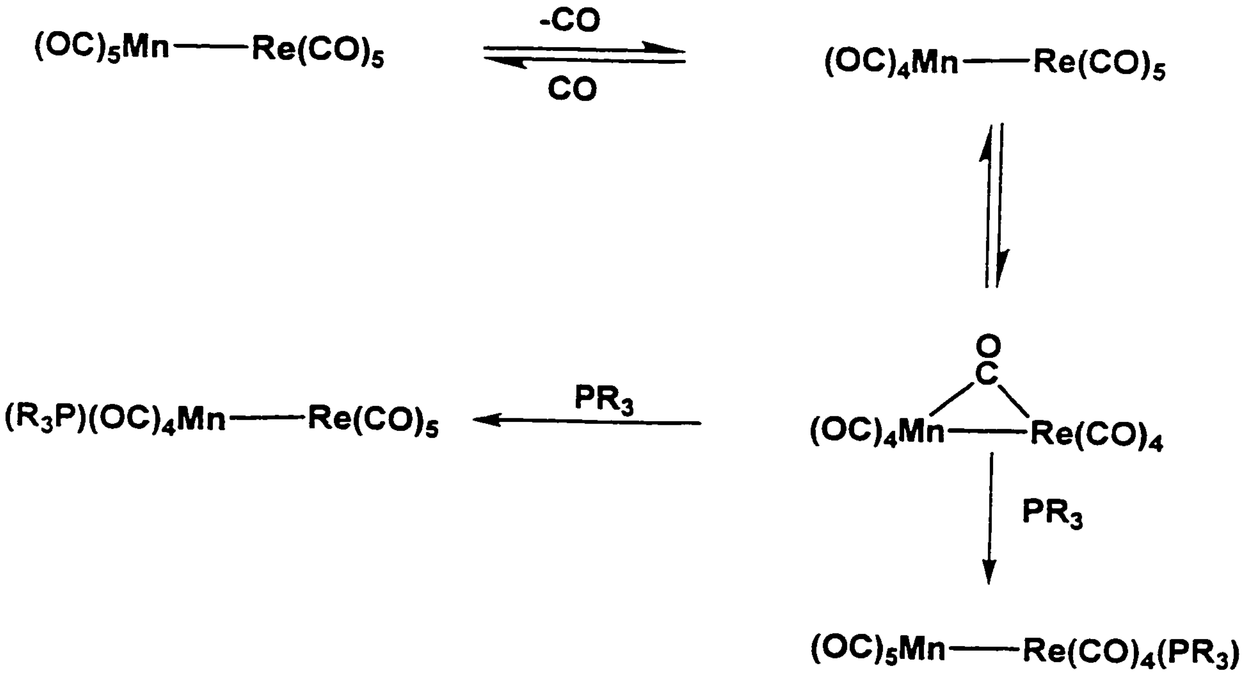


Most catalytic studies have focused on homobimetallic complexes in which both metals are the same. Of late, however, interest in heterobimetallic compounds, involving two different metals, has increased. It has been suggested that two different metals adjacent to each other, might display different chemistry than their homo-bimetallic counterparts. For example, the early-late transition metal compounds may cooperatively activate organic subtrate molecules. The electron-poor early transition metal and the electron-rich late transition metal are likely to create an ideal environment for heterolytic bond cleavage of polar substrates. In addition, the late transition metal is often more reactive due to electronic or steric saturation of the early metal center.[18] As an example, a Zr/Co complex was found to activate the reduction of CO as shown below. This could result from the oxophilicity of the early transition metal, which being electron deficient, functions as a hard Lewis acid, while the late transition metal in low oxidation state serves as either soft Lewis base or acid.[19] The principle used in such complexes was that the early metal could assist in weakening the CO bond



while the late metal could coordinate and activate dihydrogen molecules for subsequent reduction of coordinated CO. One of the significant aspects of the chemistry of heteronuclear compounds is the introduction of chemical reactivity to an inert metal center by the adjacent reactive metal center. This is exemplified by the substitution reactions occurring at the Re and Mn centers in [ReMn(CO)$_{10}$] as shown in Scheme 1.1[20] below. The more kinetically labile manganese center

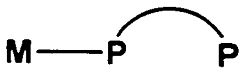
Scheme 1.1



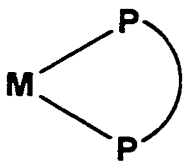
loses one carbonyl and introduces unsaturation at the adjacent Re center by the formation of the presumed carbonyl-bridged species. The monosubstituted complexes are formed upon the subsequent nucleophilic attack either on the rhenium or manganese centers by a phosphine or phosphite (PR_3; R=Ph, n-C_4H_9 or OPh). This observation is consistent with the fact that the reaction rate of $[ReMn(CO)_{10}]$ with PPh_3 is faster than that of the dirhenium carbonyl complex $[Re_2(CO)_{10}]$ due to the presence of the labile Mn center in the former.[20] Mixed-metal binuclear complexes have been studied largely for the possibilities of exhibiting novel chemistry and have elicited a great deal of interest as homogeneous catalysts.[5,21] Also, mixed-metal catalysts find extensive use in industrial scale processes such as the hydrodesulfurization of coal (Co/Mo catalyst),[22] gasoline reforming (Re/Pt)[22] and catalytic converters employed in the scrubbing of exhaust from automobiles (Rh/Pt). In addition, the formation of ethylene glycol from syn gas (CO/H_2) utilizes a Ru/Rh catalyst.[23] Although Ru and Rh used individually as catalysts are known to produce oxygenates, improved selectivity was shown for combination of these metals.[24] Most of these systems require heterogeneous conditions, although several homogeneously catalyzed processes are known including the Wacker Process in which ethylene is oxidized by a Pd/Cu[25] catalyst to give acetaldehyde, and the BP Chemicals Acetic Acid Process which employs an Ir/Ru[23] catalyst to convert a CH_3OH/CO mixture into acetic acid.

During chemical reactions involving binuclear complexes, changes in oxidation state, changes in coordination geometry, and formation of metal-ligand bonds may result in cleavage of the metal-metal bond.[26] Thus bridging ligands are often employed to prevent fragmentation of these complexes into mononuclear species in the absence of metal-metal bonding. Several bridging ligands are in current use[27] but the aryl or alkyl diphosphine ligands ($R_2P(CH_2)_nPR_2$, R = alkyl, aryl), in which two PR_2 groups are joined by one or more methylene units are the most popular. One of these is bis(diphenylphosphino)methane (dppm, or DPM = $Ph_2PCH_2PPh_2$) which has attracted the attention of numerous research groups since the synthesis of the first dppm-bridged complex $[\{CpFe(\mu\text{-}CO)\}_2(\mu\text{-}dppm)]$ by Haines and coworkers in 1968.[28] The chemistry of compounds containing dppm has been the subject of several excellent review articles by Puddephatt,[29] Balch,[17b] Poilblanc[27a] and McAuliffe.[32] However, some brief details of the chemistry relevant to the work discussed in later chapters of this thesis will be given. One of the reasons for the popularity of dppm in the synthesis of binuclear compounds is its similarity to triphenylphosphine, a ubiquitous ligand in mononuclear coordination chemistry; both are inexpensive, virtually odorless, air-stable solids that readily form complexes with late transition metals. In contrast, bis(dimethylphosphino)methane (dmpm), a similar ligand that would be attractive due to its decreased steric bulk and increased basicity[30] has been much less utilized. The comparatively high cost and pyrophoric nature of dmpm are significant drawbacks, but more importantly, reactions involving dmpm or its complexes tend to be more difficult to control, due to the tendency of the products to be highly fluxional and prone to subsequent rearrangement.[31]

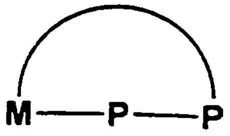
Diphosphine ligands, having the chemical formula $R_2P(CH_2)_nPR_2$, can assume a number of coordination modes from monodentate, to cis-chelating, to trans-chelating or bridging, depending on the length of the backbone (the number of methylene units) connecting the two phosphorus atoms as diagrammed below.[29,32,33] For dppm which has only one connecting methylene group, the trans-chelating mode is clearly ruled out since the backbone is far too short to span trans-related phosphorus atoms; however, all the other modes are observed. The bidentate chelating mode has substantial ring tension as shown by X-ray studies.[29b-f] The observed P-M-P angles in the chelating compounds are substantially smaller than that expected from the ideal geometry. For example, in $[Mo(CO)_4(dppm)]$ the P-M-P angle is 67.3°,[29e] which deviates significantly from the ideal bond angle in an octahedral geometry. In addition, the P-C-P angle (95.6(4)°) is significantly less than 109.5°, showing the strain within the M-P-C-P ring. The biggest advantage of dppm is its strong tendency to adopt the bridging mode instead of chelating. Dppm shows the desirable property of holding the two metal centers in close proximity while still having a large degree of flexibility in the range of metal-metal distances that can be spanned; metal-metal distances



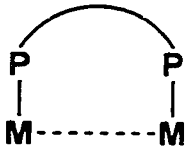
monodentate



cis-chelating



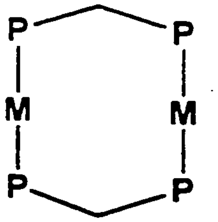
trans-chelating



bridging

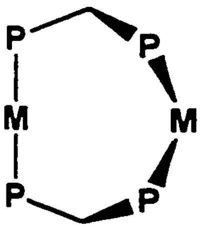
between 2.4 and 3.6 Å are commonly accommodated by bridging dppm ligands. Such flexibility is desirable as it allows the ligands to adjust to changes in the metal's oxidation state and coordination geometry that frequently accompany chemical reactions. The flexibility also allows the cleavage or formation of metal-metal bonds which often occurs in reactions involving binuclear compounds. For example, the insertion of hexafluoro-2-butyne into the metal-metal bond of $[Pd_2Cl_2(dppm)_2]$ yields a parallel-bridged alkyne compound $[Pd_2Cl_2(\mu\text{-}CF_3CCCF_3)(dppm)_2]$ accompanied by an increase in the metal-metal separation from 2.651 to 3.492 Å.[34,35]

Complexes containing two bridging dppm ligands can display a number of geometries. In a binuclear framework, the common arrangements when two diphosphine ligands bridge two metals are usually trans to each other at both metals as demonstrated in diagram **B** below in the dppm-bridged binuclear



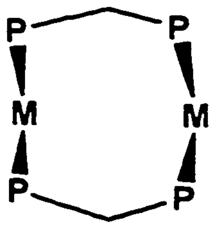
B

trans, trans



C

trans, cis



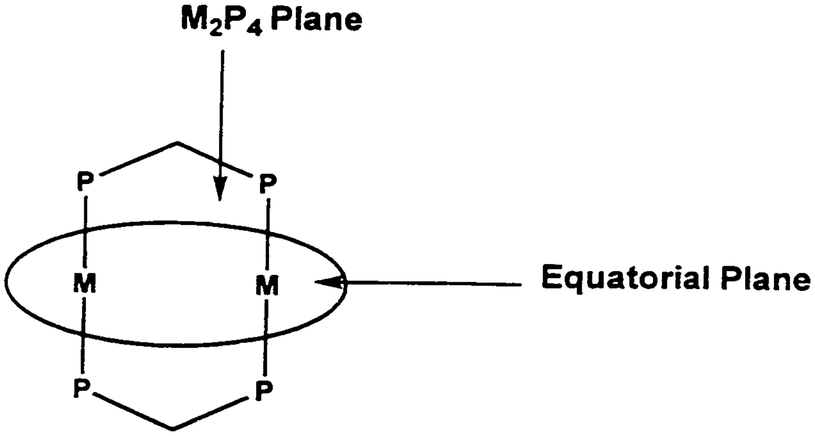
D

cis, cis

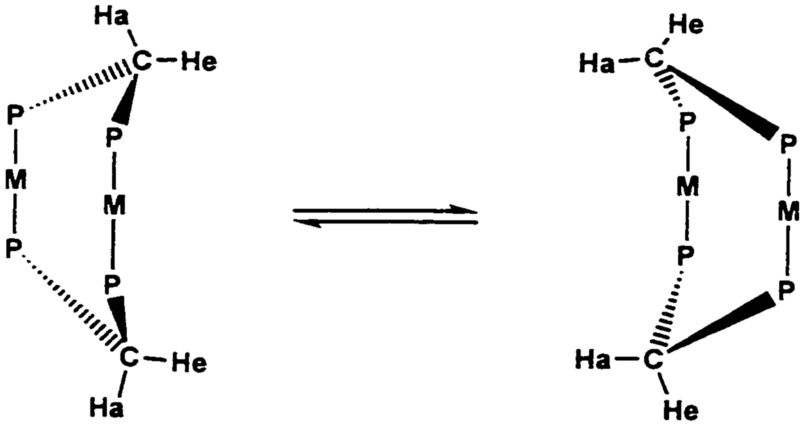
compounds $[RhCl(CO)(dppm)]_2$,[36] $[Pd_2Cl_2(\mu\text{-}CF_3C{\equiv}CCF_3)(dppm)_2]$[34] and $[Rh_2(CO)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CBu^t)(dppm)_2]$.[37] In this orientation the trans alignment can minimize any unfavorable steric interactions between bulky phenyl substituents.

However, a number of compounds in which the two phosphorus atoms are trans on one metal and cis **(C)** on the other are observed[38] and a few compounds are also known in which diphosphines occupy cis positions at both metals **(D)**.[39] All three geometries as illustrated above are also seen in a series of closely related diplatinum methyl compounds, *cis*-$[Pt_2Me_4(dppm)_2]$,[39c] *cis, trans*-$[Pt_2Me_3(dppm)_2][PF_6]$[38d,e] and *trans,trans*-$[Pt_2I_2Me_2(dppm)_2]$.[40]

Another attractive feature of dppm-containing compounds is that they are amenable to characterization in solution via multinuclear NMR[17] spectroscopy. In homobimetallic bis(dppm)-bridged species having a trans,trans geometry, the equatorial plane, as shown below, has mirror equivalence of the chemical



environment of the phosphorus atoms, resulting in the phosphorus atoms attached to one metal being equivalent. If the environments of the metal atoms are in any way different, or if the complex is heterobimetallic, the sets of phosphorus atoms attached to each metal center will be inequivalent and two multiplet resonances will be observed. If the coordination spheres of both metal centers are identical then the four phosphorus nuclei are chemically equivalent and will give rise to one resonance in the $^{31}P\{^1H\}$ NMR spectrum. Further, if the complex has 'front-back' symmetry, in other words if the environment on each side of the M_2P_4 plane is equivalent, then rapid exchange, as shown below , of



the axial and equatorial hydrogens on the CH_2 groups will equilibrate these two protons on the NMR time scale and so only one methylene proton signal is observed in the ^1H-NMR spectrum. When the chemical environment on the two sides of the M_2P_4 frame is such that there is front-back asymmetry, such as is observed in "A-frame" compounds, two methylene proton signals are observed for the dppm ligands in the ^1H NMR spectrum inspite of the axial/equatorial exchange, although one signal would still arise in the ^{31}P NMR spectrum. In all situations mentioned, precautions should be taken since an accidental equivalence of the methylene protons can give rise to only one signal in the ^1H NMR spectrum instead of the expected two.

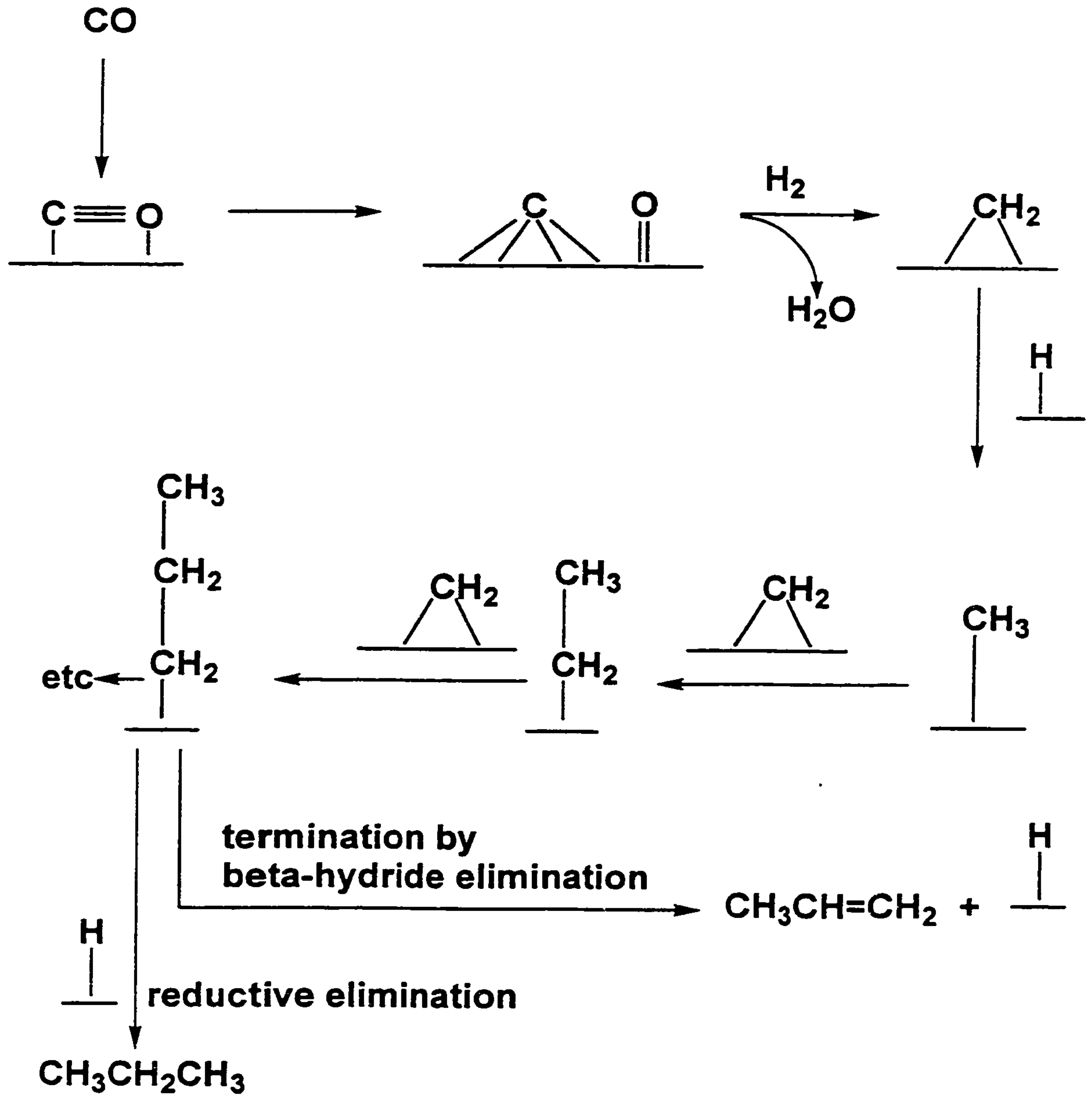
The disposition of ligands such as hydride or carbonyl groups can be determined from the multiplicities of the resonances in the respective ^1H and

$^{13}C\{^1H\}$ NMR spectra. Furthermore, in the case of asymmetric complexes the attachment of such ligands to one metal center or the other can be established through the use of selective heteronuclear decoupling techniques which produce a simplification of the multiplet observed for other spin-active ligands attached to the same metal center. Normally, the dppm ligands play an innocent role during the reactions but there are emerging reports in which deprotonations or substitutions of the dppm methylene protons[41], insertions/cleavages involving the M-P[42] or P-C bonds or orthometallation[44,41c] processes have occurred.

For carbonyl-containing compounds, IR spectroscopy plays an important role in the determination of carbonyl coordination modes. A terminal carbonyl absorbs at a higher frequency of between 2125 and 1850 cm^{-1} whereas a bridging carbonyl typically absorbs at a lower frequency of between 1860 and 1700 cm^{-1}.[45]

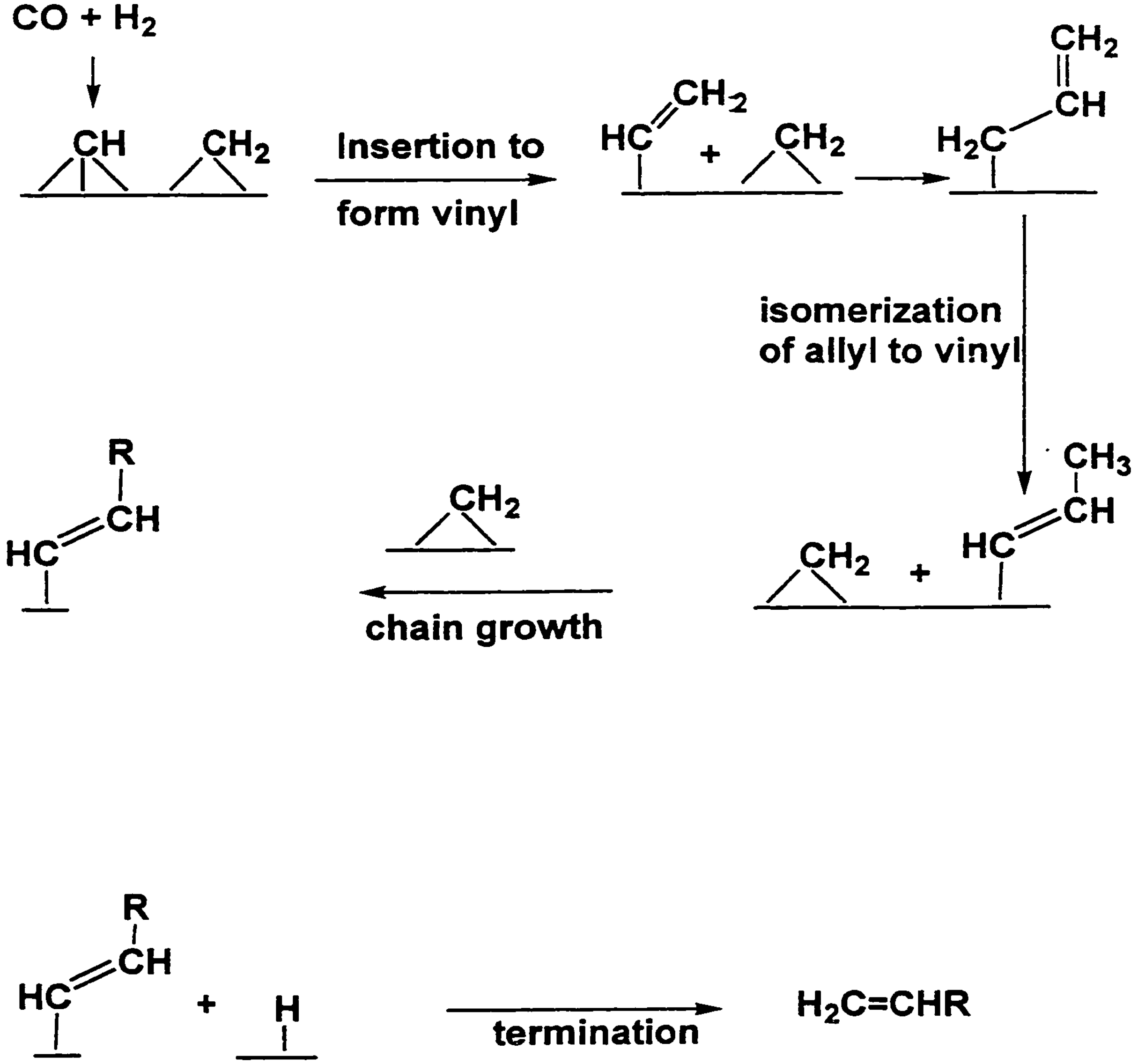
At the outset, there were two main goals of this thesis project. One objective was to synthesize and study the reactivities of methylene-bridged diiridium complexes with small molecules or molecular fragments such as diazomethane, alkynes, isocyanides, phosphines, H_2, Grignard Reagents, SO_2, and CS_2. Of special interest was the possibility of carbon-carbon bond formation involving the bridging methylene group and other organic fragments much as is known to occur in the Fischer-Tropsch (FT) process.[46] The Fischer-Tropsch reaction is an important heterogeneously catalyzed reaction that allows for the formation of valuable chemicals from inexpensive feedstocks. In this reaction, CO and H_2 react in the presence of a catalyst to form long-chain hydrocarbons and other organic products for subsequent use as fuels or chemical feedstocks. Our interest in modeling surface-bound methylene groups applies directly to the FT reaction. The use of this process has been gaining in popularity due to decreased processing costs with advancing technology, and recently Shell[47a], Exxon[48], Texaco[49] and other companies[50] have either brought online, or have plans to bring online, FT plants to produce commodity chemicals. Because of the heterogeneous nature of the process that occurs under elevated temperatures and pressures, little is presently understood about the reactions occurring on the catalyst surface, and studies using organometallic model complexes that contain the organic fragments similar to those known to exist on the FT catalyst are therefore of interest in order to gain more understanding of the individual steps in the C-C bond-formation process. By understanding how C-C bond formation occurs, it is hoped that the rational design of catalysts can be undertaken that will improve the selectivity of the process. Numerous studies have been performed with late-metal organometallic systems in an effort to model the chemistry thought to occur on the FT surfaces. In the 1980's, Brady and Pettit,[51] proposed a scheme for C-C bond formation that involved the initial formation of methylene fragments on the surface by dissociation of CO and hydrogenation of the resulting carbide fragments. Transformation of some methylene fragments into methyl groups and the insertion of methylene units into a growing alkyl chain was proposed to yield long-chain hydrocarbons as illustrated in Scheme 1.2.

Scheme 1.2 Brady & Pettit Fischer-Tropsch Mechanism for Hydrocarbon formation.



The two possibilities for termination of alkyl chain growth are: (1) reductive elimination with a surface hydride to yield alkanes and (2) β-hydride elimination to yield α-olefins. The former mechanism has been shown to be flawed because more recent studies[52] have shown that α-olefins are the primary products of FT synthesis and the second mechanism does not accurately account for the linear versus branched product distribution or explain how a β-elimination step to yield an α-olefin from a long chain alkyl would be favored on a metal surface covered in hydride ligands. More recently, Maitlis has proposed a mechanism based on model studies carried out with dirhodium compounds,[52a,53,54] in which the important species in C-C bond formation are methylene and vinyl groups that are present on the surface of FT catalysts. The Maitlis alkenyl mechanism is outlined below in Scheme 1.3. Dissociation and hydrogenation of CO generates surface-bound methyne and methylene groups. Combination of the methylene and methyne groups yields a vinyl species, which is thought to be the key species involved in the catalytic cycle. Vinyl to methylene migration yields an allyl group that isomerizes by transfer of an α-hydrogen to the γ-carbon, yielding a substituted vinyl species. Sequential vinyl-to-methylene migration steps results in the propagation of the hydrocarbon chain. Termination of the cycle occurs by reductive elimination of the vinyl group with a surface bound hydride ligand producing an α-olefin. This proposal has found support from studies under heterogenous conditions in which isotopically labelled vinyl groups are incorporated into the products, whereas other labelled C_2 fragments are not.[52b]

Scheme 1.3 **Maitlis FT Alkenyl Mechanism**



The inclusion of methylene species in both the proposed FT mechanisms (Schemes 1.2 &1.3) makes the study of methylene complexes attractive for modeling the FT reaction. The chemical properties of a bridging methylene group can be distinguished by one of two types of principal behavior: those in which the bridging methylene group is often sufficiently inert that ligand substitution can occur without disruption of the bridging methylene groups and others in which the bridging methylene is implicated in the reaction. The FT reaction is an example in which the methylene group is implicated. Other reactions where the methylene group is implicated include protonation as in the example below in which attack occurs at the bridging methylene group[55] to produce methane.

$$[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6] \xrightleftharpoons[2CH_3^-\,(-CH_4)]{2H^+\,(-CH_4)} [Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6]^{2+}$$

Hydrogenolysis of the bridging methylene was observed to occur when $[Fe(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$ was reacted with H_2 at 200 psi in benzene at 60°C producing methane (81%).[56] Carbonylation of $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ took place upon reaction with CO at 5 atm, and 60°C in benzene to yield *trans*-$[Ru(CO)_3(PMe_3)_2]$ but methane was not detected.[55] Carbene transfer from $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$ to an olefin (olefin homologation) was observed;[56] thus reaction of the complex with ethylene at 400 psi in benzene at 55°C gave C_3H_6 in more than 90% yield while reaction with C_3H_6 gave mainly isobutene and C_4H_8.

The photochemical reaction of $[(\eta^5\text{-}C_5H_5)M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)CH_3)]$ (M = Fe, Ru) with acetylene resulted in acetylene insertion into one of the M-C bonds producing a three-carbon bridging system.[57]

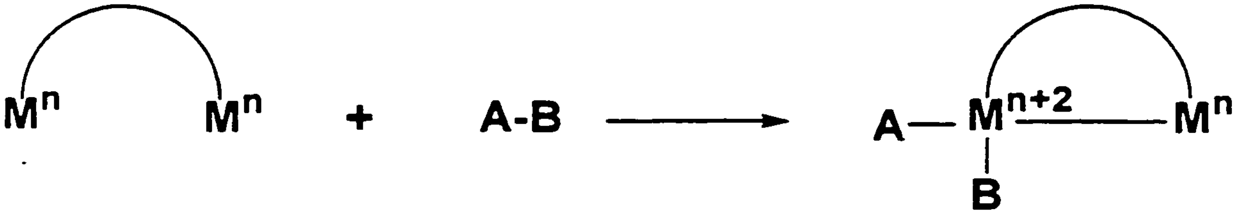
Recently in our group, the high reactivity of a bridging methylene with alkynes has been demonstrated by an Ir/Ru system in which reaction of $[IrRu(CO)_3(\mu\text{-}CH_2)(\mu\text{-}CO)(dppm)_2][BF_4]$ with acetylene resulted in formation of $[IrRu(CO)_2(H_2CCH{=}CH)(\mu\text{-}HC{\equiv}CH)(dppm)_2][BF_4]$ containing a C_3H_4 system.[58] Reaction of an analogous Rh/Os system $[RhOs(CO)_4(dppm)_2][BF_4]$ with diazomethane resulted in formation of $[RhOs(CO)_3(CH_3)(\eta^1\text{-}CH_2CH{=}CH_2)\text{-}(dppm)_2][BF_4]$ at 20°C and $[RhOs(CO)_3(CH_2CH_2CH_2CH_2)(dppm)_2][BF_4]$ unit at -60°C.[59] The selective coupling of methylene groups to give either allyl or metallacyclopentane fragments on a mixed-metal core demonstrates how metals having different properties can have applications in FT chemistry.

Reactions in which the bridging alkylidene group maintains its integrity include treatment with a neutral ligand such as PPh_3 which resulted in CO displacement by PPh_3[59] in $[(OC)_5M\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ (M= Cr or W). The reaction of $[Au(CH_2)_2PPh_2]_2$ with $Hg(CN)_2$ in THF gives the gold(II) dicyanide adduct $[Au(CH_2)_2PPh_2]_2(CN)_2$ in which the CH_2 groups are maintained. Reaction of $[Au(Br)(CH_2)_2PPh_2]_2$ with 2 eq MeLi gave $[Au(CH_3)(CH_2)_2PPh_2]_2$ in which the methyl group displaces bromide from the terminal position.[61] It is therefore of interest to study the reactivity of methylene-bridged diiridium complexes with a variety of small molecules that have varying steric and electronic properties with a view to determining the behaviour of the bridging methylene group especially with respect to C-C bond formation.

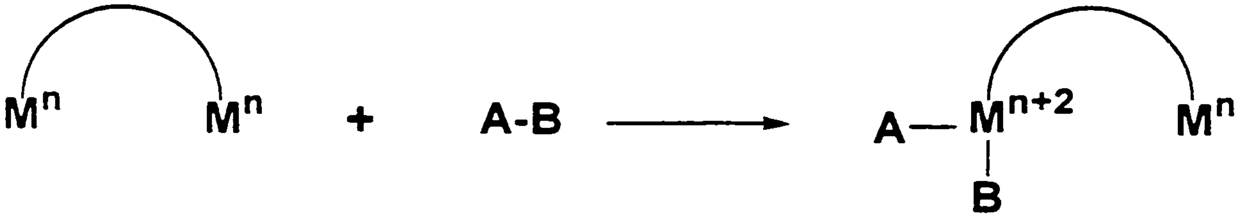
The second objective of this thesis was to study the oxidative addition of alkyl halides to the Ir(0) complex, $[Ir_2(CO)_3(dppm)_2]$. Oxidative addition in organometallic chemistry is a well established concept where a group A-B adds to and oxidizes a single metal center (M) forming M-A and M-B bonds by cleavage of the A-B bond. The metal thus behaves simultaneously as a Lewis acid and as a Lewis base.[62] For all such reactions, both the oxidation state and the coordination number of the metal increases so that the oxidative addition results in a change in electron configuration from d^n to d^{n-2} and a corresponding increase in coordination number by two. Oxidative additions can proceed by a variety of mechanisms that depend on the metal, the ligands, or the solvent system. Two-electron oxidative additions are known for virtually all d^n (n=even and $n \geq 2$) complexes; however, they are far more prevalent with the electron-rich elements to the right of the transition series. In general, factors that tend to increase the availability of electrons on the metal tend to increase oxidizability. Steric properties of the ligands must also be considered since bulky ligands tend to decrease the ease of oxidative addition by inhibiting the necessary approach of the substrate and preventing the increase in coordination number. While oxidative addition is well studied for mononuclear complexes, the special properties of a binuclear system introduce other possibilities with respect to both the mechanism and final products of oxidative additions. Hybridization of suitable metal orbitals in a bimetallic complex of appropriate symmetry may allow metal-

metal bonding, thus permitting the bimetallic species to accommodate unconventional formal oxidation states. Reaction of a substrate A-B to a bridged bimetallic species may result in one of the following reactivity patterns:

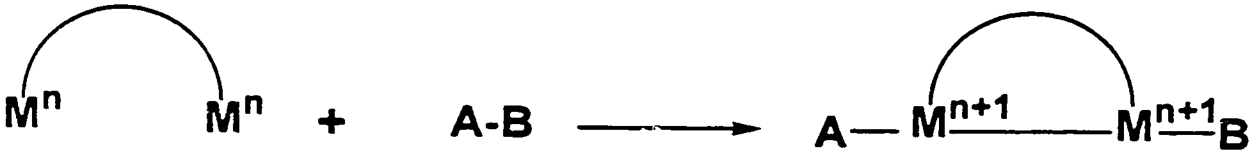
(1) A metal-metal bond is formed with a two-electron oxidation at one metal.[63]



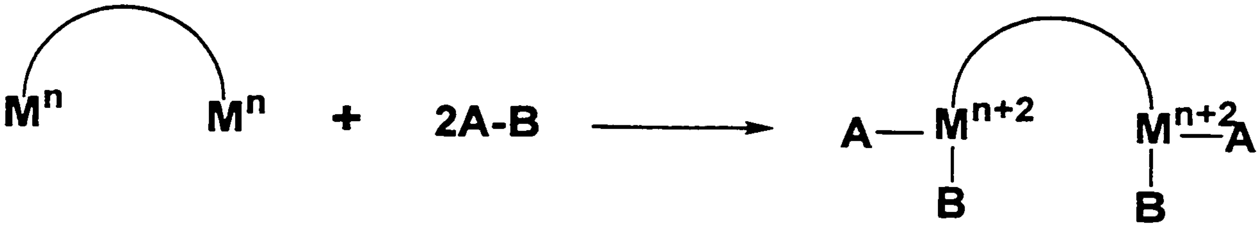
(2) A two-electron oxidation at one metal without formation of a M-M bond.[63]



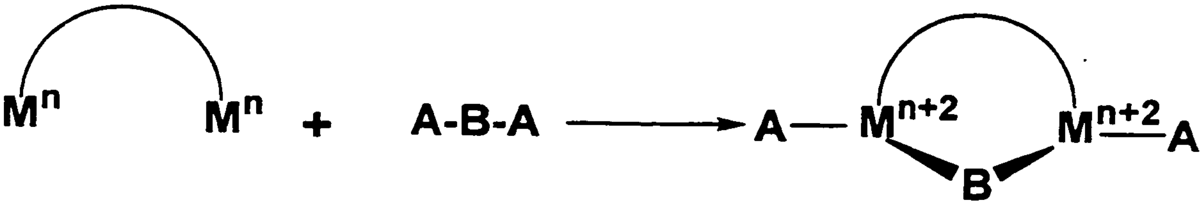
(3) One-electron oxidation at each metal with formation of a metal-metal bond.[64] This transannular oxidative addition has emerged as the most common type of reaction.



(4) A two-electron oxidative addition at each metal center without formation of a M-M bond.



(5) Oxidative addition of both A-B-A bonds to give a species bridged by a hydrocarbyl fragment.[65,66]



The oxidative addition of a polar, electrophilic substrate A-B (such as alkyl and aryl halides) to a metal complex may proceed as illustrated above by single-electron transfer and two-electron transfer. The two-electron transfer for R-X oxidation includes the S_N2 mechanism, where the metal behaves as the nucleophile characterized by an ion-pair intermediate, while the one-electron mechanism for R-X oxidative addition includes: (1) atom abstraction and combination of the resulting radical with a second metal (each metal undergoes a one-electron change); (2) inner-sphere electron transfer/caged radical-pair mechanism (the principal product (R-$M^{(n+2)}$-X) is the same as that from an S_N2 pathway except racemization occurs instead of inversion); and (3) radical chain pathway where the metal undergoes a two-electron oxidation.

The primary objective in this study was to study the oxidative addition of some alkyl halides such as benzyl bromide, allylbromide and bromoacetonitrile to $[Ir_2(CO)_3(dppm)_2]$. It had been previously determined that addition of diiodomethane and iodoacetonitrile to $[Ir_2(CO)_3(dppm)_2]$ resulted in a hydrogen abstraction from one dppm methylene group and addition of the iodine atom across the metal-metal bond[67]and it was of interest to determine the behavior of alkyl bromides. Oxidative addition of methyl iodide was also of interest considering that MeI is involved in the industrial conversion of methanol into acetic acid.[68-70] It was also of interest to investigate the oxidative addition of substituted methyl halides (XCH_2Y; X= halide, Y= substituent) as this was considered a useful route to complexes containing substituted methyl ligands. We had shown that the methyl complex $[r_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ underwent facile, and sometimes reversible, methyl C-H bond cleavage upon addition of substrate molecules,[71-73] and we were interested in generating analogous compounds in which one or more of the methyl hydrogens were replaced by different substituents, to determine the tendencies of these substituted methyl groups to undergo C-H bond activation. A recent study has suggested that C-H bond activation should be enhanced by electron-withdrawing substituents.[74] Finally, a synthetic route into methylene-bridged compounds was envisaged by oxidative addition of both carbon-halogen bonds of dihalomethane molecules.

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CHAPTER TWO

Oxidative Addition of Alkyl Halides to $[Ir_2(CO)_3(dppm)_2]$

Introduction

As part of an ongoing interest in the synthesis and reactivity of binuclear complexes containing hydrocarbyl fragments,[1] we have initiated a study into the synthesis of binuclear alkyl complexes by the oxidative addition of alkyl halides to binuclear diiridium and rhodium-iridium complexes. Oxidative-addition reactions of alkyl halides are of fundamental interest and have been much studied, particularly in the case of low-valent, late transition metals.[2] Furthermore, the addition of methyl iodide to late-metal complexes is of enormous practical significance since it represents one of the key steps in the industrial conversion of methanol into acetic acid.[3-5] Although the majority of acetic acid production is based on a rhodium-based catalyst,[3-5] which has been identified as possibly the most successful example of an industrial process catalyzed by a metal complex,[5] BP Chemicals has recently introduced a related iridium-based catalyst system.[6] Both systems continue to generate considerable interest.[5,7,8]

Although the initial interest in alkyl halide additions concentrated on mononuclear complexes,[2] there has been considerable subsequent interest in multimetal systems, particularly binuclear ones.[9-17] Even in a relatively simple binuclear complex the second metal introduces additional reactivity possibilities. In homobinuclear systems, based on an M^{n+}/M^{n+} core, the following reactivity patterns have been identified: (1) oxidative addition of one alkyl halide (RX) unit to one metal to give an $M^{n+}/M^{(n+2)+}$ product;[12,13,14b] (2) addition of one RX unit across the dimetal framework to give an $M^{(n+1)+}/M^{(n+1)+}$ core;[9,10,14a,16a,b] (3) addition of two RX units (one to each metal) to give an $M^{(n+2)+}/M^{(n+2)+}$ product; [11,13,14b] and (4) in the case in which the organic substrate contains two C-X bonds, cleavage of both C-X bonds to give an $M^{(n+2)+}/M^{(n+2)+}$ framework, bridged by the resulting hydrocarbyl fragment. [11,16c] These reactivity patterns were diagrammed and discussed in chapter one.

In addition to the intrinsic interest in oxidative addition to bimetallic frameworks, particularly those having metals (Rh, Ir) used commercially in the acetic acid synthesis, we also considered that addition of substituted methyl halides (XCH_2Y; X= halide, Y= substituent) could constitute a useful route to complexes containing substituted methyl ligands, by oxidative addition of the carbon-halide bond. We had shown that the methyl complex $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ underwent facile, and sometimes reversible, methyl C-H bond cleavage upon addition of substrate molecules,[1j,m,p] and we were interested in generating analogous compounds in which one or more of the methyl hygrogens were replaced by different substituents, to determine the tendencies of these substituted methyl groups to undergo C-H bond activation. Certainly a recent study has suggested that C-H bond activation should be enhanced by substituting a hydrogen by an electron-withdrawing substituent.[18] In this chapter we report the reactions of $[Ir_2(CO)_3(dppm)_2]$ **(1)** with various alkyl halides.

Experimental Section

General Comments. All solvents were deoxygenated and dried over the appropriate drying agents (see Appendix) prior to use and were stored under dinitrogen. Deuterated solvents used for NMR experiments were degassed and stored under dinitrogen over molecular sieves. Reactions were routinely carried out at room temperature (unless otherwise stated) and under standard Schlenk conditions. Compounds that were isolated as solids were purified by recrystallization. Ammonium hexachloroiridate (IV) was obtained from Vancouver Island Precious Metals. Methyl iodide, benzylbromide, allylbromide and bromoacetonitrile were purchased from Aldrich Chemicals and used as received. The compounds $[Ir_2(CO)_3(dppm)_2]$[19] **(1)** and $[Ir_2(I)(CH_2OCH_3)(\mu\text{-}CO)(CO)(dppm)_2]$[20] **(2)** were prepared as previously described.

All routine NMR experiments were conducted on either a Bruker AM-400 MHz spectrometer (operating at 100.614 MHz for ^{13}C and 161.978 MHz for ^{31}P) or a Bruker 200 MHz spectrometer (operating at 50.323 MHz for ^{13}C and 81.015 MHz for ^{31}P). Infra-red spectra were obtained on a Nicolet Magna-IR 750 Fourier Transform or Perkin-Elmer 883 IR spectrometer, either as Nujol mulls or as CH_2Cl_2 casts on KBr plates. Elemental analyses were performed by the microanalytical services within our department. The elemental analyses attempted on purified samples of a number of the diiridium compounds were unsatisfactory due to some contamination by traces of the previously characterized diiodo dicarbonyl species $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$,[21] the tricarbonyl iodide $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$,[21] or other uncharacterized species that could not be removed. Characterization for these compounds is based primarily on spectroscopic methods. The $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR and IR data for all new compounds are given in Table 2.1

Preparation of Compounds.

(a) $[Ir_2(I)(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ (3). A 30 mg (0.025 mmol) sample of $[Ir_2(CO)_3(dppm)_2]$ **(1)** was dissolved in 20 mL of benzene, and 18.2 µL (0.30 mmol) of CH_3I was added. The mixture was stirred overnight, resulting in a color change from yellow to orange. The volume of benzene was reduced in vacuum to about 2 mL, and the yellow product precipitated by the slow addition of pentane. Washing the product with 10 mL of pentane and drying under a slow stream of dinitrogen gave 24.3 mg of a mixture consisting of 85% of compound **3** and 15% of the previously characterized diiodo compound $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2][I]$.[21] Recrystallization attempts failed to separate these compounds, which were present in every attempt to prepare compound **3**, with the amount of impurity ranging from 15 to 30% of the total product.

(b) Reaction of compound 3 with Methyl Triflate. A 30 mg (0.023 mmol) sample of the compound $[Ir_2(I)(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ **(3)** was dissolved in 10 mL of dichloromethane, and 2.56 µL (0.023 mmol) of methyl triflate was added via syringe, resulting in a color change from yellow to red over

Table 2.1 Spectrocopic Parameters for the Compounds[a]

Compounds	IR,[b] cm^{-1}	NMR[d]		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[Ir_2(CH_3)(I)(CO)(\mu\text{-}CO)\text{-}(dppm)_2]$ **(3)**	1977 (s), 1815(m),	20.9(m), -7.4(m)	4.60(m, 2H), 4.40(m, 2H) -0.40(t, $^3J_{P\text{-}H}$=8.0 Hz, 3H),	197.6(tt, $^2J_{P\text{-}C}$=9.1, 4.3Hz, 1CO), 175.2(t, $^2J_{P\text{-}C}$=13.0 Hz,1CO), 17.5(t, CH_3, $^2J_{P\text{-}C}$= 6.3Hz),
$[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)\text{-}(Ph_2PCHPPh_2)(dppm)]$ **(4)**	–	5.5(m), -5.0(m)	4.72(m, 1H), 4.31(m, 1H), 2.10(tt, $^2J_{P\text{-}H}$=8.0 Hz, $^4J_{P\text{-}H}$=4.3 Hz, 1H)	198.6(tt, $^2J_{P\text{-}C}$=14.5, 3.5Hz, 1CO), 185.5(m, 2CO)
$[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)\text{-}(dppm)_2][BF_4]$ **(5)**	–	-4.9(s)	4.70(m, 2H),4.20(m, 2H)	206.3(q, $^2J_{P\text{-}C}$=17.3 Hz 1CO), 189.5(t, $^2J_{P\text{-}C}$=14.9 Hz, 2CO)
anti-$[Ir_2(CO)_2(Cl)(I)(\mu\text{-}CH_2)\text{-}(dppm)_2]$ **(6a)**	–	-15.1(m), -28.0(m)	6.50(tt, $^3J_{P\text{-}H}$=8.5, 7.8 Hz, 2H) 5.30 (m, 2H,), 4.40(m, 2H)	182.3(t, $^2J_{P\text{-}C}$=9.3 Hz, 1CO), 179.5(t, $^2J_{P\text{-}C}$=5.4 Hz, 1CO)
syn-$[Ir_2(CO)_2(Cl)(I)(\mu\text{-}CH_2)\text{-}(dppm)_2]$ **(6b)**	–	-8.4(m), -25.7(m)	6.60(tt, $^3J_{P\text{-}H}$=9.30, 8.4 Hz 2H),5.50(m,2H),4.60(m, 2H)	184.9(t, ,$^2J_{P\text{-}C}$=12.2 Hz, 1CO), 183.7(t, $^2J_{P\text{-}C}$=9.1 Hz, 1CO)
$[Ir_2(CH_2OCH_3)(I)(CO)_2(\mu\text{-}HC{\equiv}CH)(dppm)_2]$ **(7)**	1974(s)	-20.5(m), -28.6(m)	9.50(t, $^3J_{P\text{-}H}$=6.1 Hz, 1H), 8.00(t, $^3J_{P\text{-}H}$=5.8 Hz, 1H), 4.90(m,2H),4 40(t,$^3J_{P\text{-}H}$=5.4 Hz), 2 90(s,3H),2 50(m,2H)	177.6(t, $^2J_{P\text{-}C}$=6.3 Hz, 1CO), 174.9(t, $^2J_{P\text{-}C}$=5 3 Hz,1 CO)

Table 2.1 (contd).

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

one hour. The solution was stirred at ambient temperature for one more hour, after which the solvent was reduced to 1mL and the product precipitated by the slow addition of diethyl ether. A red precipitate of the previously described $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$[1m] was identified by $^{31}P\{^1H\}$ and ^1H NMR of the spectra. Carrying out the reaction with the use of the carbon-13 labelled methyl compound $[Ir_2(I)(^{13}CH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ and unlabelled methyl triflate yielded $[Ir_2(^{13}CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ and CH_3I with no ^{13}C label incorporated into the iodomethane, whereas reaction of unlabelled **3** with $^{13}CH_3SO_3$ resulted in no $^{13}CH_3$ incorporation into the methyl complex, but formation of $^{13}CH_3I$, as identified by $^{13}C\{^1H\}$ NMR spectroscopy.

(c) $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (4). Compound **1** (30 mg, 0.024 mmol) was dissolved in 6 mL of benzene-d_6 in an NMR tube and bromoacetonitrile 2.4 μL (0.025 mmol) was added via syringe. The solution changed color over 15 min from orange to yellow. NMR spectroscopy showed three phosphine-containing products in an approximate ratio 1:1:0.5. One of the major species was identified as $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ **(4)** on the basis of very similar NMR spectral parameters compared to the iodo analogue that was previously characterized.[22a] The other two species could not be characterized.

(d) Reaction of $[Ir_2(CO)_3(dppm)_2]$ [1] with Benzyl Bromide and Allyl Bromide. The reactions of compound **1** with benzyl bromide and allyl bromide were carried out as described in the reaction with bromoacetonitrile in part (c) above except that 2.9 μL (0.025 mmol) of benzyl bromide or 8.2 μL(0.10 mmol) of allyl bromide was used. The same three diiridium products were obtained in the same approximate proportions.

(e) Reaction of Compound 4 with HBF_4. Compound **4** was prepared as described in part (c) above except that the reaction was carried out in THF-d_8. $HBF_4 \cdot Me_2O$ (1.8 μL, 0.024 mmol) was added via a gas tight syringe resulting in an immediate color change from yellow to orange. Characterization by ^1H and $^{31}P\{^1H\}$ of the resulting mixture indicated the formation of the bromide complex $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dppm)_2][BF_4]$ **(5)** which is analogous to the previously characterized iodo and chloro-bridged complexes $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$[21] and $[Ir_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dppm)_2][BF_4]$.[23] Compound **5** was not isolated as a solid.

(f) Reaction of compound 5 with BuLi. Compound **5** was prepared in an NMR tube as described in part (e) above. Addition of a large excess (> 10 equiv.) of BuLi resulted in a color change from orange to yellow. ^1H and ^{31}P NMR analysis of the mixture showed the presence of compound **4**.

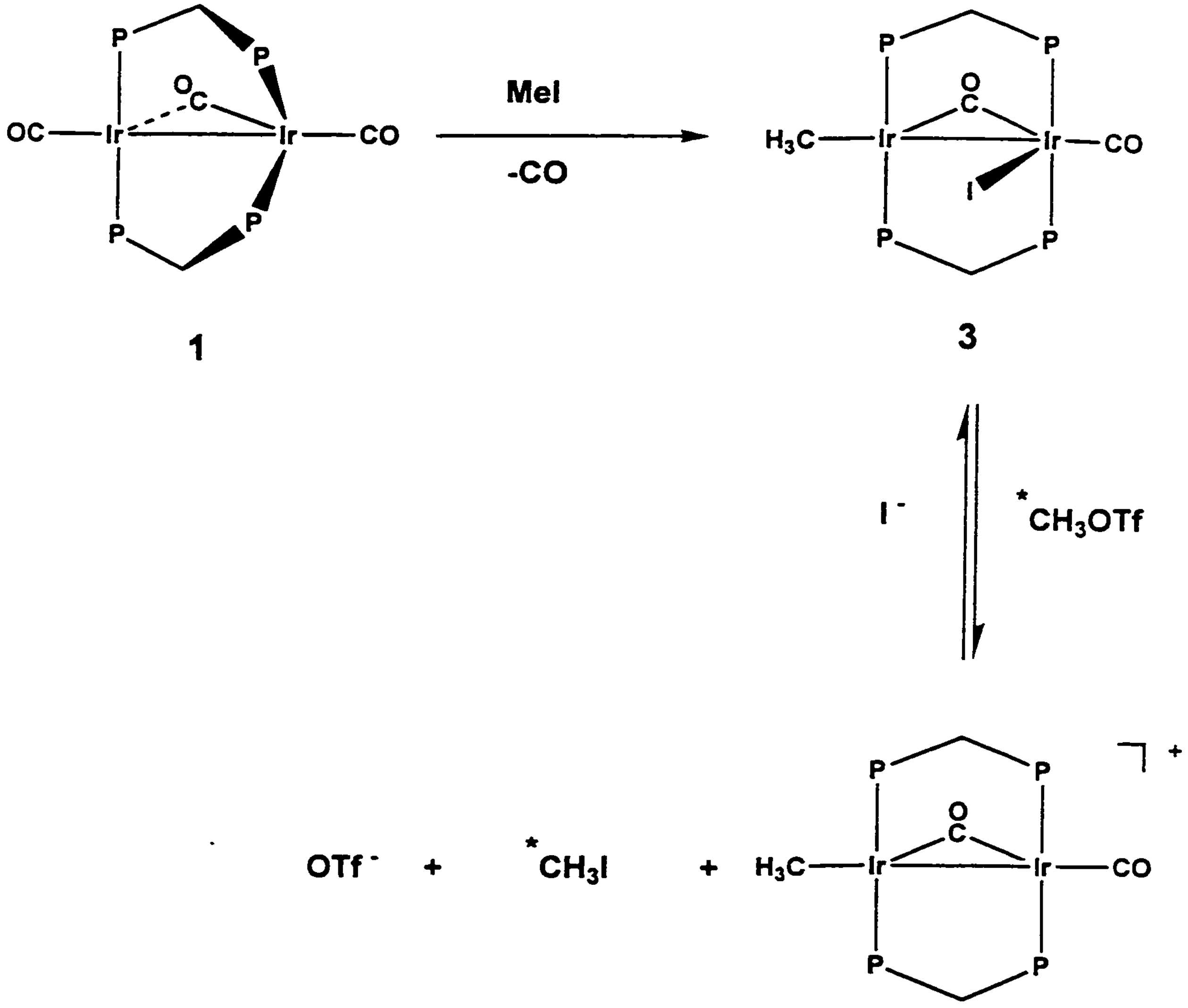
(g) Reaction of $[Ir_2(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$[22a] with HCl. The compound $[Ir_2(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ (30 mg, 0.022 mmol) was dissolved in 0.6 mL of CD_2Cl_2 and transferred via cannula into an NMR tube that was previously evacuated and placed under nitrogen. HCl gas was then passed through the solution at ~0.25 mL/sec for 1 min resulting in a color change from yellow to red. ^{1}H, ^{1}H{^{31}P} NMR broadband and selective decoupling experiments of the solution showed the presence of a mixture of the syn and anti isomers of $[Ir_2(Cl)(I)(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ **(6).**

(h) $[Ir_2(I)(CH_2OCH_3)(CO)_2(\mu\text{:}\eta^1\text{:}\eta^1\text{-}HC{\equiv}CH)(dppm)_2]$ (7). The compound $[Ir_2(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ (30 mg, 0.022 mmol) was dissolved in 10 mL of dichloromethane in a round-bottomed flask. The solution was then cooled to -78°C by immersing in dry-ice/acetone mixture. Acetylene was then passed through the solution for 2 min at ~0.25 mL/sec after which the mixture was stirred under a static atmosphere of the gas for 30 min at -78°C and then warmed to room temperature. After stirring the solution for 3 h at room temperature, during which the color changed from orange to yellow, the solvent was removed under vacuum and the yellow solid precipitated by the slow addition of pentane. Yield 85%. Anal. Calcd. for $Ir_2P_4O_3C_{56}H_{51}I$: C 47.77, H 3.65 Found: C, 47.41, H, 3.67.

Results and Characterization of Compounds.

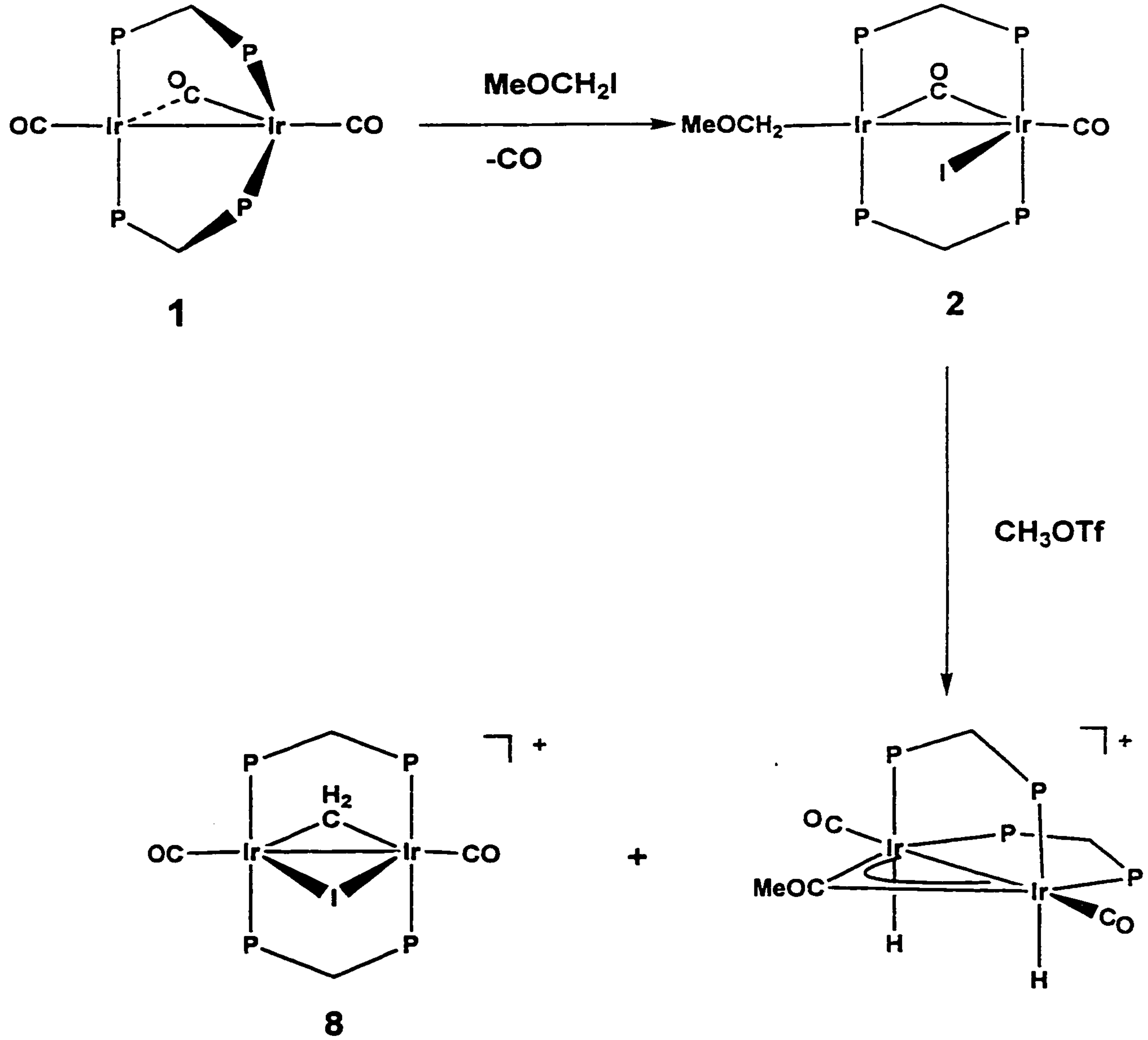
The compound $[Ir_2(CO)_3(dppm)_2]$ **(1)** reacts with methyl iodide, accompanied by loss of a carbonyl to yield the targeted oxidative-addition product $[Ir_2(CH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(3)** as shown in Scheme 2.1. The ^{31}P{^{1}H} NMR spectrum of compound **3** shows two multiplet signals typical of an AA'BB' pattern at δ 20.9 and -7.4 indicating two phosphorus environments resulting from

Scheme 2.1


P
P
P
P
OC
Ir
O
C
Ir
CO
MeI
-CO
P
P
H$_3$C
Ir
O
C
Ir
CO
I
P
P
1
3
I$^-$
*CH$_3$OTf
OTf$^-$
+
*CH$_3$I
+
H$_3$C
Ir
O
C
Ir
CO
P
P
P
P
+

the inequivalence of the two metal centers. The ^{1}H NMR spectrum shows the methyl group as a triplet ($^{3}J_{P\text{-}H}$ = 8.0 Hz) at δ -0.40 and selective ^{31}P decoupling experiments show that this group couples only to the phosphorus nuclei giving rise to the downfield signal in the $^{31}P\{^{1}H\}$ NMR spectrum. The spectroscopic data for compound **3** are very similar to those of the previously described $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(2)** which results from the oxidative addition of iodomethyl methylether to compound **1**, as represented in Scheme 2.2.[22a] The very similar spectroscopic data suggest similar structures. The dppm methylene protons for compound **3** appear as two multiplets at δ 4.60 and 4.40. The IR spectrum of a solid sample shows one carbonyl stretch at 1977 cm^{-1} indicating that it is terminally coordinated to iridium while the other carbonyl has a stretch at 1815 cm^{-1} clearly showing a bridging geometry. The terminal and bridging positions of the carbonyls are supported by the $^{13}C\{^{1}H\}$ NMR spectra of a ^{13}CO and $^{13}CH_3$-enriched samples. A signal at δ 175.2 appearing as a triplet with a coupling of 13 Hz to the phosphorus nucleus that resonates upfield, is consistent with a terminally bound carbonyl. The second carbonyl resonance, at δ 197.6 appears as a triplet of triplets ($^{2}J_{P\text{-}C}$ = 9.1, 4.3 Hz) with coupling to the two sets of inequivalent phosphorus nuclei clearly indicating of a bridging position. Based on a close similarity in spectral parameters between compounds **2** and **3** and on the X-ray structure of **2**, the structure of **3** is believed to be analogous having the carbonyls mutually cis, with one in a terminal position almost opposite the Ir-Ir bond and the other bridging in an unsymmetrical fashion. For **3** the resonance for the methyl group at δ 17.5 is a triplet ($^{2}J_{P\text{-}C}$ = 6.3 Hz) showing that it is terminally

Scheme 2.2[22a]



bound to one metal. The iodo ligand is believed to be terminally bound to the same metal as the terminal carbonyl, on the face opposite the bridging carbonyl. The methyl group is the only terminal ligand on the adjacent metal falling opposite the metal-metal bond. It is interesting that the carbonyls do not assume a symmetrical arrangement with one on each metal as found for *trans*-$[IrCl(CO)(dppm)]_2$[28c] but instead adopt the unsymmetrical arrangement as observed for $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$[21] with one of the iodo ligands being replaced by the methyl ligand. In fact, compound **3** is always contaminated with about 15-30% of this diiodo compound. The fact that these compounds have similar structures is not surprising since the methyl and iodo groups are thought to behave as electronically and sterically similar ligands.[24,25] Since this geometry does not appear to be sterically driven, we assume that the bridging carbonyl is necessary to make use of its better π-accepting properties in this position.[26] The oxidative addition of CH_3I to $[Ir_2(CO)_3(dppm)_2]$ having Ir(0)/Ir(0) puts the methyl group on one metal and the iodo ligand on the other metal giving rise to $Ir^{(+1)}/Ir^{(+1)}$ centers resulting from formal oxidation of each metal by the loss of one electron.

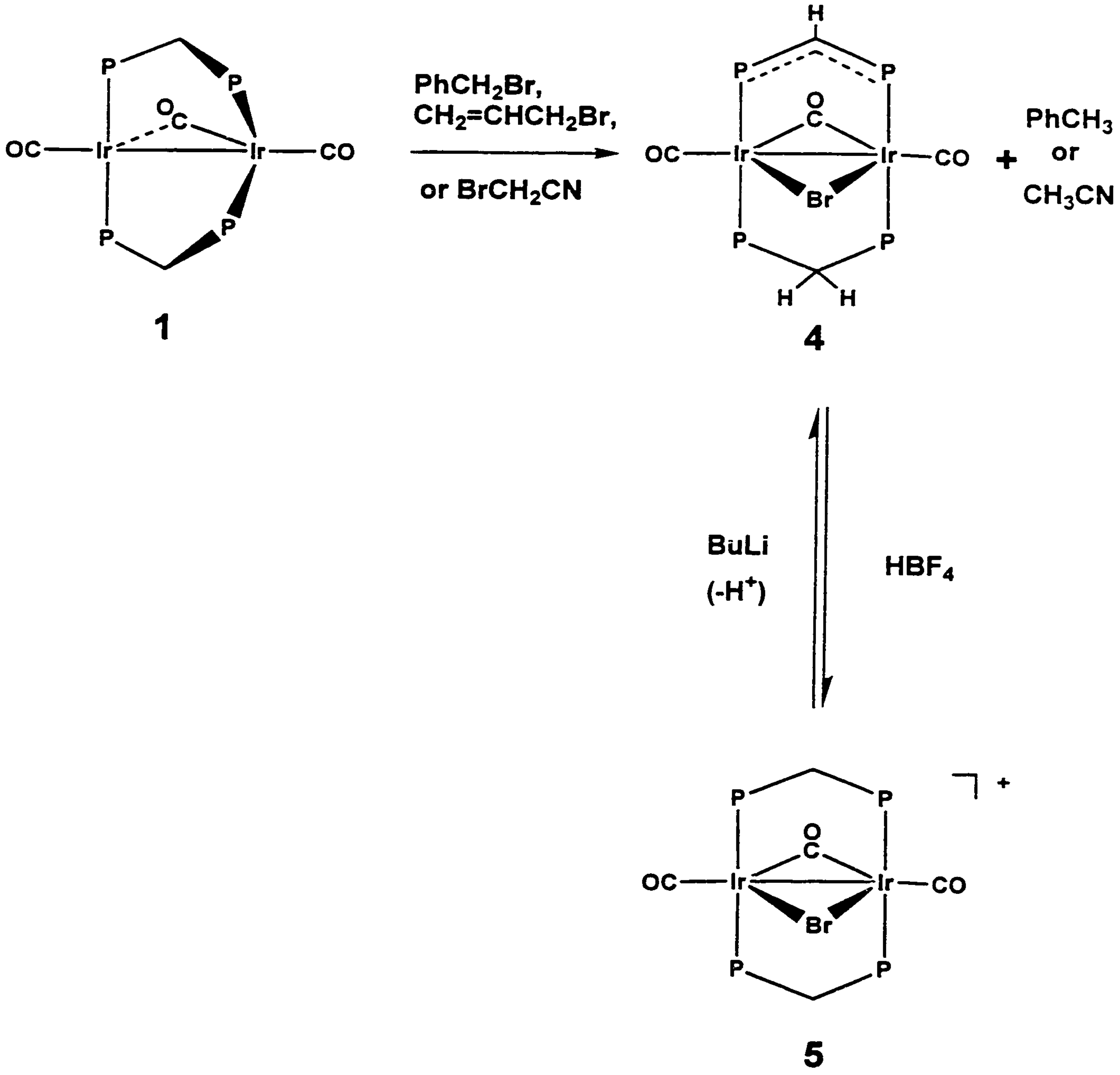
Reacting compound **3** with methyl triflate leads to iodide abstraction (the resulting methyl iodide is observed in the ^1H-NMR spectrum) to give the known compound $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$.[22a] To determine whether the methyl ligand in this product originated from the methyl triflate or from the iridium-bound methyl group two experiments were done. In the first experiment, compound **3** was reacted with carbon-13 labelled methyl triflate. No carbon-13 labelled methyl group was detected in the iridium-containing product while $^{13}CH_3I$

was detected by $^{13}C\{^1H\}$ NMR in the solution. The second experiment involved reacting the $^{13}CH_3$-labelled compound **3** ($[Ir_2(^*CH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$) with unlabelled methyl triflate. The carbon-13 labelled methyl group remained bound to the metals and none of the label was incorporated into the methyl iodide produced. These tests confirmed that the function of the methyl triflate is merely to provide the electrophilic CH_3^+ group that attacks and abstracts the iodide ion as methyl iodide. The use of silver salts to effect iodide removal is not recommended since it gives irreproducible mixtures of products. The use of methyl triflate works well as has been previously documented.[14b] Addition of methyl triflate to the iodo methoxymethyl compound $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(2)** results in the unusual double C-H activation of the methoxymethyl ligand to give the methoxy carbide-bridged product $[Ir_2(H)_2(CO)_2(\mu\text{-}COCH_3)(dppm)_2][CF_3SO_3]$ as shown in Scheme 2.2.[22a] However, this C-H activation of the methyl group was not observed upon iodide removal from compound **3** for which the expected product $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ $[CF_3SO_3]$ was obtained. It appears that incorporation of electron-withdrawing substituents on the α-carbon promotes C-H bond activation as had been reported earlier.[18,45] The ease of the double C-H activation shown by incorporation of the methoxy group remains puzzling and this is being followed in our group.

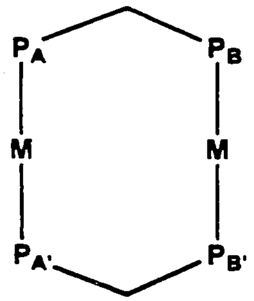
Iodide (I^-) addition to $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ regenerates the iodomethyl complex **3** as shown Scheme 2.1. This reactivity is in contrast to other reactions of this methyl compound with a number of neutral substrates (CO, SO_2, PR_3, CNR) in which the facile activation of one C-H bond yielded the corresponding methylene-bridged, hydrido product $[Ir_2(H)(CO)_2(L)(\mu-CH_2)(dppm)_2][CF_3SO_3]$[1m] (L = CO, SO_2, PR_3, CNR). We find it curious that addition of the anionic group I^- does not lead to C-H bond cleavage but instead leaves the methyl group intact. To probe this reactivity further, we sought to extend the investigation to substituted methyl groups to study the effect of different substituents on the C-H activation of an alkyl group. Our proposal was that oxidative addition of a substituted methyl halide (XCH_2Y; X= halide, Y= substituent) would constitute a useful route to complexes containing substituted methyl ligands $Ir-CH_2Y$ by oxidative-addition of the carbon-halide bond.

In the initial trials,[22a] oxidative addition of CH_2I_2 and ICH_2CN to $[Ir_2(CO)_3(dppm)_2]$ was attempted. In addition to the double-oxidative addition to binuclear complexes, generating methylene-bridged products,[11,16c] CH_2I_2 is known to undergo oxidative addition across only one C-I bond, generating CH_2I species[14a,15,16c] of the type we targeted. However, the reaction of $[Ir_2(CO)_3(dppm)_2]$ with CH_2I_2 and ICH_2CN resulted not in oxidative addition but instead, in hydrogen atom abstraction from one dppm methylene group and iodine addition to the metals to give $[Ir_2(CO)_2(\mu-I)(\mu-CO)(Ph_2PCHPPh_2)(dppm)]$ and CH_3I or CH_3CN as the organic fragments.[22a] As a continuation of this study, the addition of the substituted bromomethyl compounds benzyl bromide, allyl bromide, and bromoacetonitrile produced analogous results yielding the bromide analogue $[Ir_2(CO)_2(\mu-Br)(\mu-CO)(Ph_2PCHPPh_2)(dppm)]$ **(4)** as shown in Scheme 2.3. Product **4** has again resulted from hydrogen atom abstraction from one dppm methylene group and a bromine atom addition across the metal-metal

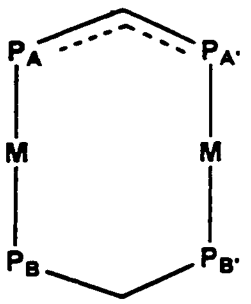
Scheme 2.3


PhCH$_2$Br,
CH$_2$=CHCH$_2$Br,
or BrCH$_2$CN
PhCH$_3$
or
CH$_3$CN
BuLi
(-H$^+$)
HBF$_4$
1
4
5

bond.The NMR data for compound **4** are very similar to that of the iodide analogue. The ^{1}H NMR spectrum shows three proton resonances, integrating as a single proton each consistent with the loss of one hydrogen from one dppm methylene group. The resonances appear as two multiplets at δ 4.72 and 4.32 and a triplet of triplets at δ 2.10. The last signal is consistent with the methyne hydrogen of the $Ph_2PCHPPh_2$ group showing coupling values of 8.0 and 4.3 Hz to the two adjacent phosphorus nuclei. When the respective reactions were monitored by ^{1}H NMR spectroscopy in the benzylbromide and bromoacetonitrile reactions, toluene and acetonitrile were detected in solution, however, propene was not detected in the allylbromide reaction. Presumably the propene signals were obscured by those of allylbromide which was added in large excess (10 equiv.) to drive the reaction to completion. The ^{31}P{^{1}H} NMR spectrum of compound **4** shows two multiplets signals at δ 5.5 and -5.0. This spectrum differs from our usual AA'BB' spin systems shown below **(E)**. In our sual AA'BB' spin



E



F

systems the P_A and P_B nuclei are bound to different metals and are coupled through the methylene unit with a coupling constant of ca. 80 Hz. In the present AA'BB' spin system of compound **4**, the A and B phosphorus nuclei are bound to the same metal as illustrated in **F** above. This spectrum differs from our usual AA'BB' due to the large coupling constants(ca. 300 Hz) between the A and B phosphorus nuclei owing to their trans alignment at the metals as illustrated in **F**. The structure of compound **4** is assumed to be like that of the iodo analogue[22a] having the bromo group on the face opposite the bridging carbonyl. This will closely resemble the carbonyl-bridged A-frames $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dppm)_2][BPh_4]$,[27] $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2][CH_3C_6H_4SO_3]$,[28] $[Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-}CO)(dppm)_2]$,[29] $[Ir_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]$ $[BF_4]$,[30] apart from the subtle differences resulting from hydrogen loss from one methylene unit in the present compound. Reacting compound **4** with $HBF_4.OEt_2$ resulted in the protonation at the CH group of the $Ph_2PCHPPh_2$ moiety generating the expected carbonyl-bridged $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dppm)_2][BF_4]$ **(5)** as shown in Scheme 2.3. This is the bromide analogue of the previously characterized iodo complex $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$.[21] The $^{31}P\{^1H\}$ spectrum of complex **5** shows one single resonance at δ -4.9, clearly consistent with a symmetrical species in which all phosphorus nuclei are chemically equivalent. The ^1H NMR spectrum shows the dppm methylene protons as two multiplets at δ 4.70 and 4.20 and the $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO enriched sample shows two signals for the carbonyl groups. The signal at δ 206.3 (integrating as one CO) is a quintet ($^2J_{P\text{-}C}$ = 17.3 Hz) and its downfield position is consistent with a bridging carbonyl whereas the highfield signal (integrating as 2CO) is a triplet at δ 189.5 ($^2J_{P-C}$ = 14.9 Hz) indicating a terminal coordination to the iridium centers. Reaction of the cationic compound **5** with the strong base, butyllithium, results in deprotonation of one dppm group to regenerate compound **4** as shown in Scheme 2.3.

In a preliminary attempt to confirm that the above reactivity resulted from a free-radical process, the reaction of $[Ir_2(CO)_3(dppm)_2]$ with alkyl halides was carried out in the presence of the radical inhibitors duroquinone, hydroquinone, 9,10-dihydroanthracene or in the presence of the radical scavenger di-tert-butylnitroxide and in darkness. The reaction was unchanged. In all cases a hydrogen atom was abstracted from one dppm ligand and a bromide atom was added across the metal-metal bond to give $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(Ph_2PCHPPH_2)(dppm)]$.

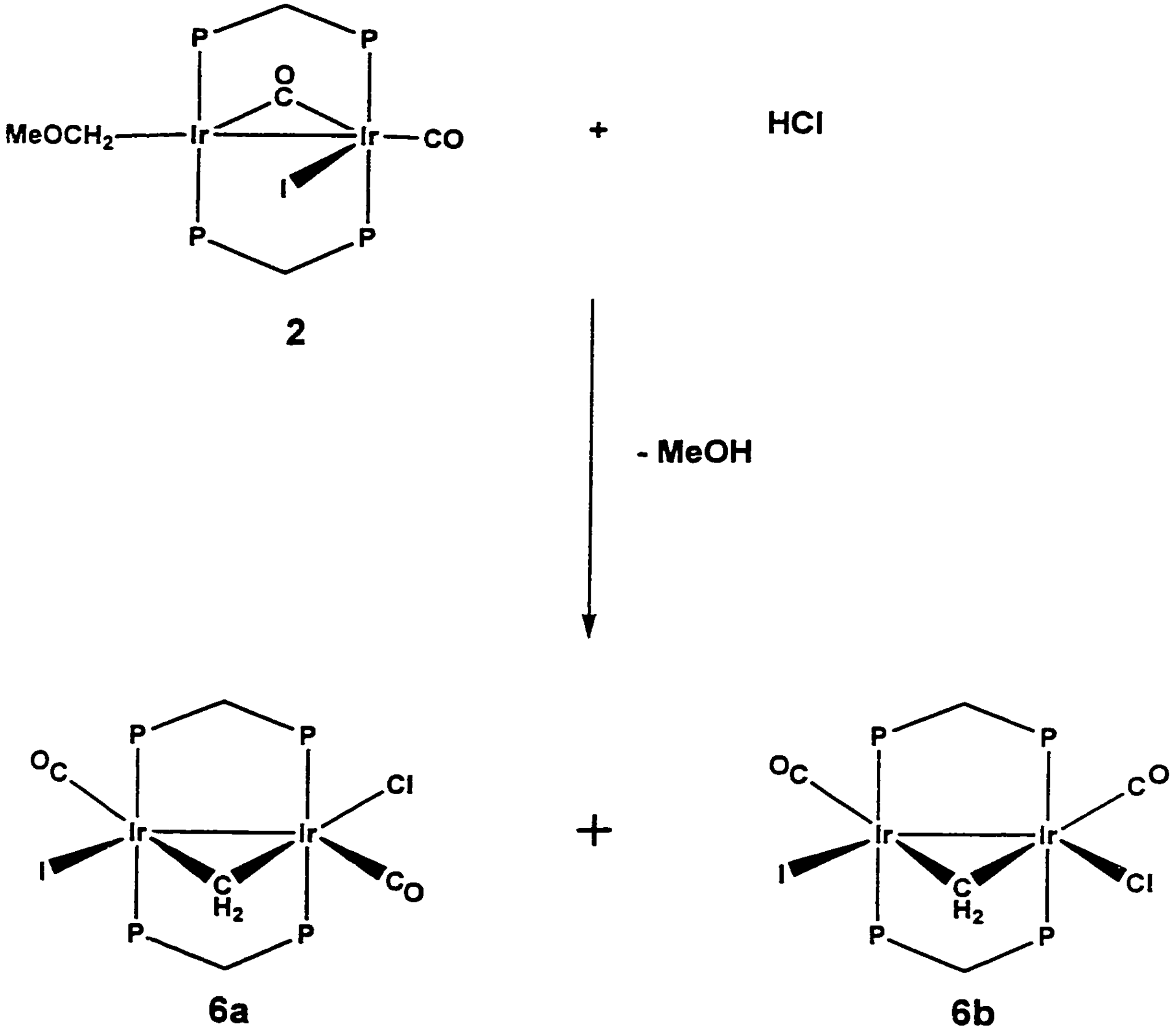
In a further attempt to synthesize a halide-substituted methyl compound $[Ir_2(CH_2X)(CO)(\mu\text{-}CO)(dppm)_2]$ (X=halide) we attempted reacting the methoxymethyl compound **2** with HCl gas. Such reactions had been used to synthesize mononuclear bromomethyl and chloromethyl complexes of iron as shown in equation 2.1 below:[35,36]

$$[MCH_2OCH_3] + HX \longrightarrow [MCH_2X] + CH_3OH \qquad (2.1)$$

$$M = CpFe(CO)_2;\ X=Cl,\ Br$$

Instead, the reaction of $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ with HCl gas resulted in the formation of a mixture of anti and syn isomers of the methylene-bridged chloroiodo species $[Ir_2(I)(Cl)(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ **(6a&b)** in the ratio 1.6:1 respectively as shown in Scheme 2.4. These isomers differ in the orientation of the iodo and chloro groups as either anti **(6a)** or syn **(6b)** on the adjacent metals. ^1H NMR experiments with selective ^{31}P decoupling of the resonances of the anti isomer **(6a)** shows the diiridium-bridged methylene resonance as a triplet of triplets at δ 6.50 ($^3J_{P\text{-}H}$ = 8.5, 7.8 Hz) showing coupling to both sets of phosphorus nuclei. The dppm methylene protons appear as multiplets at δ 5.30 and 4.40. The phosphine signals for this isomer appear as two sets of multiplets in the $^{31}P\{^1H\}$ NMR spectrum at δ -15.1 and -28.0 owing to the inequivalence of metal environments. The $^{13}C\{^1H\}$ NMR spectrum shows two triplet signals for the two carbonyls at δ 182.3 ($^3J_{P\text{-}C}$ = 9.3 Hz) and 179.5 ($^3J_{P\text{-}C}$ = 5.4 Hz) indicating terminal coordination to the metals. The spectroscopic data for the anti isomer **6a** is identical to that observed for the diiridium diiodide methylene-bridged compound that was previously characterized.[22a] The syn isomer **6b** shows two multiplets in the $^{31}P\{^1H\}$ NMR spectrum at δ -8.4 and -25.7. The methylene-bridged signals in the ^1H-NMR spectrum appears at δ 6.50 as a triplet of triplets ($^3J_{P\text{-}H}$ = 9.3, 8.4 Hz) and the dppm methylenes appear at δ 5.50 and 4.60. The $^{13}C\{^1H\}$ NMR spectrum shows two triplet signals for the carbonyls at δ 184.9 ($^3J_{P\text{-}C}$ = 12.2 Hz) and 183.7 ($^3J_{P\text{-}C}$ = 9.1 Hz) indicating terminal coordination of both carbonyls to the metals. Both carbonyls in **6b** are in similar environments opposite the bridging methylene group and both appear at similar chemical shifts in the ^{13}C NMR spectrum. It is interesting that these are also close to one of the carbonyl resonance for isomer **6a** (δ 182.3) so it is assumed

Scheme 2.4

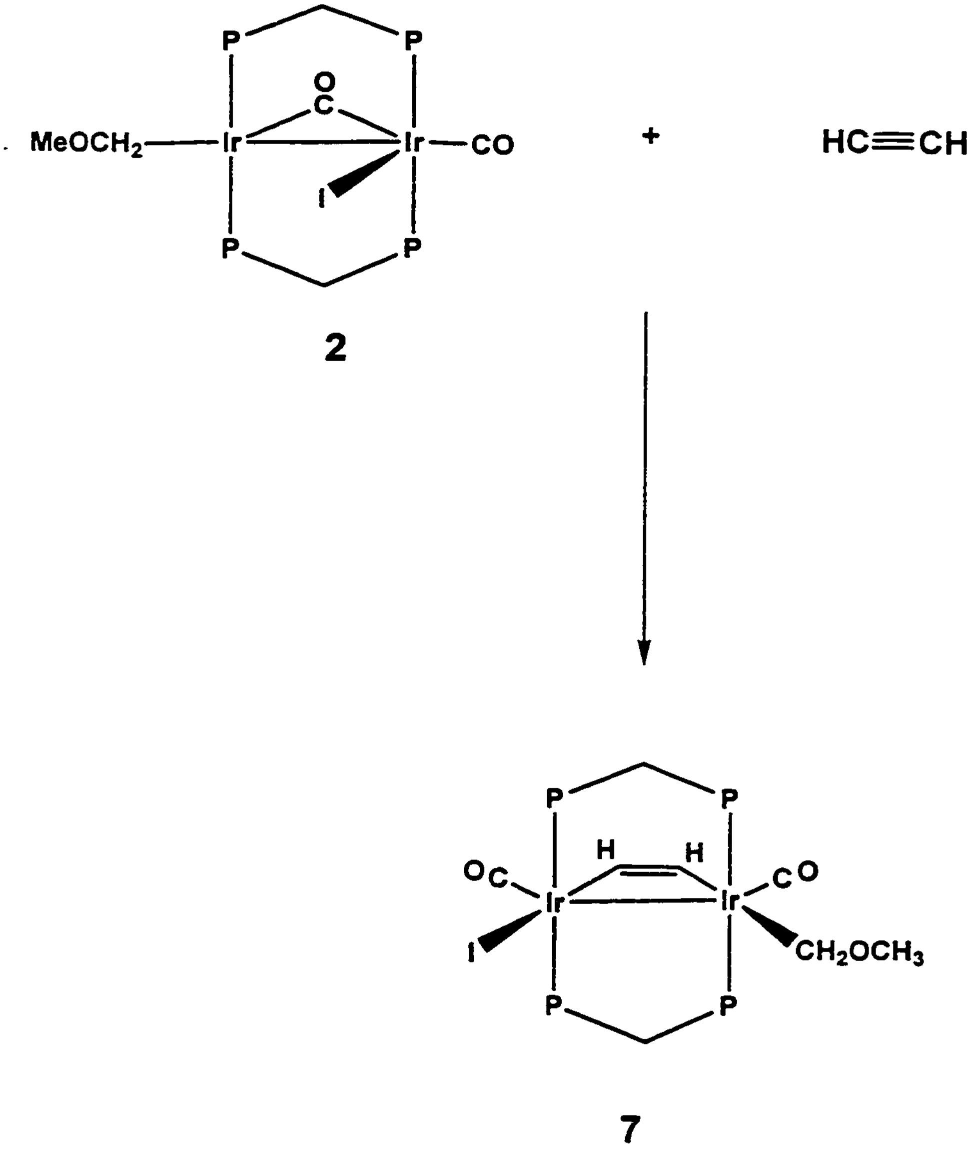


that this corresponds to that which is also opposite the methylene group in this isomer.

Although the reaction of compound **2** with HCl resulted in protonation of the methoxy group liberating methanol, this was not accompanied by a halide attack at the resulting methylene carbon, as targeted. Instead, the resulting product has the halide ion bound to one of the metals. Whether this results from the lower electrophilicity of the methylene group compared to the metals, or whether the targeted methylene chloride species $[Ir_2(CH_2Cl)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ was obtained but underwent facile subsequent C-Cl oxidative addition to yield the observed products is not known. It may also be that in a binuclear system the methylene-bridged geometry can be readily obtained, reducing the electrophilicity of the methylene carbon compared to that of a terminal carbene.

Reaction of compound **2** with acetylene gives the alkyne-bridged complex $[Ir_2(CH_2OCH_3)(I)(CO)_2(\mu\text{-}HC{\equiv}CH)(dppm)_2]$ **(7)** as shown in Scheme 2.5. The $^{31}P\{^1H\}$ NMR spectrum of complex **7** shows two multiplets at δ -20.5 and -28.6 consistent with an AA'BB' spin system. The ^1H NMR spectrum shows the proton resonances of the coordinated acetylene as two triplets at δ 9.50 ($^3J_{P\text{-}H}$ = 6.1 Hz) and 8.00 ($^3J_{P\text{-}H}$ = 5.8 Hz) respectively. In addition, the dppm methylene protons appear as multiplets at δ 4.90 and 2.50, the methylene protons of the methoxymethyl group appear at δ 4.40 as a triplet ($^3J_{P\text{-}H}$ = 5.4 Hz), while the methyl protons appear at δ 2.90 as a singlet. The $^{13}C\{^1H\}$ NMR spectrum shows

Scheme 2.5



2

7

one resonances at δ 177.6 that is a triplet with three-bond coupling to the phosphorus nuclei of 6.3 Hz and the second resonance that is a triplet at δ174.9 with a three bond coupling to the phosphorus nuclei of 5.3 Hz. The IR spectra show a very strong stretch at 1974 cm^{-1} that rules out any bridging interaction of the carbonyl. Also the IR spectrum shows a weak peak at 1624 cm^{-1} that can be assigned to the C≡C stretch of the coordinated acetylene, consistent with the bridging mode (parallel to the metal-metal axis). A conclusive structural assignment for compound **7** was not possible since it was not possible to grow crystals of this compound for X-ray structure determination.The orientation of the iodo group and the methoxymethyl ligand as cis is proposed based on steric arguments. The NMR data for compound **7** are close to those in related systems, in which the alkyne bridges two metals parallel to the metal-metal axis.[37,38] An attempt to initiate C-C bond formation between the alkyne and the methylene group by abstraction of the methoxy group with electrophiles such as H^+, Me_3Si^+ did not occur and only resulted in decomposition; perhaps the arrangement of the alkyne and the methoxymethyl group on opposite sides of the Ir_2P_4 plane as shown in Scheme 2.5, does not allow them to combine. However, it is still surprising that a methylene- and alkyne- bridged product did not result.

Discussion.

Attempts to access binuclear alkyl complexes involving the "$Ir_2(dppm)_2$" framework, through oxidative addition of alkyl halides to the respective low-valent metal precursors, has succeeded with methyl iodide but has resulted in a notable and unexpected failures, which will be discussed (*vide infra*). The diiridium complex $[Ir_2(CO)_3(dppm)_2]$ **(1)** reacts readily with CH_3I to give the targeted oxidative-addition product $[Ir_2(CH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(3)** (see Scheme 2.1). The structure of this oxidative-addition product is identical to the structure of the previously characterized compound $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(2)** that has resulted from the oxidative addition of iodomethyl methyl ether to compound **1** as shown in Scheme 2.2.[22a] Compound **2** has the methyl group on one metal and the iodo ligand on the other, giving rise to Ir(+1)/Ir(+1) centers resulting from formal oxidation of both metals. This compound bears a remarkable resemblance to the diiodo complex $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$ which is not too surprising since the methyl and iodo groups are thought to behave as electronically similar ligands[24] and are also sterically comparable.[25]

Addition of I^- to the previously characterized $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$[22a] generates the iodomethyl complex **3**. In this context we find it interesting that the addition of a number of neutral substrates (CO, SO_2, PR_3, CNR) to this methyl-containing species resulted in cleavage of one methyl C-H bond, yielding the corresponding methylene-bridged, hydrido products.[1m] It is curious that addition of the anionic group (I^-) does not also lead to C-H bond cleavage, but instead leaves the methyl group intact.

Attempts to generate species containing a substituted methyl group through oxidative addition of a single C-Br bond in $C_5H_5CH_2Br$, CH_2CHCH_2Br, and $BrCH_2CN$ to compound **1** did not proceed as anticipated. Instead, the reaction resulted in hydrogen atom abstraction from one dppm methylene group and bromide atom addition to the metals. Although these reactions appear to be free-radical processes, we observe no inhibition by the addition of the radical inhibitors duroquinone, hydroquinone, or 9,10-dihydroanthracene or by addition of the radical scavenger di-*tert*-butylnitroxide. Similarly, these reactions were unaffected when done in the dark. The participation of radical processes in the oxidative additions of alkyl halides to Rh(I) and Ir(I) is well documented[7c,31,32] and the failure of these radical inhibitors and scavengers to affect the oxidative addition in this study has been rationalized in terms of caged radical species.[7c] In the present study the alkyl halides for which a radical process appears to be involved (CH_2I_2, ICH_2CN, $CH_2{=}CHCH_2Br$), and $C_6H_5CH_2Br$, $BrCH_2CN$) are those known to give rise to more stable radicals by virtue either of resonance stabilization or by electron-withdrawing groups.[33,34] Certainly, polyhalomethanes CH_nX_{4-n} are known to display a greater tendency to undergo radical processes than the monohalo counterparts,[32b,34] in agreement with our observation of a radical-induced process involving CH_2I_2, ICH_2CN, and $BrCH_2CN$.

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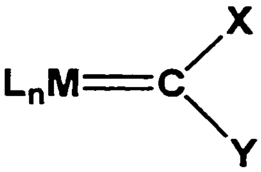
CHAPTER THREE

Methylene-Bridged Diiridium Complexes:

Introduction

By the early 1980's rarely had any field in organometallic chemistry encountered the tremendous rapid expansion experienced by the synthesis, spectroscopy, structural chemistry, theory, and reactivity of compounds characterized as mononuclear alkylidene (terminal carbene) or methylene complexes. Fischer and his group pioneered the discovery of these remarkable classes of compounds.[1,2] The several comprehensive reviews are eloquent witness to the amazing plethora of compounds this fascinating area of research had yielded.[3] Carbene complexes contain metal-carbon double bonds and have the general structure shown below.



When X and/or Y = OR, NR_2, SR, or halides these are the Fischer carbenes. When X and Y = C_xH_y or H these are the Schrock carbenes.[4] Mononuclear alkylidene complexes have shown versatile reactivities such as stoichiometric and catalytic cyclopropanation, olefin metathesis and acetylene polymerization.[5]

In the case of polynuclear complexes the alkylidene ligand is usually bridging a pair of metal atoms, although a number of complexes are known in which the alkylidene group is terminally bound to one of the metals.[6] Polynuclear methylene-bridged complexes have been extensively studied as models for surface-bound methylene species and structurally are recognized as better models for surface-bound species compared to mononuclear methylene complexes.[7] A binuclear complex represents the simplest multi-metal system in which the involvement of adjacent metals in the chemistry can be studied. The adjacent metals can somehow interact in a cooperative manner when activating organic substrates. Methylene-bridged complexes are especially important models in Fisher-Tropsch chemistry in which methylene fragments are known to be involved in the conversion of carbon monoxide and hydrogen into hydrocarbons.[7e,8] Extensive studies on their coupling reactions with hydrocarbyl species (e.g. another methylene ligand present in the complex or alkyl or vinyl fragments) have provided information on the mechanism of the carbon-chain propagation steps of catalytic CO hydrogenation.[9] Other recent examples of reactions involving methylene-bridged complexes include the specific carbon-carbon coupling of the labile diruthenium methylene-bridged complex $[Cp_2Ru_2(\mu\text{-}CH_2)(CO)_2(MeCN)]$, with diazoalkanes that was observed to lead to the alkenyl complex $[Cp_2Ru_2(\mu\text{-}CH{=}CR_2)(\mu\text{-}H)(CO)_2]$ and the alkenes, $CH_2{=}CR_2$.[10] Also reaction of the diruthenium methylene-bridged complex $[Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2]$ with hydrosilane yielding methane has been observed.[11]

Our group has recently been interested in methylene-bridged complexes that can be used to model the involvement of adjacent metals in simple organic substrate transformations known to occur in the Fischer-Tropsch process. We have chosen the bis(diphenylphosphino)methane (dppm) framework that serves to hold the metals in close proximity to facilitate interactions between the organic substrates and both metal centers. In some recent work facile selective coupling of methylene units in a Rh/Os complex to give either a C3 or C4 fragments has been observed[12] and reaction of a methylene-bridged complex of Ir/Ru with acetylene was observed to give a C3 fragment.[13] It was therefore of interest to study how the corresponding methylene-bridged complexes of diiridium would react with diazomethane, acetylene and other small molecules of catalytic significance. The results of these studies are presented in this chapter.

Experimental Section

General Comments. All solvents were deoxygenated and dried over the appropriate drying agents (see Appendix) prior to use and were stored under dinitrogen. Deuterated solvents used for NMR experiments were degassed and stored under dinitrogen over molecular sieves. Reactions were routinely carried out at room temperature (unless otherwise stated) and under dinitrogen, using standard Schlenk conditions. Compounds that were isolated as solids were purified by recrystallization. Ammonium hexachloroiridate(IV) was obtained from Vancouver Island Precious Metal. Phosphines, tert-butylisocyanide, trimethylamine oxide and methylmagnesium bromide were purchased from Aldrich Chemicals and used as received. Dihydrogen was purchased from Linde, CO and SO_2 were purchased from Matheson, and CS_2 was purchased from Merck Sharp & Dohme. All gases were used as received. The compounds $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}I)(dppm)_2][CF_3SO_3]$ **(8)** and $[Ir_2(CO)_2(I)_2(\mu\text{-}CH_2)(dppm)_2]$ **(9)** were prepared as previously reported.[14] All routine NMR experiments were conducted on either a Bruker AM-400 MHz spectrometer (operating at 100.614 MHz for ^{13}C and 161.978 MHz for ^{31}P) or Bruker 200 MHz spectrometer (operating at 50.323 MHz for ^{13}C and 81.015 MHz for ^{31}P). Infra-red spectra were obtained on a Perkin-Elmer 883 IR spectrometer, either as Nujol mulls on KBr plates or for a few select cases on Nic-Plan IR Microscope attached to a Nicolet Magna-IR 750 Fourier Transform as single crystals. Elemental analyses were performed by the microanalytical service within our department. Spectroscopic data for all compounds are given in Table 3.1.

Table 3.1 Spectrocopic Parameters for the Compounds[a]

		NMR[d]		
Compounds	IR,[b] cm^{-1}	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[Ir_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CO)\text{-}(dppm)_2][BF_4]_2$ **(10)**	2085(s), 2036(s), 2013(s), 1991(s), 1810(w)[c]	-17.6(s)	7.10(q, $^3J_{P\text{-}H}$=7.3 Hz, 2H), 6.82(m, 2H),5.13(m, 2H)	197.6(q, $^2J_{P\text{-}C}$=4.6 Hz,1CO), 166.7(t, $^2J_{PC}$=14.0 Hz,2CO), 159.4(t, $^2J_{P\text{-}C}$=13.8 Hz, 2CO),
syn-$[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ **(11a)**	2350(vw)[f], 1985(bs)	-10.1 (s)	6.44(q, $^3J_{P\text{-}H}$=7.6 Hz ,2H), 6.32(m, 2H), 4.73(m, 2H), 2.11(s, 6H)	168.2(t, $^2J_{P\text{-}C}$=7.0 Hz),
anti-$[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ **(11b)**	2350 (vw)[f], 2006 (bs)	-10.2 (m), -15.8(m)	6.52(tt, $^3J_{P\text{-}H}$=9.6, 6.7 Hz, 2H), 6.12(m, 2H) 4.51(m, 2H), 2.04(s, 6H)	171.9(t, $^2J_{P\text{-}C}$=7.7 Hz), 164.8(b)
$[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}\eta^1{:}\eta^1\text{-}HC{\equiv}CH)(dppm)_2][BF_4]_2$ **(16)**	1960(s), 1632(w)	-10.2(s)	8.84(t, $^3J_{P\text{-}H}$=4.8 Hz, 2H), 5.02(m, 2H), 4.93(m, 2H), 3.22(q, 2H),	174.2(b)
$[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}C{=}CH_2)(dppm)_2][BF_4]_2$ **(17)**	2024(s)	-12.5(s)	7.92(s, 2H) ,3.70(m, 2H), 3.53(m, 2H), 3.14(q, $^3J_{P\text{-}H}$=7.2 Hz, 2H)	172.4 (t, $^2J_{P\text{-}C}$=5.3Hz)

Table 3.1 (contd).

Compounds	IR,^{b,c}cm^{-1}	NMR^{d} δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C{^{1}H})
$[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}SO_2)\text{-}(dppm)_2][BF_4]_2$ **(18)**	2025(s),1996(s), 1029, 1150^{e}	5.0(s)	6.60(q, $^{3}J_{P\text{-}H}$=8.0 Hz, 2H), 5.62 (m, 2H), 4.48(m, 2H),	172.4(t, $^{2}J_{P\text{-}C}$=5.3 Hz)
$[Ir_2(CO)_2(CS_2)(\mu\text{-}CH_2)\text{-}(dppm)_2][BF_4]_2$ **(19)**	2000(s), 1805(w)	-8.7(m), -18.9(m)	4.74(m, 2H), 3.76(m, 2H), 3.52(m, 2H)	193.6(b), 164.3(t, $^{2}J_{P\text{-}C}$=7.8 Hz)
$[Ir_2(Br)_2(CO)_2(\mu\text{-}CH_2)\text{-}(dppm)_2]$ **(20)**	2058(ss), 1995 (ms)^{e},	-11.6(m), -23.4(m)	6.53(tt, $^{3}J_{P\text{-}H}$=9.7, 6.5 Hz, 2H), 5.34(m, 2H), 4.42(m, 2H),	184.5(t, $^{2}J_{P\text{-}C}$=14.5 Hz), 179.8(t, $^{2}J_{P\text{-}C}$=12.8 Hz),
$[Ir_2(I)(CO)_2(^{t}BuNC)\text{-}(\mu\text{-}CH_2)(dppm)_2]$ **(22)**	2171(ms), 2023(bs), 1970(s)	-15.8(m), -19.2(m)	6.62(tt, $^{3}J_{P\text{-}H}$=3.5, 2.9 Hz, 2H), 6.22(m, 2H),4.67(m, 2H), 1.03(s, 9H)	172.1(b), 165.2(b)
$[Ir_2(I)(CO)_2(PMe_3)\text{-}(\mu\text{-}CH_2)(dppm)_2]$ **(23)**	1962(s), 1991(bs)	-16.6(m), -17.6(m), -78.6(t,$^{2}J_{P\text{-}P}$ =17.7Hz)	6.67(m), 6.54(m, 2H), 4.62(m), 0.83(d, $^{2}J_{P\text{-}H}$=20.4 Hz, 9H)	169.8(t, $^{2}J_{P\text{-}C}$=15.1 Hz), 168.6(b)
$[Ir_2(I)(CO)_2(PMe_2Ph)(\mu\text{-}CH_2)(dppm)_2]$ **(24)**	1963(vs), 1990(ms)	-15.3(m), -15.4(m) -67.8(t, $^{2}J_{P\text{-}P}$=18.5Hz)	6.61(ttd, $^{3}J_{P\text{-}H}$=7.0 ,8.4, 5.4 Hz, 2H), 6.46(m, 2H), 4.42(m, 2H), 2.21(d, $^{2}J_{P\text{-}H}$=24.0 Hz, 6H)	170.0(b), 168.2(b)

Table 3.1 (contd).

[a] IR abbreviations: ss = strong sharp, sb = strong broad, ms = medium sharp, m = medium, w = weak. NMR abbreviations: t = triplet, d = doublet, dt = doublet of triplets, dd = doublet of doublets, tt = triplet of triplets, ddt = doublet of doublets of triplets, ddm = doublet of doublets of multiplets, dm = doublet of multiplets, td = triplet of doublets, bs = broad singlet, m = multiplet, q = quartet, s = singlet. [b] Nujol mull except as indicated. Values quoted are ν(CO) except as indicated. [c] single crystal microscope. [d] $^{31}P\{^{1}H\}$ chemical shifts are referenced vs external 85% H_3PO_4 while ^{1}H and $^{13}C\{^{1}H\}$ are referenced vs TMS. Chemical shifts for the phenyl hydrogens are not given in the ^{1}H NMR data. [e] ν(SO) for SO_2. [f] νC≡N.

Preparation of Compounds.

(a) $[Ir_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CO)(dppm)_2][BF_4]_2$ (10). Compound **9** (190 mg, 0.129 mmol) was dissolved in 80 mL of THF and CO was passed through the solution at ~0.25 mL/sec, causing the color of the solution to change immediately from orange to yellow. To this solution was added $AgBF_4$ (50 mg, 0.258 mmol) dissolved in 40 mL of THF, and the mixture was stirred overnight under an atmosphere of CO. The mixture was filtered under vacuum through celite and the product washed with 20 mL of acetonitrile. A clear pale yellow solution was obtained. Reducing the solution volume to 4 mL under vacuum and precipitating the product with ether/hexane (1:1) gave a cream-colored solid. Yield 82%. Anal. Calcd. for $Ir_2P_4F_8O_5B_2C_{56}H_{46}$: C 45.38, H 3.14. Found: C 44.89, H 3.23.

(b) *Syn*-$[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ (11a). Compound **10** (136 mg, 0.092mmol) was dissolved in 50 mL of acetonitrile. To this solution was slowly added Me_3NO (14.06 mg, 0.184 mmol) dissolved in 10 mL of acetonitrile and the mixture purged with a slow stream of dinitrogen for one hour, during which time the color of the solution changed from yellow to orange-pink. The solvent was reduced to 2 mL under vacuum and a pale pink product was obtained on precipitating with ether. The product was washed twice with 5 mL of ether and dried under a slow stream of dinitrogen. Yield 86%. Anal. Calcd. for $Ir_2P_4F_8O_2B_2C_{57}H_{52}N_2$: C 45.42, H 3.48. Found: C 45.28, H 3.73.

(c) *anti*-$[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ (11b). Compound **10** or **11a** when dissolved in acetonitrile gave compound **11b** after three days at room temperature. Reducing the solvent in vacuum and adding hexane precipitated a pale pink compound. Yield 90%. Anal. Calcd. for $Ir_2P_4F_8O_2B_2C_{57}H_{52}N_2$: C 45.42, H 3.48. Found C: 45.89, H 3.58.

(d) Reaction of $[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ (11a) with HC≡CH. Compound **11a** (95 mg, 0.064mmol) was dissolved in 30 mL of acetonitrile and acetylene was slowly passed (~0.25 mL/sec) through the solution for 5 minutes. The mixture was then stirred under an atmosphere of acetylene for 3 h during which the color changed from pale pink to yellow. The solvent was reduced to 2 mL under vacuum and the yellow product was precipitated with pentane. NMR analysis showed the presence of two isomers $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}\eta^1{:}\eta^1\text{-}HC{\equiv}CH)(dppm)_2][BF_4]_2$ **(16)** and $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}C{=}CH_2)(dppm)_2][BF_4]_2$ **(17)** in the ratio 5:1. Analytical results reported are for the mixture of the isomers. Anal. Calcd. for $Ir_2P_4F_8O_2B_2C_{55}H_{48}$: C 46.42, H 3.67. Found: C 46.81, H 3.64.

(e) $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}SO_2)(dppm)_2][BF_4]_2$ (18). Compound **11a** (45 mg, 0.03 mmol) was dissolved in 20 mL of acetonitrile and SO_2 slowly (~0.25 mL/sec) passed through the solution for 10 min. The mixture was then stirred overnight at room temperature during which the color of the solution changed from pale pink to brown. The solvent was then reduced to 2 mL and an orange product precipitated with pentane. Anal. Calcd. for $Ir_2P_4F_8O_4B_2C_{53}H_{46}S$: C 43.57, H 3.17, S 2.19. Found: C 44.03, H 3.25, S 2.45.

(f) $[Ir_2(CO)_2(CS_2)(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ (19). The compound **11a** (30 mg, 0.04 mmol) was dissolved in 20 mL of acetonitrile and CS_2 (12 μL, 0.4 mmol) added. After 15 min of stirring at room temperature, the color of the solution changed from pink to yellow, and stirring for 3 h gave a color change to a brown solution. The solvent was reduced to 2mL under vacuum and the brown product precipitated and washed with pentane and recrystallised from dichloromethane/pentane. Yield 72%. Anal. Calcd. for $Ir_2P_4F_8O_2B_2C_{54}H_{46}S_2$: C 44.03, H 3.15, S 4.35. Found: C 44.25, H 3.31, S 4.69.

(g) $[Ir_2(Br)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ (20). 30 mg (0.04 mmol) of compound **10** was weighed and added into a Schlenk flask. 3.2 mg (0.08 mmol) of Me_3NO was added and the flask was kept under dinitrogen. 80 μL (0.16 mmol) of vinylmagnesium bromide (1 mL solution in THF) was added followed by 20 mL of THF and the mixture was stirred for one hour resulting in a color change from pale pink to a clear yellow solution. The solvent was removed and the resulting yellow solid product was dissolved in dichloromethane and filtered through celite. The solvent was reduced to 2 mL and a yellow product was precipitated by the addition of 5mL of pentane. Yield 65%. Anal. Calcd. for $Ir_2P_4O_2C_{53}H_{46}Br_2$: C 52.03, H 3.80. Found: C 52.39, H 3.64.

(h) $[Ir_2(I)(CO)_2(^tBuNC)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (22). 30 mg (0.02 mmol) of compound **8** was dissolved in 10 mL of dichloromethane and 2.26 μL (0.02 mmol) of ^{t}BuNC added. There was an immediate color change from red to yellow. The mixture was stirred for 3 h at room temperature after which the solvent was reduced to 2 mL and a yellow solid precipitated on adding 6 mL of pentane. Yield 75% Anal. Calcd. for $Ir_2P_4F_3O_5C_{59}H_{55}IS$: C 46.43, H 3.63. Found: C 46.99, H 3.58.

(i) $[Ir_2(I)(CO)_2(PMe_3)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (23). 30 mg (0.02 mmol) of compound **8** was dissolved in 10 mL of dichloromethane and 2μL (0.02 mmol) of PMe_3 (97%) was added. There was an immediate color change from red to yellow. The mixture was stirred for 1 h at room temperature after which the solvent was reduced to 2 mL and a yellow solid precipitated on slow addition of 10 mL of pentane. Yield 82%. Anal. Calcd. for $Ir_2P_5F_3O_5C_{53}H_{53}IS$: C 45.06, H 3.65. Found: C 45.86, H 3.32.

(j) $[Ir_2(I)(CO)_2(PMe_2Ph)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (24) . 30 mg (0.02 mmol) of compound **8** was dissolved in 10 mL of dichloromethane and 2.8μL (0.02 mmol) of PMe_2Ph (97%) added. There was an immediate color change from red to yellow. The mixture was stirred for 1 h at room temperature after which the solvent was reduced to 2 mL and a yellow solid precipitated on slow addition of 8 mL of pentane. Yield 76%%. Anal. Calcd. for $Ir_2P_5F_3O_5C_{59}H_{55}IS$: C 44.81, H 3.51. Found: C 44.32, H 3.43.

(k) Reaction of $[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ with H_2. Into an NMR tube was placed 30 mg (0.04 mmol) of compound **11a** . The tube was then capped with a septa and evacuated and put under nitrogen. 0.7 mL of deuterated acetonitrile was added to form a pale pink solution. Dihydrogen was slowly passed (~0.25 mL/sec) through the solution for 5 min. After standing for one hour at room temperature the color of the solution had changed to yellow and the mixture was taken for NMR analysis which showed the presence of the known compound $[Ir_2(CO)_2(H)_2(\mu\text{-}H)_2(dppm)_2][BF_4]_2$ **(14)**.[231]

(l) Low-Temperature Reaction of Compound 11a with H_2. The above procedure was repeated using compound **11a** except that dihydrogen was slowly passed through the solution at -40°C for 5 min and the NMR of the mixture taken immediately. At -40°C only the starting material was observed. At -20°C three species were observed in the solution. The majority species was the starting material followed by the known tetrahydride $[Ir_2(CO)_2(H)_2(\mu\text{-}H)_2(dppm)_2][BF_4]_2$ **(14)**. A small amount of another species **13** was also observed. Upon warming to room temperature only compound **14** was detected.

X-ray Data Collection for Compound 20. Suitable crystals of compound **20** were grown by slow diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of the compound. Several crystals were mounted and flame-sealed in glass capillaries under solvent vapor to minimize decomposition or deterioration due to solvent loss. Data were collected at -80°C on a Bruker P4/RA/SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation. Unit-cell parameters were obtained from least-squares refinement of 8061 centered reflections. The cell parameters and systematic absences defined the space group as *Pbca*. Of the 11516 independent reflections collected, the number of observed reflections was 8425. Absorption corrections were applied using the program *SADABS*. Crystal data and X-ray collection information are given in Table 3.2.

Structure Solution and Refinement. The positions of the iridium and phosphorus atoms were found using the direct methods/fragment search program DIRDIF-96.[15] The remaining atoms were located using a succession of least-squares refinements and difference Fourier maps. Refinement of the structure proceeded using the program SHELXL-93.[16] Hydrogen atom positions were calculated by assuming idealized sp^2 or sp^3 geometries about their attached carbon atoms as appropriate and were given thermal parameters 120% of the equivalent isotropic displacement parameters of the attached carbons. The compound was found to be disordered, in which there are two superimposed orientations of the complex as diagrammed below

Table 3.2 Crystallographic Experimental Details

A. Crystal Data

formula	$C_{58}H_{58}Br_2Cl_2Ir_2O_3P_4$
formula weight	1542.04
crystal dimensions (mm)	0.34x0.21x0.18
crystal system	orthorhombic
space group	*Pbca* (No. 61)
unit cell parameters[a]	
a (Å)	16.8150 (9)
b (Å)	18.3549 (11)
c (Å)	36.442 (2)
V (Å^3)	11247.3 (11)
Z	8
ρ_{calcd} (g cm^{-3})	1.821
μ (mm^{-1})	6.401

B. Data Collection and Refinement Conditions

diffractometer	Bruker P4/RA/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	-80
scan type	ϕ rotations (0.3°)/ ω scans(0.3°) (30 s exposures)

Table 3.2 Crystallographic Experimental Details (continued)

data collection 2θ limit (deg)	52.84
total data collected	53218 ($-8 \le h \le 21$, $-22 \le k \le 22$, $-45 \le l \le 43$)
independent reflections	11516
number of observed reflections (NO)	8425 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods/fragment search (*DIRDIF-96*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL-93*[d])
absorption correction method	*SADABS*
range of transmission factors	0.4591-0.3448
data/restraints/parameters	11516 [$F_o^2 \ge -3\sigma(F_o^2)$] /12[e]/678
goodness-of-fit (S)[f]	1.036 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[g]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0347
ωR_2[$F_o^2 \ge -3\sigma(F_o^2)$]	0.0922
largest difference peak and hole	1.215 and –0.970 e Å^{-3}

[a] Obtained from least-squares refinement of 8061 centered reflections.

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

[c] Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Garcia Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. 1996. The *DIRDIF-96*

Table 3.2 Crystallographic Experimental Details (continued)

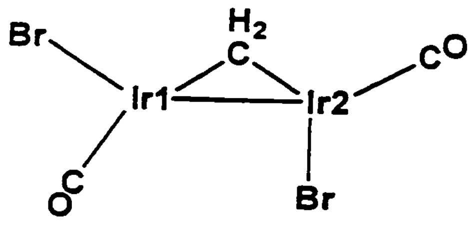
program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted *R*-factors ωR_2 and all goodnesses of fit S are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

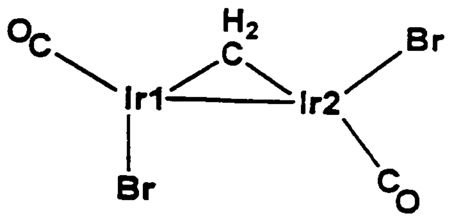
[e]Because of the superposition of carbonyl and bromine positions it was necessary to refine the positions of the carbonyl C and O atoms with a fixed linear carbonyl geometry, i.e. d(Ir-C) = 1.85Å, d(O-C) = 1.15Å, and d(Ir···O)= 3.00Å.

[f]$S = [\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $\omega = [\sigma^2(F_o^2) + (0.0494P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $\omega R_2 = [\Sigma\omega(F_o^2 - F_c^2)^2/(F_o^4)]^{1/2}$.



20a



20b

(dppm ligands are omitted for clarity). The major isomer **20a** has a 65% occupancy while isomer **20b** has 35% occupancy. Subsequent difference Fourier maps showed that the disordered carbonyls and bromides were not exactly superimposed but were slightly offset from each other. A drawing of the equatorial plane of the disordered structure (with dppm ligands omitted for clarity) is shown in Figure 3.1. Atoms Ir(1), Ir(2) and C3 are common to both disordered molecules with the black solid line connecting ligands Br(1A), Br(2A), C(1A)O(1A) and C(2A)O(2A) having the major occupancy while the white solid line connects ligands Br(1B), Br(2B), C(1B)O(1B) and C(2B)O(2B) having the minor occupancy. The atomic coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms of compound **20** are given in Table 3.3.

Dr. Bob McDonald is acknowledged for X-ray data collection and structure solution for compound **20**.

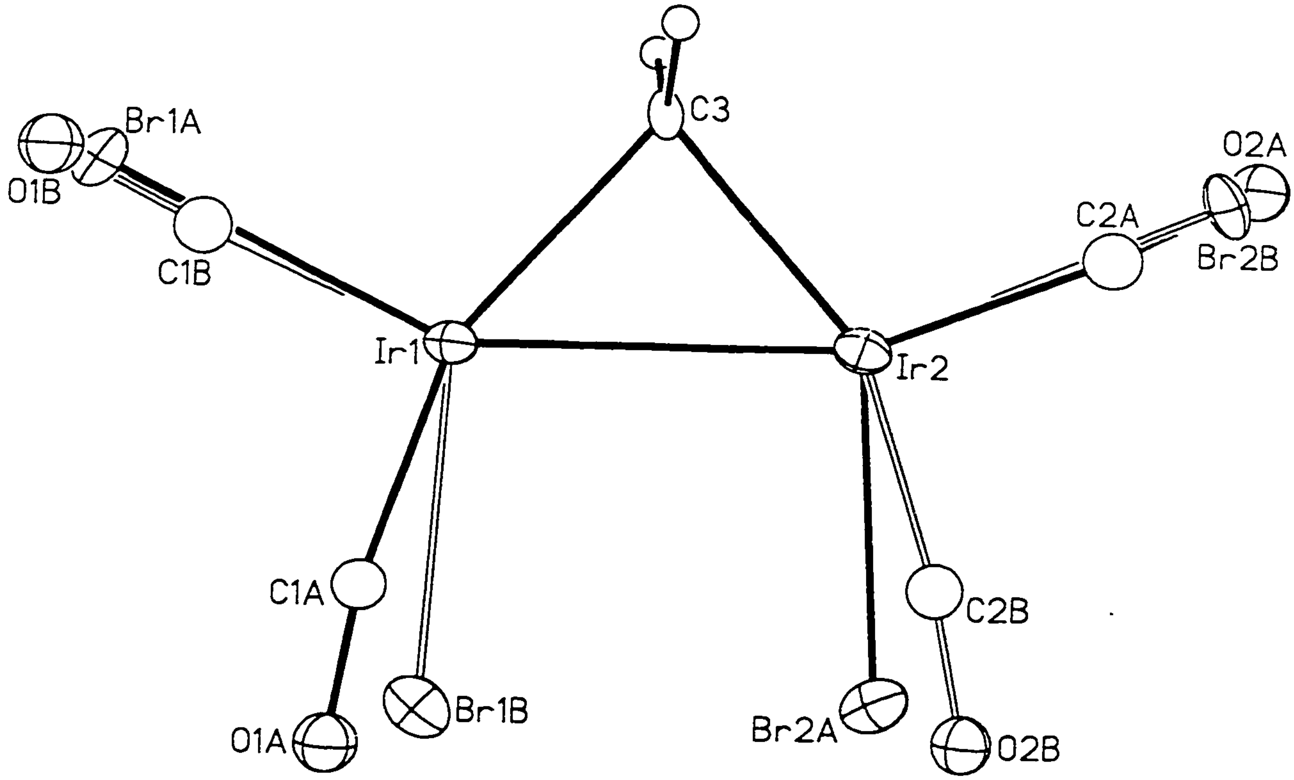


Figure 3.1 Illustration of the disordering between the carbonyl and bromide ligands. The Br(1A), Br(2A), C(1A)O(1A) and C(2A)O(2A) ligands have occupancies of 0.65 while the Br(1B), Br(2B), C(1B)O(1B) and C(2B)O(2B) ligands have occupancies of 0.35. The dppm ligands are not shown.

Table 3.3. Atomic Coordinates and Equivalent Displacement Parameters

(a) 'inner-core' atom

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Ir(1)	0.069019(9)	0.076226(9)	0.128945(6)	0.02955(9)*
Ir(2)	-0.052910(9)	0.177124(9)	0.123255(6)	0.03136(9)*
Br(1A)[a]	0.17939(7)	-0.01012(7)	0.09874(4)	0.0393(3)*
Br(2A)[a]	-0.06921(7)	0.18946(7)	0.19450(3)	0.0454(3)*
Br(1B)[b]	0.06382(15)	0.07359(14)	0.20151(7)	0.0475(6)*
Br(2B)[b]	-0.15977(12)	0.26297(17)	0.08665(11)	0.0366(6)*
P(1)	-0.01977(11)	-0.02164(10)	0.13082(5)	0.0315(4)*
P(2)	-0.15062(11)	0.08713(11)	0.12181(5)	0.0349(4)*
P(3)	0.16727(11)	0.16590(11)	0.13162(5)	0.0322(4)*
P(4)	0.03527(11)	0.27465(11)	0.12624(5)	0.0346(4)*
O(1A)[a,c]	0.0917(2)	0.0528(5)	0.20974(4)	0.046(2)
O(2A)[a,c]	-0.16925(4)	0.2740(6)	0.0843(4)	0.046(2)
O(1B)[b,c]	0.19479(3)	-0.0216(6)	0.0976(5)	0.046(2)
O(2B)[b,c]	-0.09888(10)	0.2123(9)	0.20080(10)	0.046(2)
C(1A)[a]	0.08406(16)	0.0599(6)	0.17856(4)	0.032(2)
C(2A)[a]	-0.1249(3)	0.2375(5)	0.0998(2)	0.043(3)
C(1B)[b]	0.1466(6)	0.0158(6)	0.1097(3)	0.040(5)
C(2B)[b]	-0.0822(5)	0.2001(11)	0.17082(8)	0.038(5)
C(3)	0.0155(3)	0.1251(3)	0.07971(17)	0.0203(13)*
C(4)	-0.1182(4)	0.0071(4)	0.14700(19)	0.0345(17)*
C(5)	0.1261(4)	0.2499(4)	0.15050(19)	0.0345(17)*

(b) dppm phenyl carbons

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(11)	0.0058(4)	-0.0941(4)	0.1636(2)	0.0367(17)*
C(12)	0.0690(6)	-0.1364(6)	0.1581(3)	0.095(4)*
C(13)	0.0860(7)	-0.1947(7)	0.1807(3)	0.108(5)*
C(14)	0.0424(6)	-0.2090(5)	0.2098(3)	0.065(3)*
C(15)	-0.0266(7)	-0.1700(5)	0.2154(3)	0.068(3)*
C(16)	-0.0439(6)	-0.1114(5)	0.1922(2)	0.057(2)*
C(21)	-0.0378(4)	-0.0752(4)	0.08923(19)	0.0346(16)*
C(22)	-0.0021(4)	-0.0579(4)	0.0560(2)	0.0396(18)*
C(23)	-0.0173(5)	-0.0992(5)	0.0249(2)	0.048(2)*
C(24)	-0.0671(5)	-0.1582(5)	0.0266(2)	0.054(2)*
C(25)	-0.1014(6)	-0.1774(5)	0.0597(2)	0.057(2)*
C(26)	-0.0873(5)	-0.1363(4)	0.0908(2)	0.047(2)*
C(31)	-0.1849(4)	0.0511(4)	0.0776(2)	0.0381(18)*
C(32)	-0.1641(4)	0.0846(4)	0.0445(2)	0.0427(19)*
C(33)	-0.1881(5)	0.0540(5)	0.0117(2)	0.055(2)*

Table 3.3. Atomic Coordinates and Displacement Parameters (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(34)	-0.2343(6)	-0.0084(5)	0.0119(3)	0.061(3)*
C(35)	-0.2569(5)	-0.0408(5)	0.0438(2)	0.058(2)*
C(36)	-0.2318(5)	-0.0107(4)	0.0769(2)	0.053(2)*
C(41)	-0.2433(4)	0.1136(4)	0.1446(2)	0.043(2)*
C(42)	-0.3020(5)	0.1476(5)	0.1232(3)	0.064(3)*
C(43)	-0.3714(6)	0.1734(5)	0.1402(4)	0.085(4)*
C(44)	-0.3832(6)	0.1634(5)	0.1770(4)	0.082(4)*
C(45)	-0.3248(6)	0.1292(5)	0.1977(3)	0.070(3)*
C(46)	-0.2557(5)	0.1046(5)	0.1814(2)	0.052(2)*
C(51)	0.2488(4)	0.1440(4)	0.1628(2)	0.0395(19)*
C(52)	0.3106(5)	0.1015(5)	0.1507(3)	0.062(3)*
C(53)	0.3727(6)	0.0827(6)	0.1735(3)	0.075(3)*
C(54)	0.3730(5)	0.1057(6)	0.2093(3)	0.069(3)*
C(55)	0.3115(5)	0.1472(5)	0.2225(2)	0.058(3)*
C(56)	0.2494(5)	0.1660(5)	0.1993(2)	0.048(2)*
C(61)	0.2231(4)	0.1964(4)	0.0914(2)	0.0363(17)*
C(62)	0.2094(4)	0.1691(5)	0.0560(2)	0.0436(19)*
C(63)	0.2515(5)	0.1953(5)	0.0265(2)	0.052(2)*
C(64)	0.3092(5)	0.2482(5)	0.0312(2)	0.056(2)*
C(65)	0.3254(5)	0.2752(5)	0.0660(3)	0.059(2)*
C(66)	0.2814(5)	0.2492(4)	0.0958(2)	0.050(2)*
C(71)	0.0681(4)	0.3158(4)	0.0834(2)	0.0364(17)*
C(72)	0.0300(5)	0.3009(4)	0.0504(2)	0.0437(19)*
C(73)	0.0553(5)	0.3335(5)	0.0183(2)	0.056(2)*
C(74)	0.1189(5)	0.3796(6)	0.0182(3)	0.067(3)*
C(75)	0.1556(6)	0.3963(5)	0.0504(3)	0.067(3)*
C(76)	0.1308(5)	0.3646(5)	0.0829(2)	0.051(2)*
C(81)	-0.0004(4)	0.3543(4)	0.1521(2)	0.0402(19)*
C(82)	-0.0504(6)	0.4032(6)	0.1357(3)	0.070(3)*
C(83)	-0.0795(6)	0.4632(6)	0.1543(4)	0.079(3)*
C(84)	-0.0586(6)	0.4742(6)	0.1901(3)	0.073(3)*
C(85)	-0.0114(9)	0.4264(6)	0.2062(3)	0.099(4)*
C(86)	0.0195(7)	0.3662(5)	0.1872(3)	0.080(3)*

(c) solvent dichloromethane atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Cl(1S)[d]	0.0574(7)	0.4892(5)	-0.0565(3)	0.126(4)*
Cl(2S)[d]	-0.0556(7)	0.3747(7)	-0.0725(4)	0.186(6)*
C(1S)[d]	-0.0290(18)	0.4586(18)	-0.0813(10)	0.125(11)*
Cl(3S)[d]	0.0578(6)	0.4319(10)	-0.0721(4)	0.197(7)*

Table 3.3. Atomic Coordinates and Displacement Parameters (continued)

Atom	x	y	z	U_{eq}, Å^2
Cl(4S)[d]	-0.0960(4)	0.4154(5)	-0.0468(3)	0.126(3)*
C(2S)[d]	-0.0225(16)	0.4691(16)	-0.0474(9)	0.109(10)*

(d) solvent diethyl ether atoms

Atom	x	y	z	U_{eq}, Å^2
O(10S)	0.2360(7)	0.0959(7)	-0.2276(4)	0.188(7)*
C(11S)	0.2680(9)	0.1619(8)	-0.2156(5)	0.152(8)*
C(12S)	0.2531(6)	0.1686(6)	-0.1736(3)	0.082(4)*
C(13S)	0.2582(11)	0.0567(10)	-0.2563(6)	0.172(8)*
C(14S)	0.2289(12)	0.0892(11)	-0.2938(7)	0.257(15)*

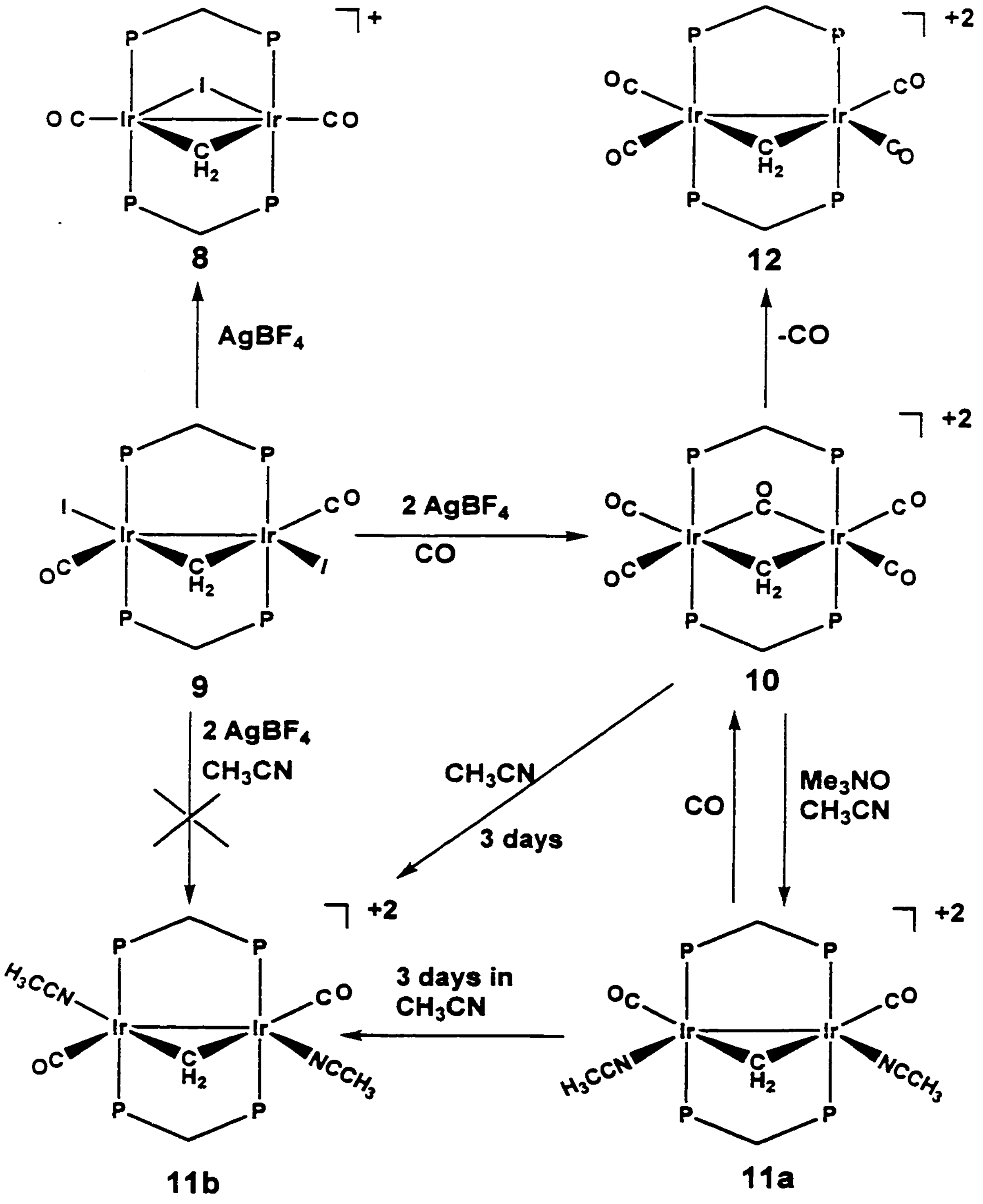
Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$. [a]Refined with an occupancy factor of 0.65. [b]Refined with an occupancy factor of 0.35. [c]Carbonyl oxygens were refined with a common isotropic displacement parameter. [d]Refined with an occupancy factor of 0.5.

Results and Characterization of Compounds

As discussed in the previous chapter, the reaction of $Ir_2(CO)_3(dppm)_2$ with iodomethyl methylether results in loss of a CO and the oxidative addition of ICH_2OCH_3 to give $[Ir_2(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)dppm)_2]$ **(2)** as shown in Scheme 2.2. Although the reaction of compound **2** with methyl triflate resulted in some abstraction of the methoxy group yielding the targeted methylene-bridged compound, varying amounts of iodide abstraction was also observed giving product of double C-H activation of the methylene group. Thus a mixture of products as shown in Scheme 2.2 was obtained. However, reaction of $[Ir_2(I)(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ with trimethyl silyliodide, (Me_3SiI) resulted in the formation of a methylene-bridged diiodo dicarbonyl complex $[Ir_2(I)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ **(9)** and Me_3SiOCH_3[14]. Methylene groups have been noted to be the key species in the carbon chain elongation observed in the Fischer-Tropsch (FT) reaction and it was of interest to investigate if this or related methylene-bridged diiridium species could be used to model the carbon chain growth observed in the FT process.

The iodide ligands in compound **9** can be abstracted with various electrophiles resulting in the conversion of **9** into a number of cationic methylene-bridged complexes. Reaction of **9** with an excess of methyl triflate, silver tetrafluoroborate $AgBF_4$, or silver triflate ($AgSO_3CF_3$), in dichloromethane, THF, or acetonitrile led to the formation of $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2][X]$ ($X = CF_3SO_3, BF_4$) **(8)** by electrophilic attack and abstraction of one iodide. However, when the reaction was done under an atmosphere of CO both iodides were abstracted to give the methylene-bridged pentacarbonyl $[Ir_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CO)(dppm)_2][BF_4]_2$ **(10)** as shown in Scheme 3.1. The failure to abstract both iodide ions in absence of CO suggests that formation of the targeted diiridium dicationic methylene-bridged dicarbonyl species $[Ir_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]^{2+}$ is unfavorable. Compound **10** has been assigned the structure shown in Scheme 3.1 on the basis of ^{31}P, ^{1}H, ^{13}C NMR and IR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum shows only one sharp singlet at δ -17.6 suggesting a species with "top-bottom" and "left-right" symmetry in which the two diphosphine ligands bridge the metals in a trans, trans geometry with both metals having equivalent chemical environments. The ^1H NMR spectrum shows the bridging methylene protons at δ 7.10 as a quintet ($^3J_{P\text{-}H}$ = 7.3 Hz) which is consistent with all four phosphorus nuclei being chemically equivalent. The dppm methylene protons were observed as multiplets at δ 6.82 and 5.13 which is also indicative of a trans, trans dppm-bridged structure in which the two faces of the "Ir_2P_4" plane are inequivalent. The IR spectrum of a solid sample of compound **10** indicates carbonyl stretches at 2085, 2036, 2013, 1991 cm^{-1}, consistent with four terminal carbonyl groups and at 1810 cm^{-1} consistent with a bridging carbonyl. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO enriched sample at room temperature shows three carbonyl signals at δ 197.6 166.7 and 159.4 in a ratio of approximately 1:2:2, respectively. This is consistent with a pentacarbonyl species having one bridging carbonyl and two carbonyls terminally bound to

Scheme 3.1


P
P
I
OC
Ir
Ir
CO
C
H2
+
8
12
+2
-CO
AgBF4
9
10
2 AgBF4
CO
2 AgBF4
CH3CN
CH3CN
3 days
CO
Me3NO
CH3CN
3 days in
CH3CN
H3CCN
NCCH3
11b
11a

each metal. The bridging carbonyl resonance at δ 197.6 appears as a quintet ($^2J_{P\text{-}C}$ = 4.6 Hz) due to coupling with the four chemically equivalent dppm phosphorus nuclei.

One carbonyl of complex **10** is labile in solution and is readily lost to form the tetracarbonyl complex with a metal-metal bond as shown in Scheme 3.1. It is the facile loss of one carbonyl in solution that made it difficult to grow crystals for X-ray structure determination of compound **10**. However, taken together, the NMR and IR spectroscopic data are very strongly suggestive of structure **10**. Reaction of compound **10** with trimethylamine oxide in acetonitrile as illustrated in Scheme 3.1 results in substitution of two carbonyls by acetonitrile, accompanied by loss of a third carbonyl to give compound **11** which exists as the syn and anti isomers **(11a&b)**. Compound **11**, formulated as $[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ is coordinatively saturated but the labile acetonitrile ligands are very readily displaced. It was anticipated that acetonitrile loss from **11** would be facile, allowing their substitution by more interesting substrates. Such reactivity was observed in other methylene-bridged compounds such as $[Cp_2Ru_2(\mu\text{-}CH_2)(CO)_2(CH_3CN)]$[10], in which acetonitrile substitution led to C-C bond formation and in the compound $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]^+$ in which the presence of one-electron oxidizers caused decomposition of the compound to give propene as a result of C-C coupling between the methyl and methylene ligands[19]. Compound **11** exists as the syn and anti isomers depending upon the relative positions of the acetonitrile ligands as shown in Scheme 3.1. The syn isomer (**11a)** has a single phosphorus peak at δ -10.1 as expected of this symmetric compound. The bridging methylene protons appear as a quintet in the ^{1}H NMR spectrum at δ 6.44 ($^3J_{P\text{-}H}$ = 7.6 Hz) consistent with a compound having all four phosphorus nuclei chemically equivalent. The dppm methylene protons are observed as multiplets at δ 6.32 and 4.73 while the acetonitrile protons are observed as a singlet at δ 2.11. The ^{13}C{^{1}H} NMR spectrum of a ^{13}CO enriched sample shows one triplet signal at δ 168.2 ($^2J_{P\text{-}C}$ = 7.0 Hz) which is consistent with the two carbonyls being chemically equivalent. The IR spectrum shows the acetonitrile νC≡N peak at 2350 cm^{-1} and the terminal carbonyls as a broad peak at 1985 cm^{-1}. The anti isomer (**11b)** has one acetonitrile ligand cis and the other trans to the bridging methylene group. ^{1}H NMR experiments of **11b** with selective ^{31}P decoupling of the resonances shows the bridging methylene resonance as a triplet of triplets at δ 6.52 with coupling to the two sets of inequivalent phosphorus nuclei of 9.6 and 6.7 Hz. Although the acetonitrile ligands in **11b** are inequivalent, only one resonance for the methyl protons is observed as a singlet at δ 2.04. The phosphines appear as two sets of multiplets in the ^{31}P{^{1}H} spectrum at δ -10.2 and -15.8 owing to the inequivalent metal environments (one metal has a carbonyl trans to the bridging methylene while the other has an acetonitrile in the trans position). The dppm methylene protons appear as multiplet signals at δ 6.12 and 4.51. The ^{13}C{^{1}H} NMR spectrum of a ^{13}CO enriched sample shows a triplet at δ 171.9 ($^{2}J_{P\text{-}C}$ = 7.7Hz) and a broad unresolved peak δ 164.8. The IR spectrum supports the assignment of two terminal carbonyls at a frequency of 2006 cm^{-1} and 1980 cm^{-1} with the acetonitrile C≡N stretch appearing at 2350 cm.$^{-1}$

Over a period of three days in acetonitrile at room temperature the syn isomer **11a** completely transforms into the thermodynamically favored anti isomer **11b**. This could be due to the unfavorable steric interactions in complex **11a** between the acetonitrile groups on one face of the complex with the dppm phenyl groups. Transforming into the anti isomer puts the acetonitrile groups as far apart as possible, this relieves these steric interactions resulting into a more stable isomer. It is anticipated that acetonitrile dissociation and recoordination would be the most favorable process for this transformation and has been previously proposed in the reactions of the diiodo methylene-bridged complex $[Ir_2(I)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$[14] and the diiodo carbonyl-bridged $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$.[21]

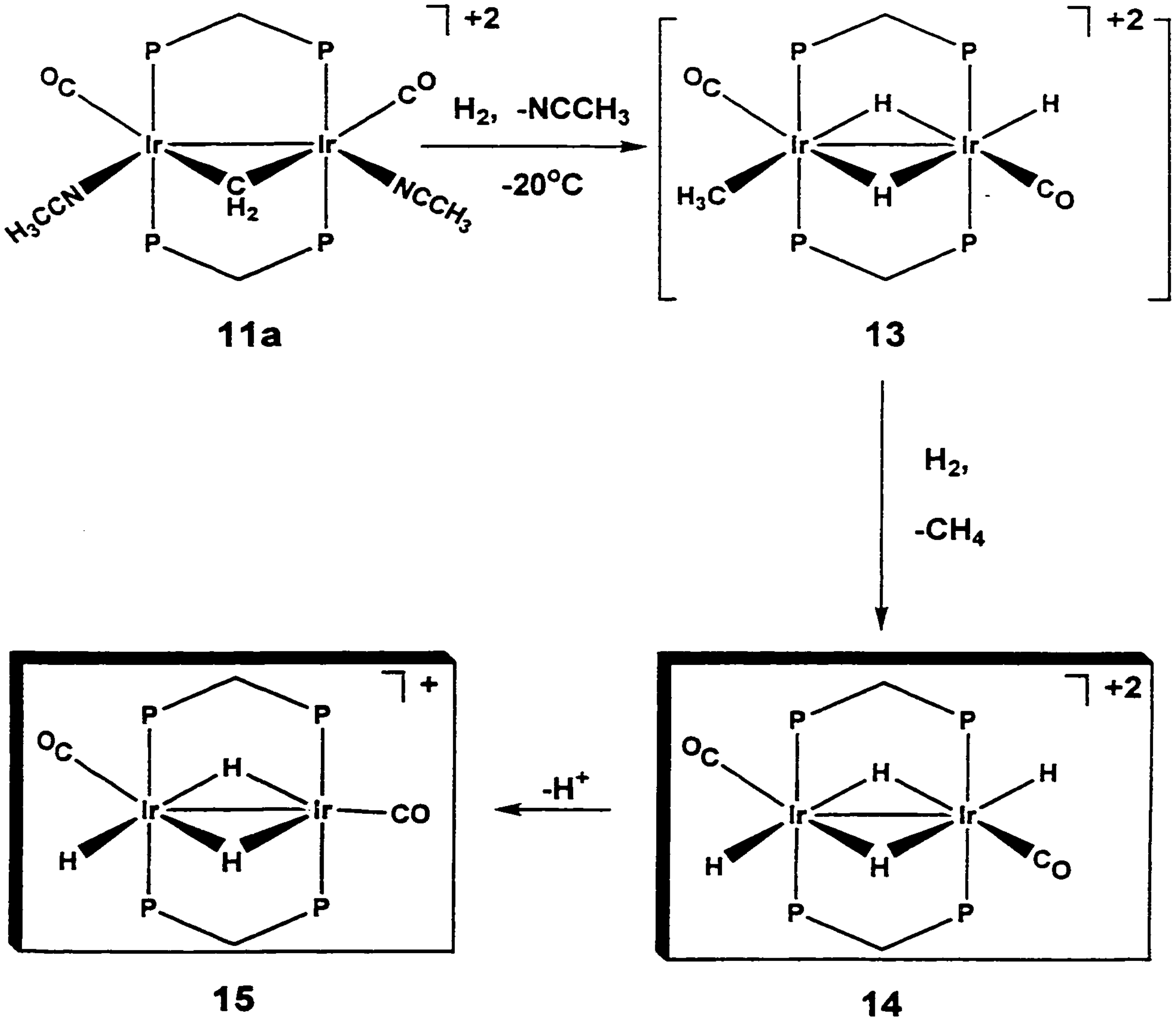
Reactivity Studies

Having prepared the methylene-bridged "Ir_2" species **11a** there were several aspects of its potential reactivity that were of interest. Reactivity of compound **11a** was of interest owing to the acetonitrile arrangement in this species. Having both potentially labile groups adjacent to the methylene groups was desirable for any potential migratory insertion reactions that might result upon replacing these acetonitriles by groups that were capable of combining with the methylene ligand. We were interested in inducing carbon-carbon bond formation involving the bridging methylene group with a number of hydrocarbyl fragments. Recent studies in our group had demonstrated carbon-carbon bond formation involving reactions of methylene-bridged complexes with diazomethane,[12] allenes and acetylene.[13] It was also of interest to induce carbon-carbon bond formation through reaction with other sources of hydrocarbyl groups such as olefins, Grignard reagents and alkyllithium reagents. The second aspect of additional interest was to investigate the reactivity of compounds **8**, **10** and **11a** with a number of ligands having different steric and electronic properties such as H_2, PR_3, ^tBuNC, SO_2 and CS_2. We were interested in the site of ligand attack and subsequent ligand rearrangement that might occur with particular interest in possible migratory insertions into the $Ir\text{-}CH_2$ bonds.

All attempts to form longer-chain hydrocarbon fragments by reacting the methylene-bridged compounds **8**, **10** and **11a** with diazomethane, substituted alkynes, allenes, ethylene and Grignard reagents failed. However, the complexes showed some reactivity with some small molecules such as H_2, $HC{\equiv}CH$, ^tBuNC, SO_2, CS_2, RMgX and PR_3.

Reaction of compound **11a** with H_2 at ambient temperature yields the known tetrahydride species $[Ir_2(H)_2(CO)_2(\mu\text{-}H)_2(dppm)_2][BF_4]_2$[23l] **(14)** and methane as shown in Scheme 3.2. Also observed in the reaction solution was 36% of the known trihydride $[Ir_2(H)(CO)_2(\mu\text{-}H)_2(dppm)_2][BF_4]$ **(15)** which has

Scheme 3.2

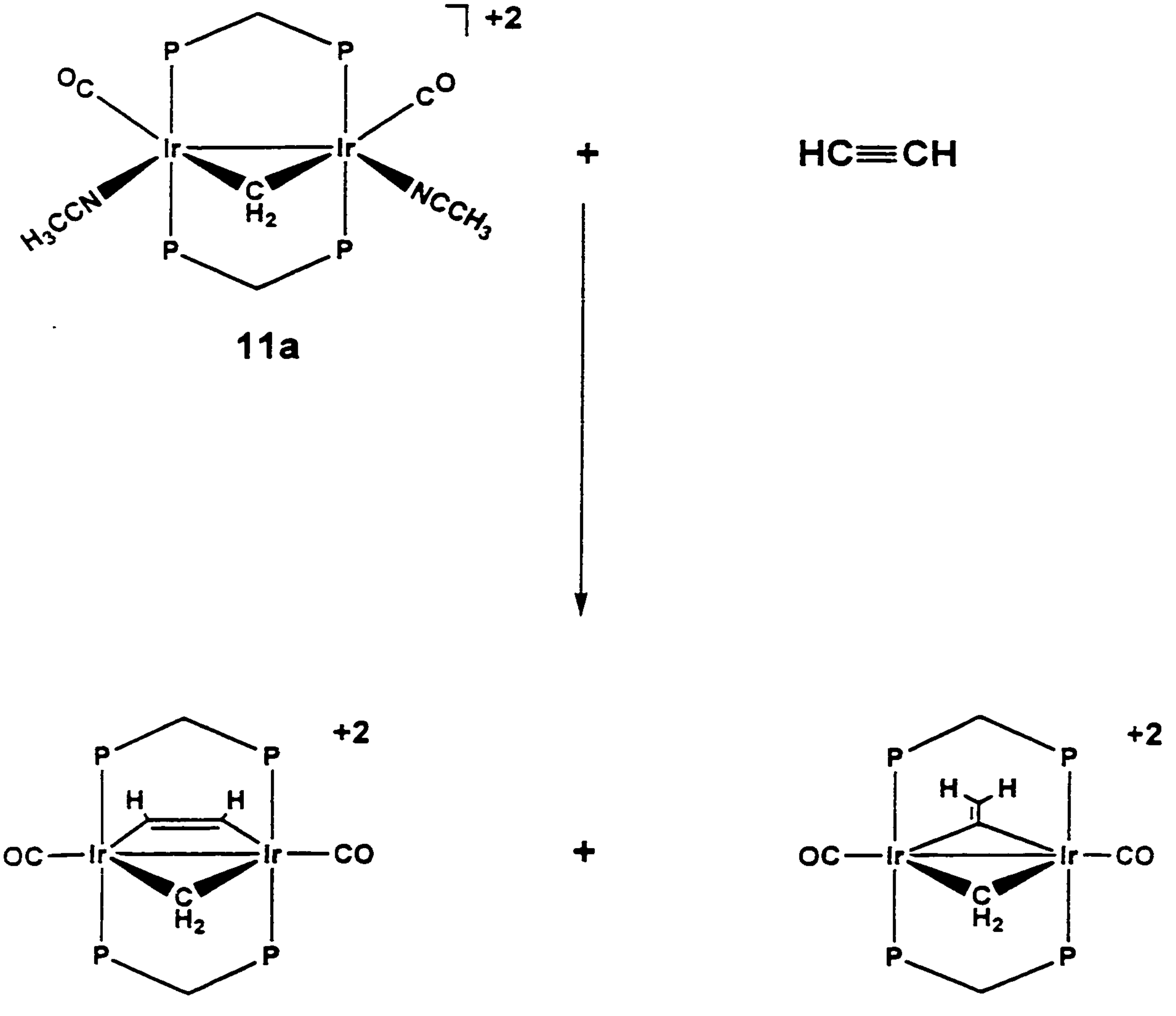


Boxed Compounds have been previously described

been shown to result from deprotonation of the tetrahydride complex in acetonitrile.[23] The reaction of compound **11a** with dihydrogen at ambient temperature and pressure to produce the tetrahydride and methane represents an unusually facile example of hydrogenolysis of the M-CH_2 bonds. Other hydrogenolysis reactions involving bridging methylene groups found in the literature include the reaction of the iron compound $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$ with dihydrogen that occurred at 200 psi and 60°C in benzene to produce methane.[24] It was of interest to establish the reductive elimination process of methane from the reaction of compound **11a** with H_2 and to establish the natures of any hydrido-methyl intermediates in the elimination of methane from the iridium centers. When H_2 was passed through a solution of compound **11a** in CD_3CN at -20°C in an NMR tube, and the NMR spectra of the mixture taken immediately, three species were observed in solution in the ratio 10:2:1. The majority species is the starting material, followed by the tetrahydride product $[Ir_2(H)_2(CO)_2(\mu\text{-}H)_2(dppm)_2][BF_4]_2$ **(14)**. The minor species is proposed to be the trihydride-methyl species $[Ir_2(H)(CH_3)(CO)_2(\mu\text{-}H)_2(dppm)_2][BF_4]_2$ **(13)** as outlined in Scheme 3.2. The ^1H NMR of intermediate **13** shows the methyl resonance as a broad signal at δ 2.32 together with three hydride resonances that appear at δ -10.51, -11.93 and -12.42. The $^{31}P\{^1H\}$ NMR spectrum of **13** shows two multiplet signals at δ -11.3 and -14.8. On warming and after standing at room temperature for about three hours, compound **13** disappears accompanied by a substantial increase in the tetrahydride and small amounts of the trihydride products. Due to the relatively high freezing point of acetonitrile (-44°C) (the starting material is not soluble in any other solvent) the reaction could not be studied at a lower temperature and therefore NMR characterization of the intermediate compound **13** was not conclusive. However, on the basis of the data available and from the literature where μ-methylene groups have been eliminated as methane,[10] the reaction sequence shown in Scheme 3.2 is proposed. Oxidative addition of H_2 to compound **11a** occurs with subsequent hydride migration to the methylene group to yield the methyl-containing intermediate **13** which eliminates methane with concomitant addition of another molecule of H_2 to give the tetrahydride product **14**.

Reaction of compound **11a** with acetylene at ambient temperature resulted in the formation of a mixture of $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}HC{\equiv}CH)(dppm)_2][BF_4]_2$ **(16)** and $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}C{=}CH_2)(dppm)_2][BF_4]_2$ **(17)** in the ratio 5:1 as shown in Scheme 3.3. Compound **16** contains the intact acetylene molecule while compound **17** is a vinylidene-bridged species resulting from a 1,2-hydrogen shift of an acetylene hydrogen. The $^{31}P\{^1H\}$ NMR[22] spectrum of compound **16** is a singlet at δ -10.2 suggesting a symmetrical compound. In the ^1H-NMR spectrum of compound **16** the bridging methylene resonance is a quintet at δ 3.22 and the proton resonances of the coordinated acetylene is a triplet at δ 8.84 ($^3J_{P\text{-}H}$ = 4.8 Hz). The dppm methylene protons appear as multiplets at δ 5.02 and 4.93. The IR spectrum shows a broad

Scheme 3.3



11a

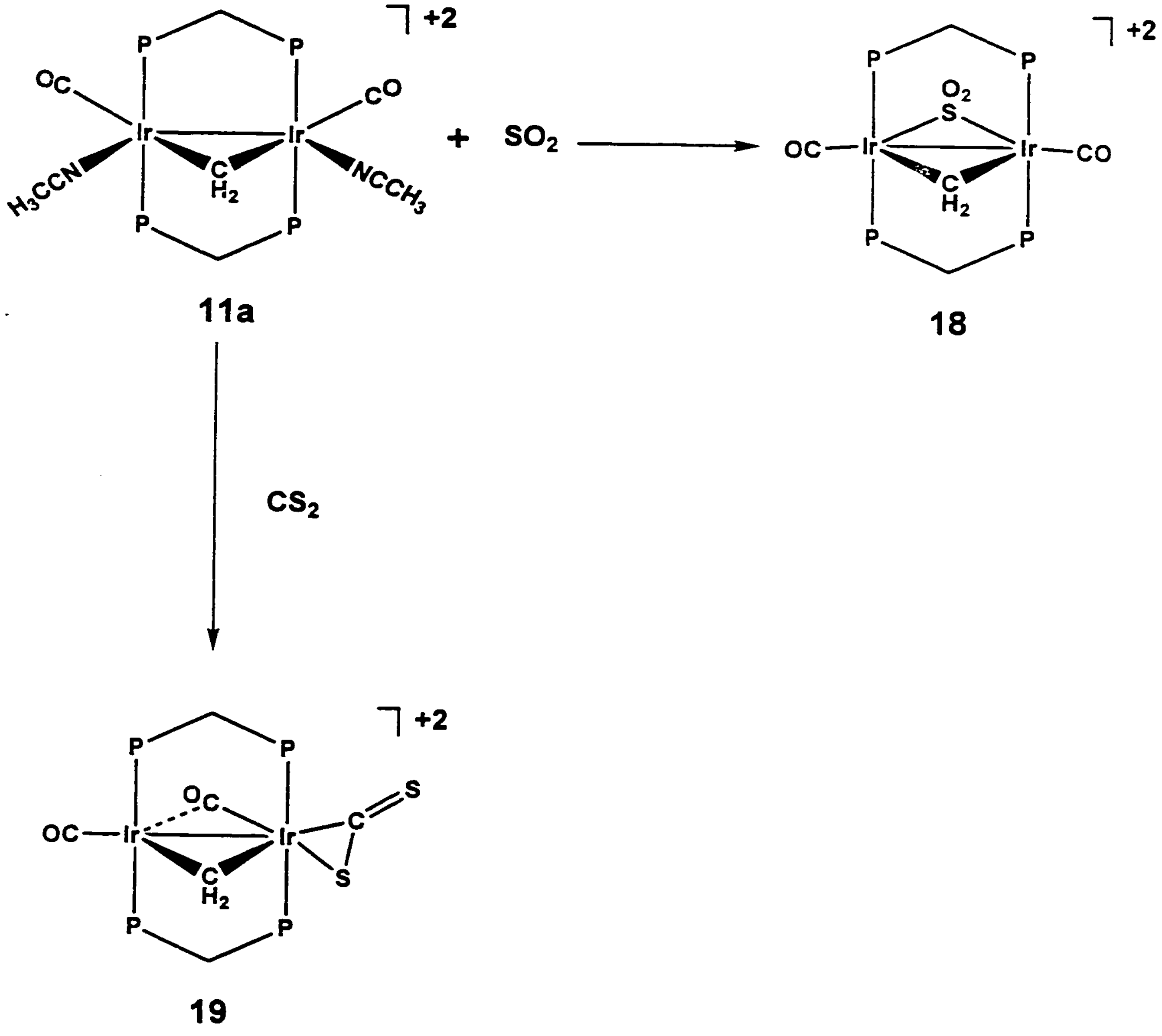
16

17

carbonyl stretch at 1960 cm^{-1} indicating the presence of terminally bound carbonyl ligands. Also in the IR spectrum, the peak at 1632 cm^{-1} is assigned to the C≡C stretches of the coordinated acetylene. This is within the range of 1530-1642 cm^{-1} observed in closely related dppm-bridged binuclear complexes in which the alkyne bridges the two metals parallel to the metal-metal axis.[18] The $^{31}P\{^1H\}$ NMR spectrum of compound **17** shows a singlet at δ -12.5 while the ^1H NMR spectrum shows the vinylidene proton resonances as a singlet at δ 7.92 indicating no observable coupling to the phosphines. The bridging methylene protons appear as a quintet ($^3J_{P\text{-}H}$ = 7.2 Hz) at δ 3.14. The IR spectrum shows a single broad stretch of the carbonyls at 2024 cm^{-1} indicating terminal coordination. The NMR data for the alkyne-bridged compound **16** and the vinylidene-bridged compound **17** are in close agreement with those of another alkyne-bridged and vinylidene-bridged mixture that was previously characterised in this research group.[18]

Reaction of compound **11a** with SO_2 produces an SO_2-bridged adduct $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}SO_2)(dppm)_2][BF_4]_2$ **(18)** as shown in Scheme 3.4. The $^{31}P\{^1H\}$ NMR spectrum of compound **18** shows a singlet at δ 5.0 indicating the equivalence of the four phosphorus nuclei and the ^1H NMR spectrum shows the bridging methylene group as a quintet ($^3J_{P\text{-}H}$ = 8 Hz) at δ 6.60. The dppm methylenes appear as multiplets at δ 5.62 and 4.48. In the $^{13}C\{^1H\}$ NMR spectrum, the carbonyls appear as a triplet signal at δ 172.4, while the IR

Scheme 3.4


+2
P
P
OC
CO
Ir
Ir
H3CCN
C
H2
NCCH3
+ SO2
OC
Ir
S
O2
Ir
CO
11a
18
CS2
OC
Ir
Ir
C
S
19

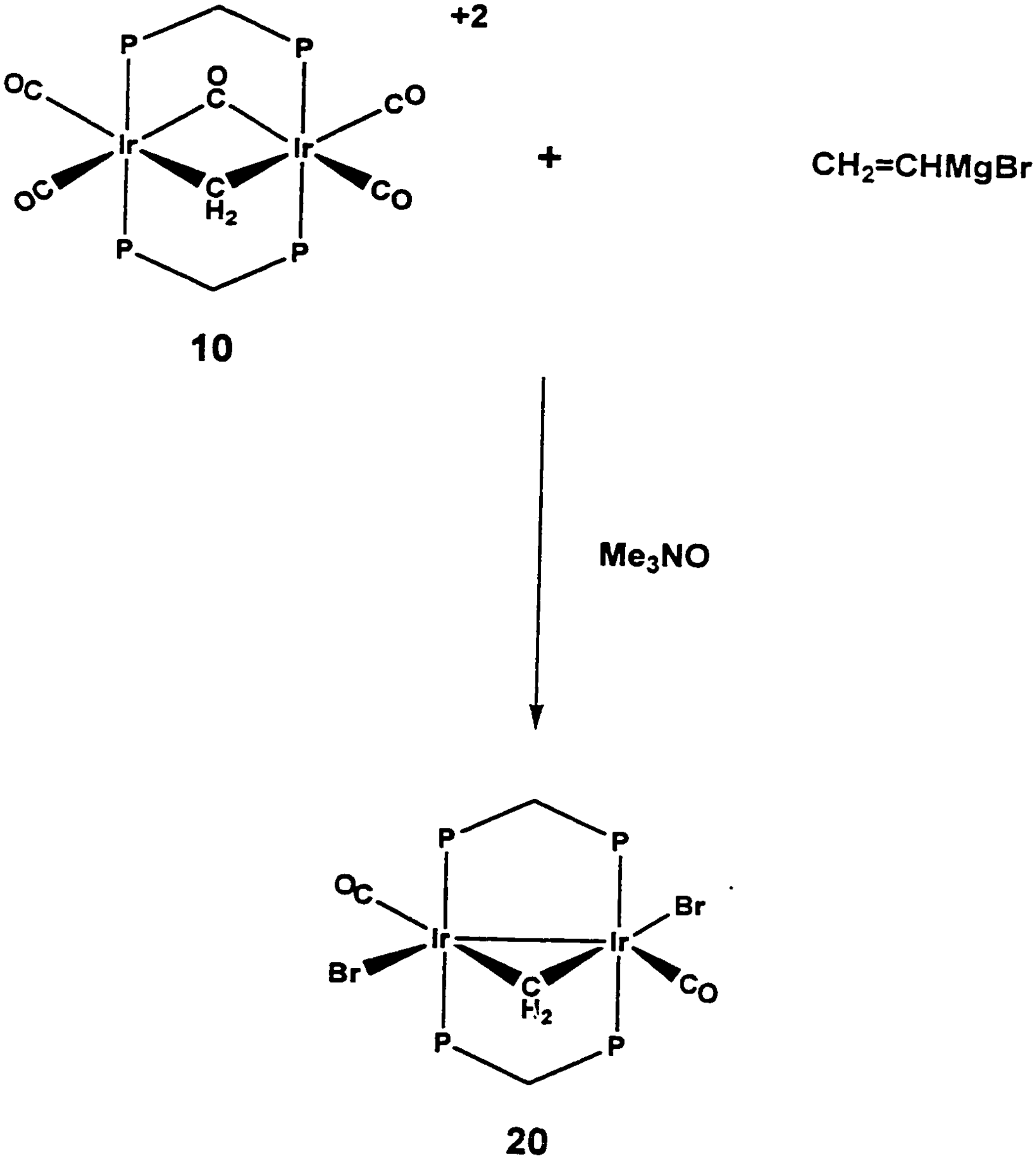
spectrum shows CO stretches at 2025 and 1996 cm^{-1} indicating two terminally bound carbonyl ligands in compound **18**. The asymmetric and symmetric S-O stretches of the bridging SO_2 group appear at 1150 and 1029 cm^{-1} respectively. Although the spectroscopic data do not unambigously establish the binding mode of the SO_2 ligand, a bridging mode is proposed based on this favored mode of coordination as previously observed in several related binuclear SO_2 adducts[20] including one that was recently characterized by X-ray crystallography in our lab.[17] The low S-O stretches are supportive of the SO_2-bridged structure for compound **18**. The behavior of compound **11a** in its reaction with SO_2 is similar to that observed for the complex $[Ir_2(H)(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$[18] and $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$,[17] in that it does not lead to insertion of the SO_2 ligand into the M-C (methylene or alkyl) bond.

Carbon disulfide (CS_2) is known to undergo a wide range of reactions with polynuclear complexes of transition metals; it can act as a terminal or a bridging ligand,[28] it can undergo carbon-sulphur bond cleavage or insertion reactions into M-C bonds.[5a,29,30] CS_2 can also undergo self condensation reactions in which two or three of these units can combine.[25,32,33] Compound **11a** reacts with only one equivalent of CS_2 to give a CS_2 adduct $[Ir_2(CO)(\eta^2\text{-}CS_2)(\mu\text{-}CH_2)(\mu\text{-}CO)(dppm)_2][BF_4]_2$ **(19)** in which one CS_2 has coordinated to one of the iridium center as shown in Scheme 3.4. Even in the presence of a large excess of CS_2 no further reaction was observed. The $^{31}P\{^1H\}$ NMR spectrum of compound **19** shows two multiplets at δ -8.7 and -18.9. The ^1H NMR spectrum shows the bridging methylene group as a multiplet at δ 4.74 and the dppm methylenes as multiplet signals at δ 3.76 and 3.52 whereas the $^{13}C\{^{1}H\}$ NMR spectrum shows two carbonyl signals at δ 193.6 and 164.3. The low-field resonance at δ 193.6 is suggestive of a semi-bridging carbonyl and this is supported by the IR absorption at 1805cm^{-1}. The high-field signal, a triplet at δ 164.3 ($^{2}J_{P\text{-}C}$ = 7.8 Hz), is consistent with a terminally bound carbonyl that is coupled to two adjacent ^{31}P nuclei. No ^{13}C NMR signal was observed for the CS_2 ligand in the absence of $^{13}CS_2$. However, the presence of a bridging methylene and a bridging CO implies that the CS_2 has to be terminally bound to one iridium as illustrated in Scheme 3.4. This coordination mode for the CS_2 is similar to that one observed in the reaction of the phenylacetylide-bridged complex $[RhIr(CO)_2(\mu\text{-}CCPh)(dppm)_2][BF_4]$ with CS_2.[25]

The reaction of the pentacarbonyl compound $[Ir_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CO)\text{-}(dppm)_2][BF_4]_2$ (**10**) with vinylmagnesium bromide was carried out in attempts to generate a compound containing the vinyl group. It would then be of interest to observe C-C bond formation between the vinyl group and the methylene group as had been observed by Maitlis in the reaction of $[(C_5Me_5)Rh(\mu\text{-}CH_2)(CH{=}CH_2)]_2$ with HCl to give $[(C_5Me_5)Rh(\eta^3\text{-}C_3H_5)Cl]$,[19] or as Maitlis has proposed occurs in the Fischer-Tropsch process to give an η^1-allyl.[9] However, the reaction of compound **10** with vinylmagnesium bromide in presence of Me_3NO resulted in the formation of a dibromide species $[Ir_2(Br)_2(CO)_2(\mu\text{-}$

$CH_2)(dppm)_2]$ **(20)** as shown in Scheme 3.5. No species incorporating the vinyl group was observed and no coupling occurred with the bridging methylene group. This result was disappointing in that it was anticipated that the vinyl groups would transfer to the metal instead of the bromides. Compound **20** has two multiplets on the $^{31}P\{^1H\}$ NMR spectrum at -11.6 and -23.4. The bridging methylene protons appear as a triplet of triplets at δ 6.53. Selective ^{31}P decoupling experiments show coupling to phosphorus of 9.7 and 6.5 Hz. The dppm methylene hydrogens appear as multiplets at δ 5.34 and 4.42. The $^{13}C\{^1H\}$ NMR spectrum shows two triplets at δ 184.5 ($^2J_{P\text{-}C}$ = 14.5 Hz) and δ 179.8 ($^2J_{P\text{-}C}$ = 12.8 Hz). The anti orientation of the bromides on the adjacent metals is responsible for the two sets of inequivalent phosphine environments, the chemical shifts of which are very close to those described for the anti isomer of the diiodo methylene-bridged compound $[Ir_2(I)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ **(9)** that has been previously characterized.[14] The carbonyl stretches of 2058 and 1995 cm^{-1} indicate that there are two terminally bound carbonyls. The structure of compound **20** was confirmed by a single crystal X-ray structure determination, a representation of which is shown in Figure 3.2, with the interatomic distances given in Table 3.4 and angles given in Table 3.5. Figure 3.2 clearly shows the anti orientation of the carbonyls and the bromides on the two metals while the methylene group almost symmetrically bridges the two metals with Ir(1)-C(3) bond length of 2.198(6)Å, Ir(2)-C(3) 2.180(6)Å and

Scheme 3.5



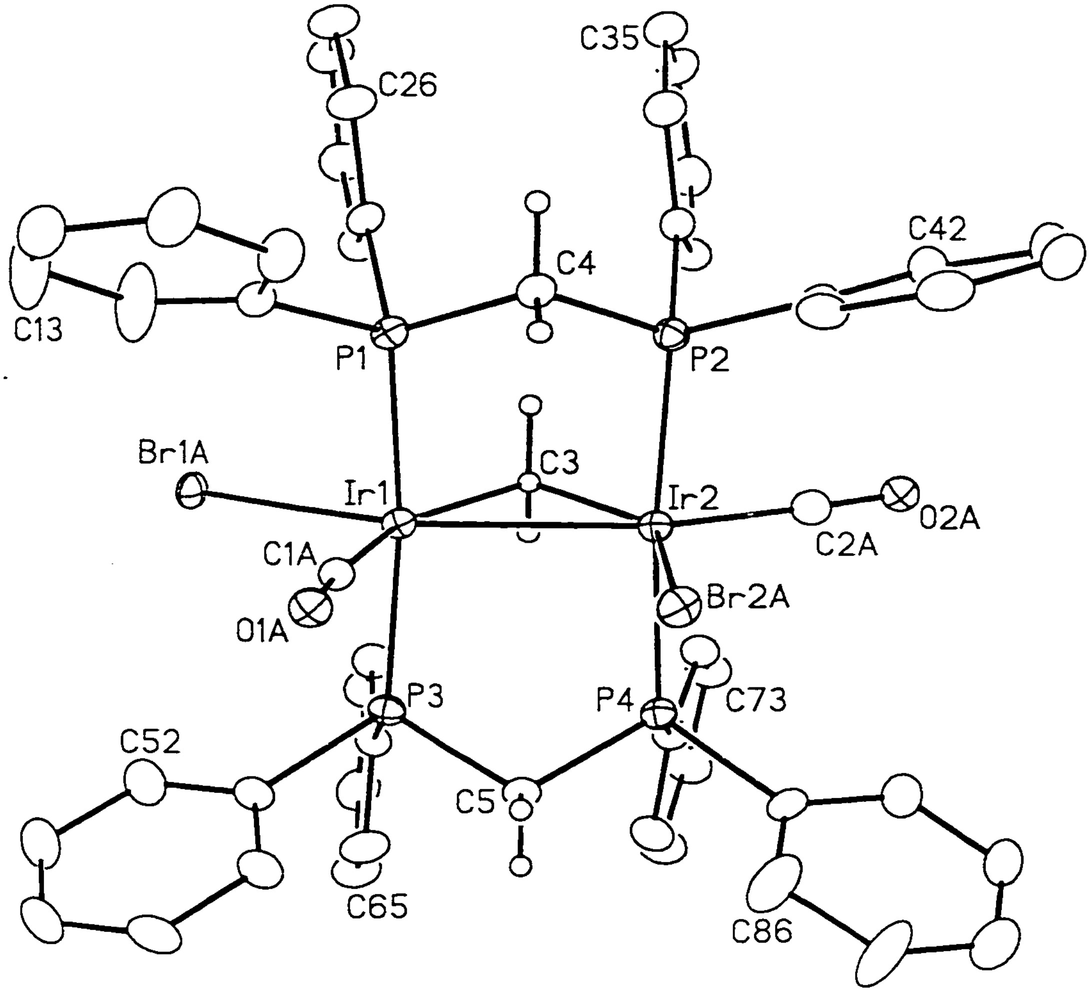


Figure 3.2 **Perspective view of the $[Ir_2Br_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms of the methylene groups are shown with arbitrarily small thermal parameters; dppm phenyl hydrogens are not shown.**

Table 3.4. Interatomic Distances (Å) for Compound 20

(a) involving 'inner-core' atoms

Atom1	Atom2	Distance
Ir(1)	Ir(2)	2.7706(4)
Ir(1)	Br(1A)	2.6773(12)
Ir(1)	Br(1B)	2.646(2)
Ir(1)	P(1)	2.3367(19)
Ir(1)	P(3)	2.3341(19)
Ir(1)	C(1A)	1.85†
Ir(1)	C(1B)	1.85†
Ir(1)	C(3)	2.198(6)
Ir(2)	Br(2A)	2.6204(13)
Ir(2)	Br(2B)	2.737(2)
Ir(2)	P(2)	2.3304(19)
Ir(2)	P(4)	2.3269(19)
Ir(2)	C(2A)	1.85†
Ir(2)	C(2B)	1.85†
Ir(2)	C(3)	2.180(6)
P(1)	C(4)	1.835(7)
P(2)	C(4)	1.816(7)
P(3)	C(5)	1.825(7)
P(4)	C(5)	1.822(7)
O(1A)	C(1A)	1.15†
O(2A)	C(2A)	1.15†
O(1B)	C(1B)	1.15†
O(2B)	C(2B)	1.15†

†Distance fixed during refinement.

(b) involving dppm phenyl carbons

Atom1	Atom2	Distance
P(1)	C(11)	1.838(7)
P(1)	C(21)	1.831(7)
P(2)	C(31)	1.835(8)
P(2)	C(41)	1.831(8)
P(3)	C(51)	1.826(8)
P(3)	C(61)	1.828(7)
P(4)	C(71)	1.820(7)
P(4)	C(81)	1.839(8)
C(11)	C(12)	1.331(11)
C(11)	C(16)	1.376(11)
C(12)	C(13)	1.379(13)
C(13)	C(14)	1.315(13)
C(14)	C(15)	1.379(13)
C(15)	C(16)	1.398(12)
C(21)	C(22)	1.388(10)
C(21)	C(26)	1.398(10)
C(22)	C(23)	1.387(10)
C(23)	C(24)	1.371(11)
C(24)	C(25)	1.383(12)
C(25)	C(26)	1.381(11)
C(31)	C(32)	1.398(10)
C(31)	C(36)	1.381(10)
C(32)	C(33)	1.382(11)
C(33)	C(34)	1.384(12)
C(34)	C(35)	1.361(12)
C(35)	C(36)	1.392(11)
C(41)	C(42)	1.405(11)
C(41)	C(46)	1.370(11)
C(42)	C(43)	1.404(13)
C(43)	C(44)	1.366(16)
C(44)	C(45)	1.389(15)
C(45)	C(46)	1.381(11)
C(51)	C(52)	1.373(11)
C(51)	C(56)	1.391(10)
C(52)	C(53)	1.377(12)
C(53)	C(54)	1.371(14)
C(54)	C(55)	1.372(13)
C(55)	C(56)	1.385(10)
C(61)	C(62)	1.402(10)
C(61)	C(66)	1.388(10)
C(62)	C(63)	1.377(10)
C(63)	C(64)	1.383(11)
C(64)	C(65)	1.385(12)
C(65)	C(66)	1.399(10)
C(71)	C(72)	1.389(10)
C(71)	C(76)	1.383(10)

Table 3.4. Interatomic Distances for Compound 20 (continued)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C(72)	C(73)	1.380(11)	C(81)	C(86)	1.341(13)
C(73)	C(74)	1.363(11)	C(82)	C(83)	1.382(14)
C(74)	C(75)	1.360(12)	C(83)	C(84)	1.368(15)
C(75)	C(76)	1.384(11)	C(84)	C(85)	1.320(14)
C(81)	C(82)	1.366(12)	C(85)	C(86)	1.403(13)

(c) within the (disordered) solvent dichloromethane molecule

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Cl(1S)	C(1S)	1.80(3)	Cl(3S)	C(2S)	1.76(3)
Cl(2S)	C(1S)	1.63(3)	Cl(4S)	C(2S)	1.58(3)

(d) within the solvent diethyl ether molecule

Atom1	Atom2	Distance	Atom1	Atom2	Distance
O(10S)	C(11S)	1.395(15)	C(11S)	C(12S)	1.554(18)
O(10S)	C(13S)	1.323(19)	C(13S)	C(14S)	1.57(3)

Table 3.5 Interatomic Angles (deg) for Compound 20

(a) involving 'inner-core' atoms

Atom1	Atom2	Atom3	Angle
Ir(2)	Ir(1)	Br(1A)	151.39(4)
Ir(2)	Ir(1)	Br(1B)	93.59(6)
Ir(2)	Ir(1)	P(1)	92.48(5)
Ir(2)	Ir(1)	P(3)	93.18(5)
Ir(2)	Ir(1)	C(1A)	106.4(2)
Ir(2)	Ir(1)	C(1B)	153.4(4)
Ir(2)	Ir(1)	C(3)	50.46(15)
Br(1A)	Ir(1)	P(1)	89.99(5)
Br(1A)	Ir(1)	P(3)	86.79(5)
Br(1A)	Ir(1)	C(1A)	102.2(2)
Br(1A)	Ir(1)	C(3)	100.93(9)
Br(1B)	Ir(1)	P(1)	86.31(7)
Br(1B)	Ir(1)	P(3)	89.69(7)
Br(1B)	Ir(1)	C(1B)	113.0(4)
Br(1B)	Ir(1)	C(3)	144.05(9)
P(1)	Ir(1)	P(3)	173.26(6)
P(1)	Ir(1)	C(1A)	86.2(3)
P(1)	Ir(1)	C(1B)	90.0(5)
P(1)	Ir(1)	C(3)	94.37(15)
P(3)	Ir(1)	C(1A)	88.7(3)
P(3)	Ir(1)	C(1B)	86.6(5)
P(3)	Ir(1)	C(3)	92.05(15)
C(1A)	Ir(1)	C(1B)	100.2(4)
C(1A)	Ir(1)	C(3)	156.9(3)
C(1B)	Ir(1)	C(3)	102.9(4)
Ir(1)	Ir(2)	Br(2A)	93.50(3)
Ir(1)	Ir(2)	Br(2B)	155.11(9)
Ir(1)	Ir(2)	P(2)	92.84(5)
Ir(1)	Ir(2)	P(4)	92.25(5)
Ir(1)	Ir(2)	C(2A)	156.8(3)
Ir(1)	Ir(2)	C(2B)	106.2(3)
Ir(1)	Ir(2)	C(3)	51.04(15)
Br(2A)	Ir(2)	P(2)	90.57(6)
Br(2A)	Ir(2)	P(4)	87.35(5)
Br(2A)	Ir(2)	C(2A)	109.7(3)
Br(2A)	Ir(2)	C(3)	144.50(9)
Br(2B)	Ir(2)	P(2)	86.23(7)
Br(2B)	Ir(2)	P(4)	89.90(7)
Br(2B)	Ir(2)	C(2B)	98.7(3)
Br(2B)	Ir(2)	C(3)	104.12(9)
P(2)	Ir(2)	P(4)	174.61(7)
P(2)	Ir(2)	C(2A)	87.3(3)
P(2)	Ir(2)	C(2B)	89.7(6)
P(2)	Ir(2)	C(3)	92.60(16)
P(4)	Ir(2)	C(2A)	88.7(3)
P(4)	Ir(2)	C(2B)	87.2(7)
P(4)	Ir(2)	C(3)	91.98(16)
C(2A)	Ir(2)	C(2B)	97.1(4)
C(2A)	Ir(2)	C(3)	105.7(3)
C(2B)	Ir(2)	C(3)	157.2(3)
Ir(1)	P(1)	C(4)	111.4(2)
Ir(2)	P(2)	C(4)	110.5(2)
Ir(1)	P(3)	C(5)	110.0(2)
Ir(2)	P(4)	C(5)	111.4(2)
Ir(1)	C(3)	Ir(2)	78.5(2)
P(1)	C(4)	P(2)	109.9(4)
P(3)	C(5)	P(4)	110.2(4)

(b) involving dppm phenyl carbons

Atom1	Atom2	Atom3	Angle
Ir(1)	P(1)	C(11)	115.2(2)
Ir(1)	P(1)	C(21)	119.6(2)
C(4)	P(1)	C(11)	102.1(3)
C(4)	P(1)	C(21)	105.7(3)
C(11)	P(1)	C(21)	100.8(3)
Ir(2)	P(2)	C(31)	119.8(3)
Ir(2)	P(2)	C(41)	113.7(3)
C(4)	P(2)	C(31)	104.3(3)
C(4)	P(2)	C(41)	103.9(3)
C(31)	P(2)	C(41)	103.0(4)
Ir(1)	P(3)	C(51)	113.7(3)
Ir(1)	P(3)	C(61)	123.1(2)
C(5)	P(3)	C(51)	103.7(3)
C(5)	P(3)	C(61)	103.8(3)

Table 3.5. Interatomic Angles for Compound 20 (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(51)	P(3)	C(61)	100.4(3)	C(43)	C(44)	C(45)	119.5(9)
Ir(2)	P(4)	C(71)	118.2(2)	C(44)	C(45)	C(46)	120.5(10)
Ir(2)	P(4)	C(81)	115.3(2)	C(41)	C(46)	C(45)	120.7(10)
C(5)	P(4)	C(71)	105.4(3)	P(3)	C(51)	C(52)	119.5(6)
C(5)	P(4)	C(81)	102.9(3)	P(3)	C(51)	C(56)	122.5(6)
C(71)	P(4)	C(81)	102.0(4)	C(52)	C(51)	C(56)	117.9(8)
P(1)	C(11)	C(12)	120.9(6)	C(51)	C(52)	C(53)	121.5(9)
P(1)	C(11)	C(16)	121.2(6)	C(52)	C(53)	C(54)	119.9(10)
C(12)	C(11)	C(16)	117.6(8)	C(53)	C(54)	C(55)	120.1(9)
C(11)	C(12)	C(13)	122.0(9)	C(54)	C(55)	C(56)	119.5(9)
C(12)	C(13)	C(14)	121.4(10)	C(51)	C(56)	C(55)	121.1(9)
C(13)	C(14)	C(15)	118.9(9)	P(3)	C(61)	C(62)	122.9(6)
C(14)	C(15)	C(16)	119.1(9)	P(3)	C(61)	C(66)	119.0(6)
C(11)	C(16)	C(15)	120.6(9)	C(62)	C(61)	C(66)	118.1(7)
P(1)	C(21)	C(22)	121.9(6)	C(61)	C(62)	C(63)	120.7(8)
P(1)	C(21)	C(26)	119.6(6)	C(62)	C(63)	C(64)	120.5(8)
C(22)	C(21)	C(26)	118.5(7)	C(63)	C(64)	C(65)	120.3(8)
C(21)	C(22)	C(23)	120.6(7)	C(64)	C(65)	C(66)	119.0(8)
C(22)	C(23)	C(24)	120.4(8)	C(61)	C(66)	C(65)	121.5(8)
C(23)	C(24)	C(25)	119.7(8)	P(4)	C(71)	C(72)	121.4(6)
C(24)	C(25)	C(26)	120.4(8)	P(4)	C(71)	C(76)	120.8(6)
C(21)	C(26)	C(25)	120.4(8)	C(72)	C(71)	C(76)	117.8(7)
P(2)	C(31)	C(32)	121.3(6)	C(71)	C(72)	C(73)	120.4(7)
P(2)	C(31)	C(36)	119.5(6)	C(72)	C(73)	C(74)	120.9(8)
C(32)	C(31)	C(36)	119.3(7)	C(73)	C(74)	C(75)	119.5(8)
C(31)	C(32)	C(33)	119.6(8)	C(74)	C(75)	C(76)	120.4(8)
C(32)	C(33)	C(34)	119.8(8)	C(71)	C(76)	C(75)	120.9(8)
C(33)	C(34)	C(35)	121.5(8)	P(4)	C(81)	C(82)	120.0(7)
C(34)	C(35)	C(36)	118.8(8)	P(4)	C(81)	C(86)	122.5(7)
C(31)	C(36)	C(35)	121.0(8)	C(82)	C(81)	C(86)	117.5(9)
P(2)	C(41)	C(42)	117.7(7)	C(81)	C(82)	C(83)	121.9(10)
P(2)	C(41)	C(46)	122.8(7)	C(82)	C(83)	C(84)	119.6(10)
C(42)	C(41)	C(46)	119.4(8)	C(83)	C(84)	C(85)	118.7(11)
C(41)	C(42)	C(43)	119.2(10)	C(84)	C(85)	C(86)	121.8(12)
C(42)	C(43)	C(44)	120.6(11)	C(81)	C(86)	C(85)	120.5(11)

(c) within the (disordered) solvent dichloromethane molecule

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl(1S)	C(1S)	Cl(2S)	114.7(18)	Cl(3S)	C(2S)	Cl(4S)	111(2)

Table 3.5. Interatomic Angles for Compound 20 (continued)

(d) within the solvent diethyl ether molecule

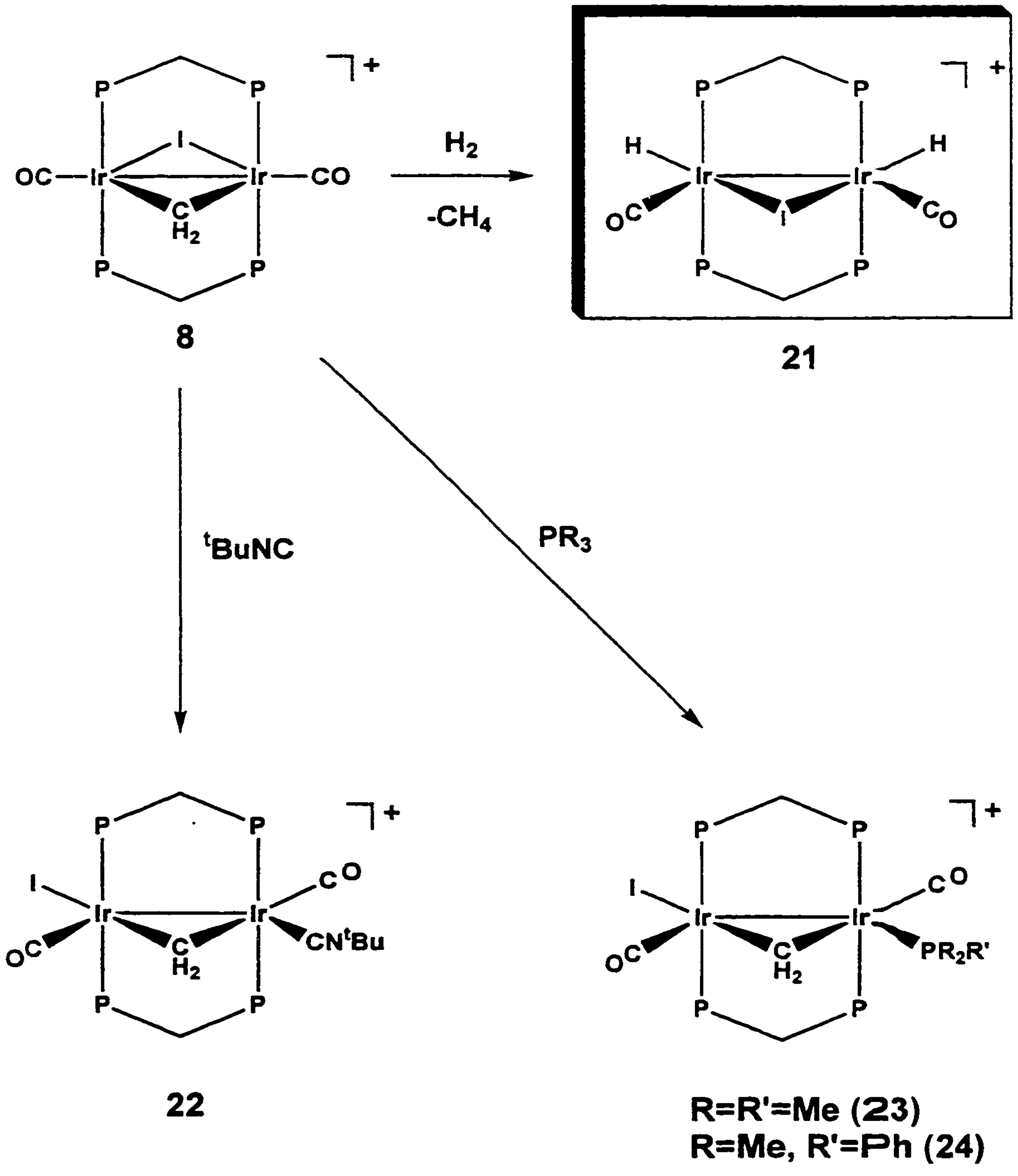
Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(11S)	O(10S)	C(13S)	127.7(15)	O(10S)	C(13S)	C(14S)	113.1(17)
O(10S)	C(11S)	C(12S)	108.3(13)				

Ir(1)-C(3)-Ir(2) bond angle of 78.5(2)°. The Ir(1)-Ir(2) bond distance of 2.7706(4)Å is consistent with the presence of a metal-metal bond for compound **20** and the Ir(1)-C(3) and Ir(2)-C(3) bond distances of 2.198(6) and 2.180(6)Å respectively are all closely comparable to those of other structurally characterized $Ir_2(\mu\text{-}CH_2)$[26] and other[7a,b] binuclear methylene-bridged complexes that contain metal-metal bonds.

The reactivity of $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ **(8)** was also investigated. In compound **11a** the vacant site for substrate attack is assumed to result from loss of the labile $NCCH_3$ ligand whereas in compound **10** coordinative unsaturation was achieved by abstracting the coordinated carbonyls with Me_3NO. In compound **8**, coordinative unsaturation can result from the movement of the bridging iodide ligand to a terminal position on one metal, creating unsaturation at the adjacent metal. Compound **8** reacts with dihydrogen in an NMR tube to give the previously described iodo dihydride $[Ir_2(H)_2(CO)_2(\mu\text{-}I)(dppm)_2][CF_3SO_3]$ **(21)**[31] and methane as illustrated in Scheme 3.6. This represents another interesting hydrogenolysis reaction of a methylene-bridged diiridium complex that occurs at room temperature and pressure.

Reaction of compound **8** with one equivalent of ^tBuNC results in the formation of the adduct $[Ir_2(I)(CO)_2(^tBuNC)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ **(22)** in which the ^tBuNC is terminally bound to iridium, as shown in Scheme 3.6. The $^{31}P\{^1H\}$ NMR spectrum shows two multiplets at δ -15.8 and -19.2 consistent

Scheme 3.6



Boxed Compound has been Previuosly Characterised with an unsymmetrical species. The ^{1}H NMR spectrum of compound **22** shows the resonances for the t-butyl group protons as a singlet at δ 1.03 as well as three multiplets at δ 6.62, 6.22 and 4.67. Selective $^1H\{^{31}P\}$ decoupling experiments established that the multiplet at δ 6.62 is a triplet of triplets ($^3J_{P\text{-}H}$ = 3.5, 2.9 Hz) corresponding to the methylene group bridging the two metals, while the other two are those of the dppm methylene ligands. The $^{13}C\{^1H\}$ NMR spectrum shows two broad signals at δ 172.1 and 165.2 indicating two carbonyls and the IR spectrum shows the CO stretches at 2023 and 1970 cm^{-1} confirming that they are terminally bound to the metals. There is also a characteristic C≡N stretch at 2171 cm^{-1} which is consistent with a terminally bound isocyanide ligand. The increase in frequency of the C≡N stretch in compound **22** compared to the value of 2130 cm^{-1} observed in free ^{t}BuNC, is consistent with strong RNC→Ir σ donation and very little Ir→CNR π backdonation[31] consistent with the cationic charge of the complex.

Compound **8** also reacts with phosphines to give the phosphine adducts. Reaction with PMe_3 at ambient temperature results in formation of $[Ir_2(I)(CO)_2(PMe_3)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ **(23)** and the structurally analogous product $[Ir_2(I)(CO)_2(\mu\text{-}CH_2)(PMe_2Ph)(dppm)_2]$ $[CF_3SO_3]$ **(24)** was also obtained by addition of PMe_2Ph. Both phosphine adducts are spectroscopically similar and are assigned the structures shown in Scheme 3.6. No reaction was observed with PPh_3 even after prolonged reaction times; presumably the approach of this bulky substrate is sterically hindered by interaction with the phenyl groups of the dppm ligands. Compound **23** $[Ir_2(I)(CO)_2(PMe_3)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$, has three signals in the $^{31}P\{^1H\}$ NMR spectrum at δ -16.6, -17.6 that are multiplets and a triplet signal at δ -78.6 ($^2J_{P\text{-}P}$ = 17.7 HZ) in a ratio 2:2:1 respectively. The first two multiplets can be attributed to the dppm phosphines and the broad signal as due to the PMe_3 group in a pattern that is consistent with an AA'BB'M spin system. The ^1H NMR spectrum shows three multiplets at δ 6.67, 6.54, 4.62 and a doublet at δ 0.83. $^1H\{^{31}P\}$ NMR experiments with ^{31}P broadband decoupling indicates that the multiplet at δ 6.54 is due to the bridging methylene while the other two multiplets are those of the dppm methylene protons. The doublet at δ 0.83 ($^2J_{P\text{-}H}$ = 20.4 Hz) is due to the PMe_3 methyl protons. The $^{13}C\{^1H\}$ NMR spectrum shows a triplet at δ 169.8 ($^2J_{P\text{-}C}$ = 15.1 Hz) and a broad resonance of equal intensity at δ 168.6 indicating two CO ligands that are terminally bound. The CO stretches at 1962 and 1991 cm^{-1} in the IR spectrum confirms the terminal coordination mode of the carbonyls thus precluding any bridging interaction. Compound **23** has similar spectroscopic parameters to those of compound **24** indicating that they have similar structures as shown in Scheme 3.6. As summarized in Table 3.1 the IR, and the ^{31}P, ^1H, and ^{13}C NMR spectroscopic parameters for compounds **23** and **24** are very comparable to those of compound **22** which is not surprising considering all added groups are neutral electron pair donors.

Discussion

Iodomethyl methylether oxidatively adds to $[Ir_2(CO)_3(dppm)_2]$ accompanied by loss of a carbonyl to give the methoxymethyl compound $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(2)**.[14] Compound **2** reacts with electrophiles that have both coordinating and non-coordinating anions. Reaction with methyl triflate results in iodide removal as methyl iodide and a double C-H activation of the methoxymethyl ligand to give the methoxycarbyne-bridged product $[Ir_2(CO)_2(H)_2(\mu\text{-}COCH_3)(dppm)_2][CF_3SO_3]$ as shown in Scheme 2.2. Reaction with trimethylsilyltriflate ($Me_3SiOSO_2CF_3$) produces the methylene- and iodo-bridged compound $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ **(8)** by removal of the methoxy group. Addition of trimethylsilyliodide to compound **2** produces the syn and anti isomers of a methylene-bridged, diiodide species $[Ir_2(I)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ **(9)**. Carbon-Carbon bond formation in the Fischer-Tropsch process involves surface methylene groups and it was therefore of interest for us to synthesize complexes containing bridging methylene groups as models for these surface-bound methylene groups. Reaction of **9** with two equivalents of $AgBF_4$ in the presence of CO produces the dicationic, methylene-bridged pentacarbonyl complex $[Ir_2(CO)_4(\mu\text{-}CO)(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ **(10)**. One carbonyl in complex **10** is very labile therefore loss of the bridging carbonyl is accompanied by formation of a metal-metal bond. Attempts to remove the iodo ligand from compound **9** with silver salts were not reproducible, and gave rise to mixtures of products that were difficult to characterize. All attempts to abstract iodides from complex **9** by using electrophiles in the absence of CO resulted in the loss of only one halide ion, generating $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2]^+$ **(8)**.

Reaction of compound **10** with Me_3NO in acetonitrile results in loss of three carbonyls ligands and generation of *cis*-$[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ **(11a)**. The acetonitrile ligand are labile and are easily substituted. Reaction of the cis isomer **11a** with CO regenerates complex **10**, further illustrating the facile displacement of the $NCCH_3$ ligands. The cis isomer in solution, transforms into the anti isomer **11b** in 3 days. The anti isomer **11b** is presumably more thermodynamically stable due to the less steric interactions between the acetonitrile ligand and the dppm phenyl groups. Isomer **11b** is spontanoeusly formed when complex **10** is dissolved in acetonitrile.

All attempts to form a carbon-carbon bond between the bridging methylene group of compounds **8** and **11a** with diazomethane, alkynes, allenes and olefins were unsuccessful. For each of these substrates no reaction with the bridging methylene complex was observed. The complexes are sufficiently inert that not even ligand substitution was observed. It is proposed that the dicationic nature of the complexes taken together with the presence of carbonyls ligands in the complexes effectively limits the metal electron density available for bonding with the substrates and also diminishes the electron density on the bridging methylene group. The result is that no substrate attack occurs on the metal. A typical C-C bond formation reaction of electrophilic bridging methylene complexes with diazoalkanes is the migratory insertion of an η^1-alkylidene intermediate into one of the two metal-CH_2 bonds. However, an η^1-alkylidene intermediate is perhaps not formed due to the low electron density on the iridium which does not allow back donation of electrons into the vacant p orbital of the η^1-CH_2 fragment. Also, it is most likely that the strong metal-CH_2 bond inhibits migratory insertion of a substrate.

The reactions of complexes **8** and **11a** with dihydrogen results in hydrogenolysis of the bridging methylene group to produce methane and the tetrahydride $[Ir_2(H)_2(CO)_2(\mu\text{-}H)_2(dppm)_2][BF_4]_2$ **(14)** for compound **11a** and $[Ir_2(H)_2(CO)_2(\mu\text{-}I)(dppm)_2][CF_3SO_3]$ **(21)** for compound **8**. Unlike other hydrogenolysis reactions involving bridging methylene groups these reactions occurred under very mild conditions of room temperature and pressure. In the case of **11a** a methyl intermediate $[Ir_2(H)(CH_3)(CO)_2(\mu\text{-}H)_2(dppm)_2][BF_4]_2$ **(13)** was observed at -20°C which upon warming lost methane illustrating a very facile hydrogenolysis. The lability of the NCMe ligands in **11a** was demonstrated in the reactions of complex **11a** with $HC{\equiv}CH$, SO_2, and CS_2. Each reaction resulting in displacement of the acetonitrile ligand with these substrates and leaving the bridging methylene group intact.

The reaction with acetylene gives the alkyne-bridged product $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}\eta^1{:}\eta^1\text{-}HC{\equiv}CH)(dppm)_2][BF_4]_2$ **(16)** and the vinylidene-bridged $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}C{=}CH_2)(dppm)_2][BF_4]_2$ **(17)** product in the ratio 5:1. Compound **16** has the acetylene ligand bound in a bridging arrangement parallel to the Ir-Ir bond as is commonly observed. Compound **17** has resulted from isomerization of the acetylene to a vinylidene group. Such isomerization are common in binuclear complexes.[18] It is not clear why the alkyne-bridged product **16** is favored over the vinylidene-bridged species, although it may be that the dicationic charge favors the simple alkyne adduct instead of the oxidative addition product (acetylide/hydride species) which is presumably a precursor to the vinylidene product.

Reaction of compound **11a** with SO_2 results in formation of an SO_2-bridged adduct $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}SO_2)(dppm)_2][BF_4]_2$ **(18)**. The SO_2 ligand bridges the iridium centers and this is not surprising since this is the coordination mode that has been observed in several binuclear SO_2 adducts in this research group.[17] Reaction with CS_2 affords a CS_2 adduct $[Ir_2(CO)_2(CS_2)(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ **(19)**, where the CS_2 becomes η^2-terminally bound to one iridium center presumably adjacent to the bridging methylene group. It was interesting that even in the presence of a huge amount of carbon-disulphide no self condensation of the CS_2 was observed or coupling to the bridging methylene group. The failure of the acetylene and SO_2 complexes to undergo subsequent coupling with the methylene group is understandable in terms of the position of these groups, which are on the opposite face of the complex from the methylene groups. However, the CS_2 and methylene groups in compound **19** appear reasonably placed for coupling although this was not observed.

Maitlis has suggested that a key step in the Fisher-Tropsch reaction is the migration of a vinyl group to a surface bound methylene. We therefore became interested in generating a vinyl-containing compound by reaction of $[Ir_2(CO)_4(\mu\text{-}CO)(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ **(9)** with vinylmagnesium bromide. However only the dibromo compound $[Ir_2(Br)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ **(20)**, which is the product of bromide transfer to iridium was obtained. This was unexpected but not surprising since similar behavior involving Grignard reagents have been observed before in this research group.

The reaction of $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ **(8)** with t-butyl isocyanide and phosphines resulted in substrate addition to give the respective adduct. For ^{t}BuNC no migratory insertion to the bridging methylene was observed.

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CHAPTER FOUR

Conclusions

The first objective of this thesis was to study the oxidative addition of alkyl halides to [$Ir_2(CO)_3(dppm)_2$]. Oxidative addition of methyl iodide was of interest considering that CH_3I is involved in the industrial conversion of methanol into acetic acid.[1-3] It was also important to investigate the oxidative addition of substituted methyl halides (XCH_2Y; X=halide, Y=substituent) as this was considered a useful route to complexes containing substituted methyl ligands. Previous studies in this research group had established that the methyl group in the complex [$Ir_2(CH_3)(CO)_2(dppm)_2$][CF_3SO_3] underwent facile, and sometimes reversible C-H bond activation upon addition of the substrate molecules CO, SO_2, CNR, PR_3 and we were interested in generating analogous compounds in which one or more of the methyl hydrogens were replaced by different substituents, to determine the tendencies of these substituted methyl groups to undergo C-H activation. A recent study has suggested that C-H activation is enhanced by electron-withdrawing groups.[7]

The second goal of this thesis was to synthesize some methylene-bridged diiridium compounds. The second step, after these alkylidene complexes had been synthesized, was to investigate and study their reactivities with small molecules in order to obtain information on their potential utility as models for some of the transformations involving methylene groups in catalysis. Of most interest was to model the C-C bond formation chemistry of surface-bound methylene groups known to occur in the Fischer-Tropsch process. Also of interest was the possible formation of C-heteroatom bonds involving the bridging methylene group.

The diiridium complex $[Ir_2(CO)_3(dppm)_2]$ reacts readily with CH_3I to give the targeted oxidative-addition product $[Ir_2(CH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ **(3)**. This product has the methyl group on one metal and the iodo ligand on the other, giving rise to Ir(+1)/Ir(+1) centers resulting from formal oxidation of both metals. Iodide abstraction from compound **3** using methyl triflate gives the known compound $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ thus providing an alternative synthetic route to this highly reactive species. It was interesting that iodide removal from compound **3** does not lead to C-H activation of the methyl group as had been observed in the methylene group of $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$, the oxidative addition product of iodomethyl methylether to $[Ir_2(CO)_3(dppm)_2]$. This demonstrates the ease of C-H bond activation on addition of electron-withdrawing groups as recently proposed.[7] Iodide (I^-) addition to $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ reforms compound **3**. This is an unexpected result considering the facile and reversible methyl C-H activation observed on addition of neutral substrates (CO, SO_2, CNR, PR_3, RC≡CR' (R, R'= Me, Et, Ph)) to this methyl compound.[4-5] To further study this C-H activation process, we sought to synthesize substituted methyl compounds by oxidative addition of substituted methyl bromides to $[Ir_2(CO)_3(dppm)_2]$. However, the addition of benzyl bromide, allyl bromide and bromoacetonitrile did not generate the targeted oxidative-addition products [$Ir_2(Br)(R)(CO)_2(dppm)_2$] (R= $CH_2C_6H_5$, CH_2CHCH_2, CH_2CN). Instead, in each case a hydrogen was abstracted from one dppm methylene group and a bromine atom added to the metals to give [$Ir_2(CO)_2(\mu$-Br)(μ-CO)-($Ph_2PCHPPh_2$)(dppm)] **(4)** and the respective organic fragments. Although toluene and acetonitrile were observed in their respective reactions of benzyl bromide and bromoacetonitrile, propene could not be observed due to the large amount of allyl bromide required to complete the reaction. The above reactivity behavior parallels that of CH_2I_2 and ICH_2CN that was previously observed,[8] except that the iodo compound [$Ir_2(CO)_2(\mu$-I)(μ-CO)($Ph_2PCHPPh_2$)-(dppm)] was observed in this case.

Another attempt to generate a chloro-substituted methyl group by replacement of the methoxy group in the compound [$Ir_2(CH_2OCH_3)(I)(CO)(\mu$-CO)$(dppm)_2$] **(2)** by chloride ion through a reaction with HCl met with failure. Only the methylene-bridged chloroiodo complex [$Ir_2(Cl)(I)(CO)_2(\mu$-$CH_2)(dppm)_2$] **(6)** was obtained. Other HX sources such as HCN and HF should be tested.

Attempts to prepare a series of methylene-bridged diiridium complexes by methoxide removal from the methoxymethyl complex **2** were successful. So reaction of complex **2** with MeSiI yielded [$Ir_2(I)_2(CO)_2(\mu$-$CH_2)(dppm)_2$] **(9)** which could be converted into cationic methylene-bridged complexes by iodide removal. The methylene-bridged diiridium complex [$Ir_2(CO)_4(\mu$-$CH_2)(\mu$-CO)$(dppm)_2$][BF_4]$_2$ **(10)** has been synthesized by reacting [$Ir_2(I)_2(CO)_2(\mu$-

$CH_2)(dppm)_2]$ **(9)** with $AgBF_4$ under CO, and subsequent reaction of compound **9** with Me_3NO in acetonitrile affords $[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ which can exist as syn **(11a)** and anti **(11b)** isomers. The syn isomer spontaneously transforms into the more thermodynamically stable anti isomer perhaps due to steric interactions between the acetonitrile and the dppm phenyl groups. The reactivities of the compounds **10** and **11a** and the previously characterised compound **8** with a selection of small molecules were investigated in order to probe the possibility of activating these molecules and formation of a C-C or C-heteroatom bond with the bridging methylene group. All attempts to form a C-C bond by reacting these complexes with diazomethane, Grignard reagents, substituted alkynes and alkyllithiums were not successful. However, the compounds showed some reactivities with H_2, acetylene, SO_2, CS_2, vinylmagnesium bromide, isocyanides and phosphines. Their reactivities with the small molecules can be grouped into the following categories:

(1) Incorporation of the new ligand with retention of the bridging methylene group. This occurred in the following reactions: reaction of complex **11a** with acetylene to give the alkyne-bridged $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}HC{\equiv}CH)\text{-}(dppm)_2][BF_4]_2$ **(16)** and the vinylidene-bridged $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}C{=}CH_2)\text{-}(dppm)_2][BF_4]_2$ **(17)**; reaction with SO_2 to give the SO_2 adduct $[Ir_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}SO_2)dppm)_2][BF_4]_2$ **(18)**; reaction with CS_2 to give the CS_2 adduct $[Ir_2(CO)_2(\mu\text{-}CH_2)(CS_2)dppm)_2][BF_4]_2$ **(19)**; and in the reaction of complex **8** with ^tBuNC, PR_3 to give the products $[Ir_2(I)(CO)_2(L)(\mu\text{-}CH_2)dppm)_2][CF_3SO_3]$ (L= ^tBuNC, PR_3).

(2) Substitution of a CO by a new ligand but with retention of the bridging methylene group as occurred in the reaction of compound **10** with vinyl magnesium bromide to give $[Ir_2(Br)_2(CO)_2(\mu\text{-}CH_2)(dppm)_2]$ **(20)**. In this reaction incorporation of the vinyl group into the product did not occur. Presumably, the bromo species is more favorable than the vinyl compound. Also substitution of carbonyls was observed in the reaction of compound **10** with $NCCH_3$ to yield anti-$[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CH_2)(dppm)_2][BF_4]_2$ **(11b)**.

(3) Oxidative addition of H_2 at the coordinatively unsaturated iridium center followed by conversion to a methyl hydride complex and eventual reductive elimination of methane as occurred in the reaction of compound **11a** and **8** with H_2. This reaction is a successful modeling of the hydrogenolysis of M-C bonds that occurs in the Fisher-Tropsch process.

Unfortunately, the targeted C-C bond formation involving the bridging methylene groups was not observed. Possibly insertion of substrates into the $Ir\text{-}CH_2$ bond is inhibited by the strength of the $Ir\text{-}CH_2$ bonds and certainly the location of some of the substituted ligands on the opposite face of the dimer from the bridging methylene group did not allow migration to occur.

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Appendix

Solvents and Drying Agents

Acetone	Calcium sulphate
Benzene	Sodium benzophenone ketyl
Dichloromethane	Phosphorus pentoxide
Diethyl ether	Sodium benzophenone ketyl
Pentanes	Sodium benzophenone ketyl
n-Hexanes	Sodium benzophenone ketyl
Methanol	Magnesium
Tetrahydrofuran	Sodium benzophenone ketyl
Acetonitrile	Calcium hydride