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University of Alberta

Binuclear Complexes of Rhodium and Iridium Bridged by Bis(diphenylphosphino)methane and 2-Mercaptothiazolinate Ligands

by

Jianliang Xiao

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

Department of Chemistry

Edmonton, Alberta
Spring, 1992

ISBN 0-315-73084-6

University of Alberta

Release Form

Name of Author: Jianliang Xiao

Title of Thesis: **Binuclear Complexes of Rhodium and Iridium Bridged by Bis(diphenylphosphino)methane and 2-Mercaptothiazolinate Ligands**

Degree: Doctor of Philosophy

Year this Degree Granted: 1992

(Signed)

Jianliang Xiao

Date: April 22 1992

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 **Binuclear Complexes of Rhodium and Iridium Bridged by Bis(diphenylphosphino)methane and 2-Mercaptothiazolinate Ligands** submitted by Jianliang Xiao in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Date: April 14 1992

To those closest to me

Mother, Father, Xiaolong and Xiao Ye

Abstract

Binuclear complexes of Rh and Ir bridged by both the bifunctional anion, 2-mercaptothiazolinate (mtz), and the neutral diphosphine ligands, $PPh_2(CH)_nPPh_2$ (n=1, dppm; 2, dppe), have been synthesized. Treatment of the mtz-bridged, open-book species, $[M(CO)_2(\mu\text{-mtz})]_2$ (M=Rh, Ir), with one equiv of L (L=dppm, dppe) yields complexes $[M_2(CO)_2(\mu\text{-L})(\mu\text{-mtz})_2]$. These complexes undergo oxidative addition of iodine to give $[M_2I_2(CO)_2(\mu\text{-L})(\mu\text{-mtz})_2]$.

When the complexes $[M(CO)_2(\mu\text{-mtz})]_2$ (M=Rh, Ir) are reacted with two equiv of dppm, the open-book species are converted to the A-frame complexes, $[M_2(\eta^1\text{-mtz})(CO)_2(\mu\text{-mtz})(dppm)_2]$. These complexes are also obtained by treatment of *trans*-$[MCl(CO)(dppm)]_2$ (M=Rh, Ir) with two equiv of the mtz anion. When one equiv of the anion is used, the complexes $[M_2Cl(CO)_2(\mu\text{-mtz})(dppm)_2]$ are produced.

The reactivity of the peroxo-bridged complex $[Ir_2I_2(CO)_2(\mu\text{-O}_2)\text{-}(dppm)_2]$ has been investigated. Its reaction with NO_2 and NO gives the complexes $[Ir_2I_2(CO)_2(\mu\text{-X})(dppm)_2][NO_3]$ (X=NO_3, NO), respectively. The reaction of the peroxo complex with CO yields $[Ir_2(CO)_2(\mu\text{-I})(\mu\text{-CO})\text{-}(dppm)_2][I]$ together with CO_2, and the new peroxo-bridged complex, $[Ir_2I_2(CO)_2(\mu\text{-CO})(\mu\text{-O}_2)(dppm)_2]$. The structure of this dioxygen complex has been confirmed by X-ray crystallography. In the reaction with RNC (R = ${}^iPr$, ${}^tBu$), methanol solvent is involved yielding $[Ir_2(CO_2CH_3)(RNC)_3(\mu\text{-CO})(\mu\text{-OH})(dppm)_2][I]_2$. Attempted reaction of the peroxo complex $[Ir_2I_2(CO)_2(\mu\text{-O}_2)(dppm)_2]$ with $HBF_4{\cdot}OEt_2$ and $CH_3SO_3CF_3$

gives rise to the cationic complex $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2]^+$, which is also produced when the peroxo species is reacted with NO^+ in damp CH_2Cl_2. Protonation of the dioxygen species with H_2SO_4 or SO_2 affords $[Ir_2I_2(CO)_2(\mu\text{-}SO_4)(dppm)_2]$, which is also formed in the reaction with $CuSO_4$. With HCl two isomers of $[Ir_2Cl_2I_2(CO)_2(dppm)_2]$ are obtained. These protonation reactions are accompanied by release of H_2O_2.

The diiodo compound $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ reacts with acetylene and phenylacetylene to give the vinylidene-bridged complexes, $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ (R=H, Ph). With acetylene the first species observed is proposed to be the alkyne-bridged $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}HC_2H)(dppm)_2][I]$. This compound transforms to $[Ir_2I(CO)_2(\mu\text{-}HC_2H)\text{-}(dppm)_2][I]$, in which it is proposed that the alkyne has slid towards one of the iridium centers. At ambient temperature this compound transforms to the vinylidene-bridged product within ca. 20 h. When the reaction of the diiodo compound with phenylacetylene is carried out at -40°C, the only species detected is the acetylide-bridged hydrido complex, $[Ir_2(H)(I)(CO)_2(\mu\text{-}C_2Ph)(dppm)_2][I]$. However, at temperatures above 0°C, only the phenylvinylidene-bridged product is observed. A mechanism is proposed for the acetylene-to-vinylidene transformation. The vinylidene-bridged complex reacts with additional acetylene to give products containing both a vinylidene and an acetylene bridge.

The neutral diiodo complex and the cationic complex, $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$, react with ethylene to yield $[Ir_2(CO)(C_2H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]^+$, in which ethylene is terminally bound to one iridium.

Acknowledgements

I wish to express my genuine gratitude to Dr. Martin Cowie for his supervision, encouragement and enthusiasm throughout the course of my study. The assistance given to me and my family by Marty and his family in matters unrelated to chemistry have been greatly appreciated.

My stay here could not be more enriched without all the help and friendship from my friends, in and out of the group. I am especially indebted to Dr. Bob McDonald, to whom I owe much of my expertise (if any) in areas ranging from NMR, and X-ray structure determination to the use of the computer. I also acknowledge the following: Dr. Rob Hilts, Dr. Yuming Xu, John Yule, Wenyi Fu, Lisheng Wang, Fred Antwi-Nsiah, Dr. Bernie Santarsiero, Dr. Giovanni Moro, and Dr. James Jenkins.

I am also grateful to all my friends in China for their unwavering help when I was in China, particularly Xiuepin Wang, Jingxinu Hu and Ningfong Mao.

I thank the staff of the NMR, Spectral Services, and Elemental Analysis Laboratories, the Machine Shop, the Glass Shop and the Store room for their talented assistance.

Especially I thank my parents and my grandfather for all their support throughout the hardest time of the family, when it was almost always difficult to get enough food for the family, yet they always managed to provide me with basic needs at school. I dedicate this thesis to my grandfather, who had given so much support in my early years of education, who unfortunately died just before I went to a university.

I am also indebted to my parents in law, Xiaofeng and Wu Jing for their support, and for being always there when their help was needed.

This thesis could never be compiled today without the support of my family. My wife, Xiaolong, has taken much of the heavy load at home though she was also working from dawn until dusk every weekday. More important were her understanding and encouragement which contributed so much to whatever I have achieved. The little guy, Xiao Ye, my son, who has brought much joy into my life, always asked to accompany me to the lab at night. To them, go my very special gratitude and thanks.

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List of Schemes

Chapter 2

Chapter 4

List of Abbreviations and Symbols

anal	analyses
ca.	circa (approximately)
calcd	calculated
dppm	bis(diphenylphosphino)methane
dppe	bis(diphenylphosphino)ethane
Et	ethyl
h	hour(s)
IR	infrared
Me	methyl
MeOH	methanol
mg	milligrams
min	minute(s)
mL	milliliters
mmol	millimoles
mtz	2-mercaptothiazolinate
Hmtz	2-mercaptothiazoline
NMR	nuclear magnetic resonance
Ph	phenyl
Pz	pyrazolyl
THF	tetrahydrofuran
µL	microliters

Crystallographic Abbreviations and Symbols

a, b, c	lengths of the x, y and z axes, respectively, of the unit cell
B	isotropic thermal parameter
deg (or °)	degrees
F_c	calculated structure factor
F_o	observed structure factor
h, k, l	Miller indices defining lattice planes, where the plane intersects the unit cell axes at $1/h$, $1/k$ and $1/l$ of the respective lengths of a, b, and c
p	experimental instability factor (used in the calculation of $\sigma(I)$ to downweight intense reflections)
R	residual index (a measure of agreement between calculated and observed structure factors)
R_w	weighted residual index
V	unit cell volume
w	weighting factor applied to structure factor
Å	Angstrom(s) (1 Å = 10^{-10} meters)
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 1

Introduction

To a large extent, modern transition-metal chemistry is based on the principles of coordination theory developed by Alfred Werner around 1900.[1] The essential concept of this theory is that a metal ion is surrounded by a set of ligands which function as electron-pair donors to the metal. The properties of the complex are then determined by the nature of the metal and the ligands, as well as by the geometry of the complex. On the other hand, much of today's transition-metal chemistry is not merely a simple extrapolation of Wernerian theory, and there are several areas which find no place in this scheme. Among these are the transition-metal clusters in which there are substantial and direct bonds between the metals. This is in contrast to the classical Wernerian complexes, in which there is no significant metal-metal bonding.[2]

The chemistry of transition-metal clusters has become one of the most rapidly expanding areas within inorganic and organometallic chemistry.[3] One of the driving forces behind the extensive research in this area stems from the suggestion that adjacent metals may react with substrate molecules in a cooperative manner, displaying reactivity patterns not observed for the mononuclear analogues.[4] The cooperative activation of organic or inorganic substrates by metal centers in close proximity could lead to unique stoichiometric and catalytic reactions which are difficult or impossible to conduct on a mononuclear metal complex.[5,6] In catalysis, for example, although alkene and alkyne hydrogenation is readily effected by homogeneous complexes such as Wilkinson's catalyst,[7] hydrogenation of triple bonds in species such as CO, CN^- and N_2, and hydrogenolysis of hydrocarbons, generally require heterogeneous catalysts such as metals, alloys and metal oxides, in which multi-metal-atom sites are available.[8,9] Because of their closer resemblance to the active sites in such catalysts than mononuclear complexes, it is conceivable that metal-cluster complexes might also effect reactions such as those noted above, but under homogeneous conditions.[6] The analogies between ligation in organo-cluster complexes and chemisorption on metal surfaces have been drawn in many aspects such as metal-metal and metal-ligand bond energies,[10-13] therefore cluster complexes could also be used to model heterogeneous catalysis.

The vast majority of isolable metal clusters are coordinatively saturated, and reactions of such systems frequently require activation by some means in order to generate the needed coordinative unsaturation. This is usually achieved by loss of ligands or by opening of metal-metal bonds.[6,14] Because in many cases, the metal-ligand and metal-metal bond energies are comparable,[15] such activation may involve a simultaneous breaking of both types of bonds. When cleavage of the metal-metal bonds is prevalent, fragmentation of the cluster may take place, which, in fact, has been the main problem in the application of clusters to catalysis.[14b]

The prototypical clusters are binuclear complexes, containing only two metal centers. Because of their simplicity, they are ideally suited to the study of the effects of cooperativity by adjacent metals. However, like the other members of the cluster family, disrupture of the binuclear framework is also encountered. To prevent the fragmentation of these binuclear complexes, bridging ligands are often used, which can hold the metals together even during processes involving metal-metal bond breaking. The many classes of bridging ligands utilized can be conveniently grouped into two categories: those involving neutral bridging groups, and those involving anionic bridging groups. One class of neutral groups which is commonly used as a bridging ligand is the diphosphine, $R_2P(CH_2)_nPR_2$, in which the two phosphorus atoms coordinate to the two metals. Among this group of ligands, bis(diphenylphosphino)methane (dppm, n=1, R=Ph) has received the most attention,[16-18] owing to its remarkable tendency to bridge two metal centers, and to its similarity to PPh_3, which has played a major role in the development of the chemistry of mononuclear complexes.[19] The popularity of dppm also stems from its ease of handling and availability, as well as its use as a spectroscopic probe in the molecule through use of ^{31}P NMR spectroscopy. Dppm-chelated mononuclear complexes are known, but the four-membered rings so formed tend to be highly strained and less favourable.[20] Mononuclear compounds involving chelated diphosphines are most often seen when bis(diphenylphosphino)ethane (dppe, n=2, R=Ph) is utilized, since chelate formation by this diphosphine is favoured.[21]

The remarkable versatility of dppm in bridging two metal centers is exemplified in the structural diversity of the complexes it forms, as shown in Figure 1.1. Complexes with structures I, II and III are usually described as face-to-face, A-frame and double A-frame complexes, respectively.

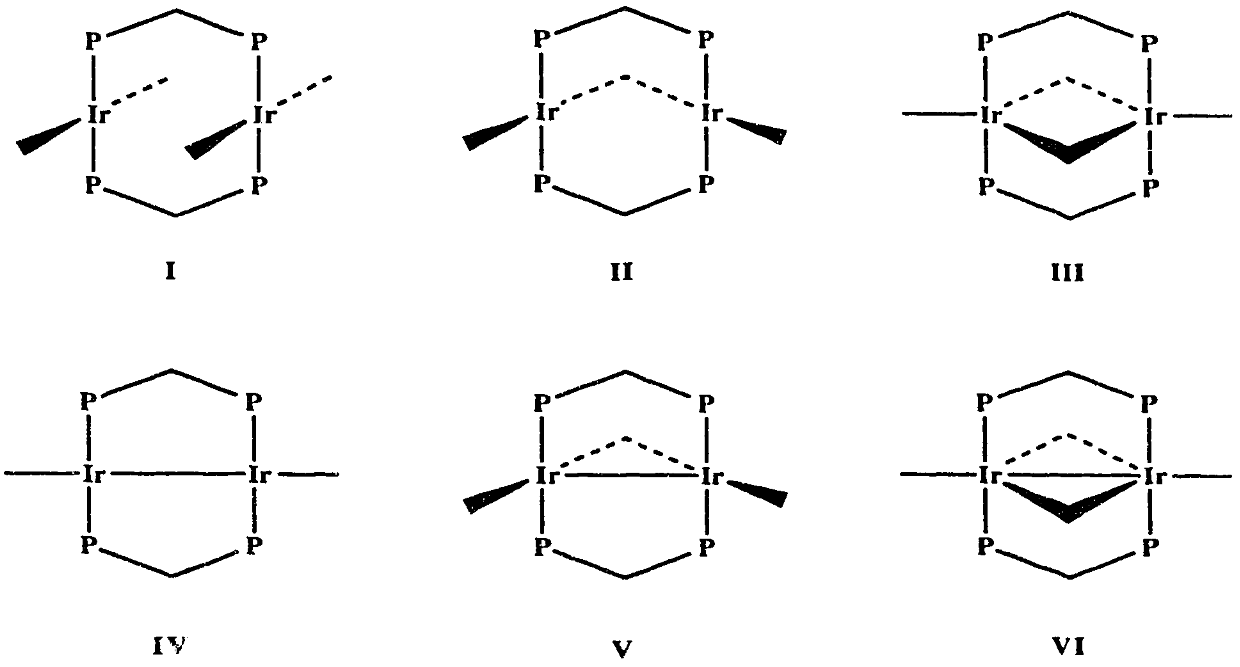


Figure 1.1. Common structures of dppm-bridged complexes

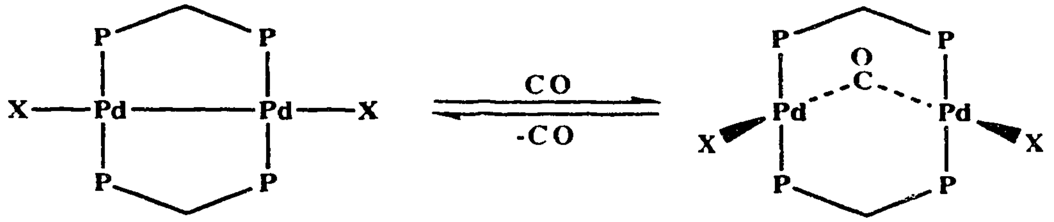
These structures, as shown, contain no metal-metal bonds, however related structures(IV-VI) which do contain metal-metal bonds are also known, and interconversion between the metal-metal bonded and non-bonded forms is common.[18] In addition, a number of variations of these structures having more ligands than shown are also known.[16-18] The structures shown in Figure 1.1 are only those having trans-oriented-dppm groups, but compounds in which the dppm ligands are disposed in a cis arrangement, at one or both metals, are also known,[22] and compounds in which one [23] or three [24] dppm molecules are incorporated into the binuclear skeletal framework have also been synthesized.

Frequently the metals involved in the frameworks of these binuclear complexes are those of the Fe, Co and Ni triads. To a large extent, the use of these metals is inspired by the involvement of the mononuclear complexes containing such metals in a wide range of substrate-activation reactions that are of relevance to important catalytic processes such as the Wacker process, alkene hydroformylation and methanol carbonylation.[2,8,9] Although initial studies on binuclear complexes were primarily focused on homobinuclear species, increasing attention has recently been given to heterobinuclear compounds,[25] in the expectation that unique chemistry may arise by virtue of the differing properties of the two distinct metals.[26]

Many of the dppm-bridged binuclear complexes undergo reactions with a variety of inorganic and organic substrates such as H (H^+, H^-),[27] H_2,[27a,28] S_8,[5b,29] CO,[5b,27a,28c,30] alkynes,[5b,28b,31] RNC,[30d,32] R_2S(R=H, alkyls),[33] SO_2,[29,30d] CS_2,[5b,34] RI,[35] R_2CN_2[29,36] halogens,[37] hydrogen halides,[27d,e] $AlMe_3$,[38] silanes,[22,39] O_2,[40] RNCS,[32a] SC(Cl)NMe_2,[41] HgCl,[42] RO^-(R=H, alkyls),[27c,43] N_2R^+,[44] RC_2^-,[45] RCO_2^-,[46] and NHR^-.[47] In reactions with these and other species, the most unique reactivity patterns of the binuclear compounds involve metal-metal bond making and breaking, and the migration of ligands from one metal to another. The former is often associated with insertion and de-insertion of the substrates between the two metal centers, and with trans-annular or double oxidative-addition reactions. These reactions generally occur on the metal centers, with the bridging dppm groups remaining intact. However, dppm is not always innocent, and phosphorus-carbon bond cleavage occasionally takes place.[48]

in phosphine-containing catalysts, such cleavage has been recognized as one of the major deactivation pathways of the catalysts.[49] Orthometallation involving dppm has recently been reported,[50] and deprotonation of the me[illegible]e carbons of the dppm ligand can also occur in the presence of base, such as $LiN(SiMe_3)_2$.[51] The chemistry of the dppm-bridged binuclear complexes has been covered in several reviews,[5a,16-18] therefore a detailed survey is not attempted here; instead several examples are selected, which either illustrate the unique aspects of the binuclear compounds or have relevance to subsequent chapters of this thesis.

As mentioned, one of the unique aspects of binuclear compounds compared to mononuclear ones relates to the making and breaking of metal-metal bonds. Shown below is an example involving insertion and

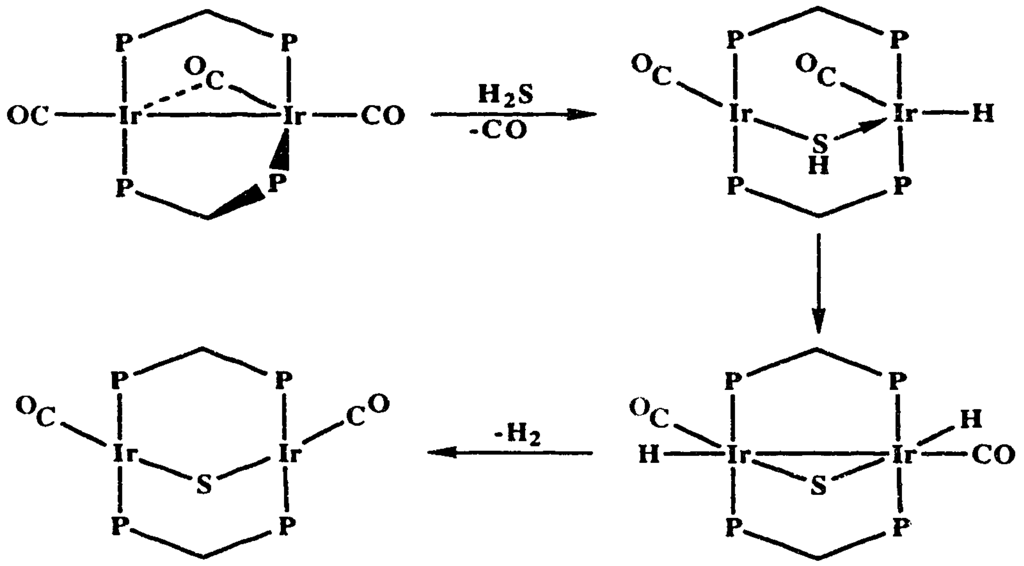


(1)

de-insertion of CO concomitant with Pd-Pd bond breaking and making.[5a,30b] The CO-inserted compound also reveals a very interesting bonding type that is almost unique to dppm-bridged binuclear compounds, in which CO bridges two metal centers between which there is no metal-metal bond.[18] In this unusual CO-binding mode the metal-carbon-metal angle at the bridging carbonyl is close to 120° and the carbonyl stretching freqency in the IR spectrum is very low, consistent with sp^2 hybridization of this group.

Another unusual CO-binding mode is the σ, π bridging mode, found in $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. In this mode, the bridging CO is a 4-electron donor, contributing two from its lone pair on carbon and two more from one of its π orbitals. This side-on mode is often cited in support of proposed intermediates in the dissociative chemisorption of CO on metal surfaces.[11,52]

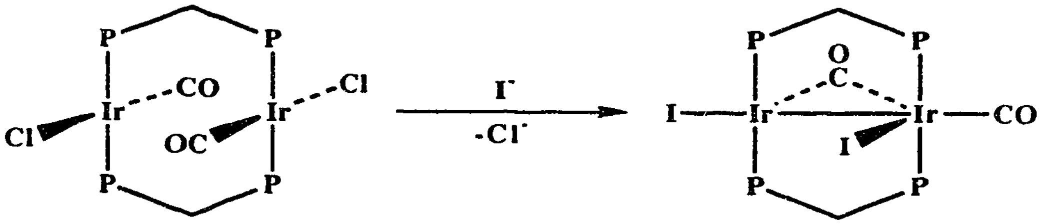
The so-called double oxidative addition of substrates to binuclear complexes is demonstrated in the reaction in which H_2S is reacted with $[Ir_2(CO)_2(\mu\text{-}CO)(dppm)_2]$.[33a] Herein lies a potentially important application of binuclear species in which both metals are involved in activation of bonds within the substrate molecule. An abbreviated reaction scheme shown in eq. 2 also reveals that ligand migration in binuclear complexes



(2)

can be quite facile. In this particular case, facile migration of a hydride ligand from one iridium center to the other, followed by elimination of H_2, occurs. Reactions of this type could provide further insight into catalyst poisoning, since H_2S is known as one of the most severe poisons for metal catalysts.[8,9,53]

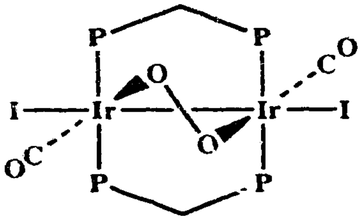
Much of our understanding about oxidative-addition reactions in mononuclear complexes is derived from studies of Vaska's compound, *trans*-[IrCl(CO)(PPh$_3$)$_2$], and related species.[7,54,55] Based on these studies, it appears that more electron-releasing ligands promote faster reaction rates, and stronger binding of the substrates to the metal centers. This is clearly exemplified in the reactions of O_2 with [IrX(CO)(PPh$_3$)$_2$], in which oxygenation is reversible when X=Cl or Br but irreversible for X=I.[55] In this respect, it was of interest to us to determine the extent of this parallel upon substitution of the chloride ligands in the well-known *trans*-[IrCl(CO)(dppm)]$_2$ by the better π-donor iodide ligand. This substitution was observed to give rise to an unusual structural change as shown in eq.3.[31e] Although a symmetrical structure was observed for the dichloro



(3)

precursor, in which the two square-planar Ir(+1) centers were parallel, the iodo analogue was found to have an unsymmetrical structure in which both of the carbonyl and both of the iodo ligands were mutually cis on adjacent metals, with one of the carbonyls occupying a bridging position. Although the observed geometry may be the result of steric interactions caused by the bulky iodo ligands, it may also be that the presence of the bridging carbonyl group serves to relieve the metal centers of some of the excess electron density, resulting from the good electron-donor iodo ligands.[31e]

It was of interest to pursue the chemistry of this unusual species in anticipation that the greater basicity of the metal centers compared with that of the chloro precursor might give rise to unusual reactivity. One example of this unusual reactivity is the oxygenation of this species. Thus reaction of the diiodo complex with O_2 afforded a remarkable dppm-bridged dioxygen complex, with a structure as shown.[40] In the context of metal-dioxygen compounds, this compound was extremely unusual, being the first in which the dioxygen ligand bridges two metal centers having an accompanying metal-metal bond.[56] Examples of binuclear dioxygen complexes, except for cobalt,[56] are rather rare. However, such complexes play a crucial role in biological dioxygen metabolism.[57] Studies of the dioxygen coordination and its subsequent reactions have been extensive,



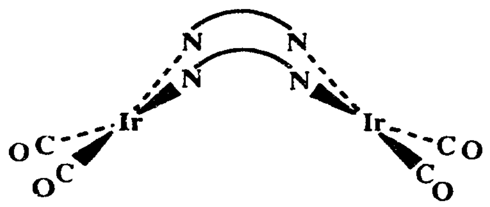
in hopes of understanding its functions relevant to biochemistry, and to gain insight into catalytic oxidations.[58,59]

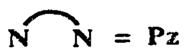
Direct oxidation of organic substrates by molecular oxygen is prohibited by spin conservation; however, this can be circumvented by coordination of O_2 to metals either on surfaces or in complexes.[60] Dioxygen is involved in the oxidation of ethylene on silver surfaces, but the mechanism is not well understood. Whether dioxygen or atomic oxygen, or both, is responsible for the selective formation of epoxide is not known,[61] although studies have shown that chemisorbed dioxygen exists on metal surfaces and may coordinate to two metal atoms.[61] With this information in mind, it was of interest to investigate the reactivity of the above unusual binuclear dioxygen compound.

The enhanced basicity of the metal centers in the diiodo complex $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)]_2$ also prompted us to pursue its reactivity with other substrates, in particular, unsaturated molecules such as olefins and alkynes. There are numerous dppm-bridged binuclear complexes in which alkyne molecules bridge two metal centers,[16,18] but in most cases these alkynes are activated by strong electron-withdrawing substituents (e.g. $CF_3C_2CF_3$). Reactions involving terminal alkynes are few,[31a-d] and there appears to be no example in which an olefin is coordinated to a dppm-bridged binuclear compound of the group VIII metals, although there are numerous mononuclear complexes that contain these unsaturated molecules, and such complexes have played a significant role in the development of organo-transition-metal chemistry.[2,7] It was anticipated that the diiodo species might show unusual reactivity towards these unsaturated molecules.

Although the emphasis within our group has primarily been on the use of diphosphines as bridging ligands,[22,25,27a-d,28a-c,30d,31c,e,33a,40,50] complexes involving anionic bridging groups have received a great deal of attention from others and to a lesser degree from our own group.[62-79] In the remaining part of this chapter, a brief survey of this area is provided.

The common bridging anionic ligands studied have been pyrazolates,[62-66] thiolates,[67,68] phosphides,[69] halides,[70] sulfides,[71] hydrides,[72] hydroxypyridinates,[73-75] thiophosphinates,[76] 2-mercaptopyridinate and related groups.[77-79] These ligands can be grouped for convenience into three categories as outlined in Figure 2.2, in which it is shown that the metals can be separated by one, two or three atoms within the bridging framework. Typically, these ligands form compounds having an open-book structure, as exemplified by the pyrazolyl(Pz)-bridged iridium dimer as shown.[80] This is particularly true for the two-atom and three-atom bridges, where the open-book structure is most often encountered. However for the one-atom bridges, the $M(\mu\text{-}X)_2M$ cores of the binuclear complexes are often planar or nearly planar. Shown below is

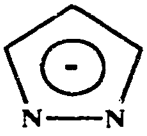




(a). one-atom bridges

H^-, S^{-2}, RS^-, Cl^-, PR_2^-

(b). two-atom bridges



R_2PS^-

(c). three-atom bridges

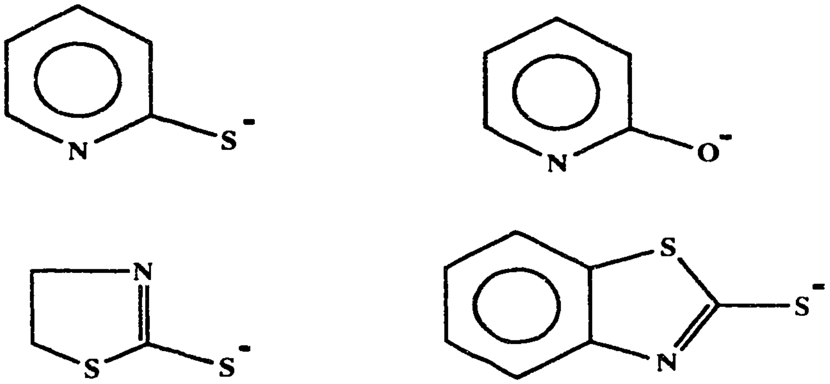
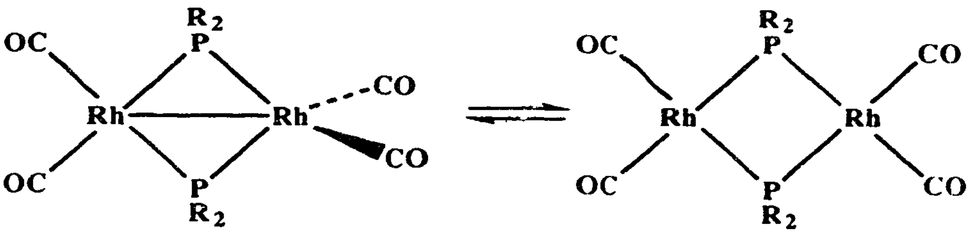


Figure 2.2. Common bridging anionic ligands

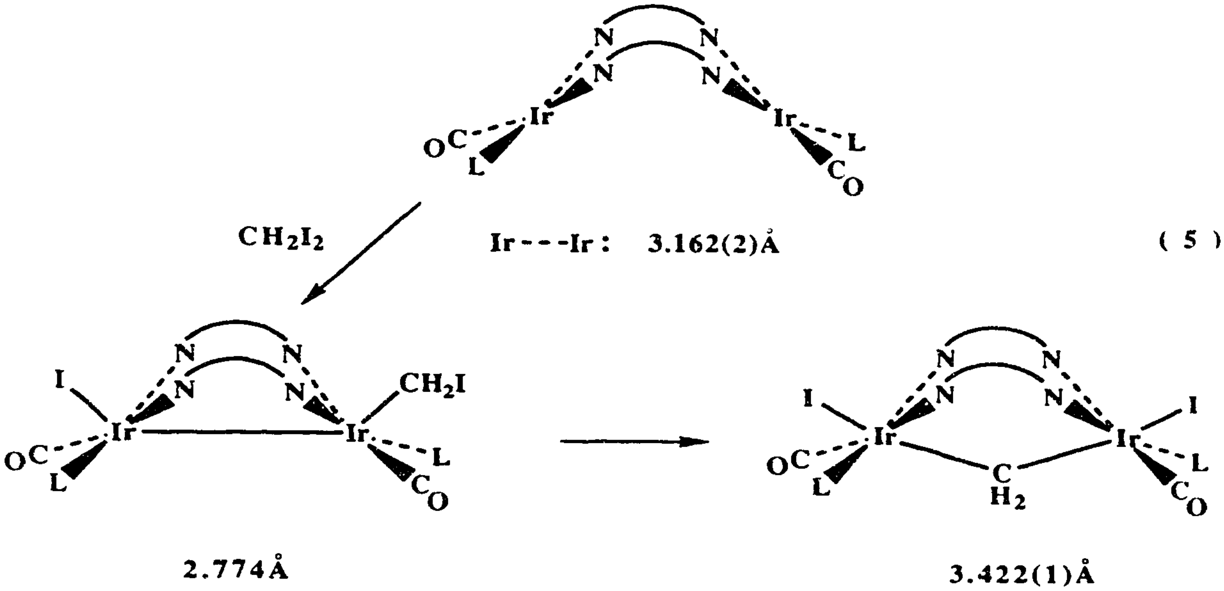
such a compound, which also exhibits an interesting geometric isomerization.[81]



(4)

Among the anionic ligands shown above, we were particularly interested in the three-atom bridges since these most resemble dppm, which is a neutral three-atom bridge. Such anionic bridges have the additional advantage of being capable of incorporating bifunctional character since many of the ligands noted earlier contain both hard and soft ligating atoms. Such bifunctionality is of interest since the combination of different bonding atoms in a bridge serves to make the metals electronically different. In addition, for ligands with a combination of strong and weak donor atoms, coordinative unsaturation can be induced through displacement of the weak end of the bridging group.[82,83]

Like the dppm-bridged compounds, the open-book complexes of group VIII metals formed by the three-atom, as well as the two-atom bridges also react with a number of substrates, although the scope of the substrates used appears much smaller than in the former case. The most extensively studied reactions are oxidative additions involving molecules such as halogens,[62g-i,64,65b,68b,78,79] CH_3I,[62g,h,78,84a] H_2,[67b,c,d,f,g,85] CH_2I_2[62c,d,67a,84a] and alkynes.[62g,h,67c,84b] A good example is seen in the reaction shown in eq. 5,[62c,i] in which the oxidative additions are associated with metal-metal bond forming and breaking.[84a] Reactions with halogens and alkyl halides generally afford complexes analogous to the metal-metal bonded species in eq. 5, and in the case of alkynes, the generation of alkyne-bridged species has been reported.[62e,84b] Although detailed mechanistic studies have not appeared, it has been proposed that reactions involving substrates such as halogens and alkyl halides may proceed via a free-radical pathway.[68b,79] Oxidative addition of H_2 to $[Ir(CO)L(\mu\text{-}SR)]_2$



(5)

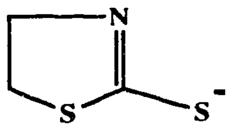
(L=tertiary phosphine ligands), on the other hand, appears to occur via initial coordination of H_2 at one iridium center followed by the migration of one hydride to the other center.[67d,g] In the case of the triply-bridged $[Ir_2(CO)_2L_2(\mu\text{-}SR)_2(\mu\text{-alkyne})]$, it has been shown that the first step in the addition of H_2 is the opening of one of the Ir-S bonds to create a vacant site at one iridium.[67b]

Like the dppm-bridged complexes, substantial stuctural changes may take place in reactions of the open-book complexes. For example, the chair conformation of the $M(\mu\text{-}X)_2M$ core in $[RhCl(\eta^5\text{-}C_5Me_5)(\mu\text{-}Pz)]_2$ transforms to an open-book structure upon treatment of the compound with Ag^+ followed by Zn/Cu reduction, affording $[Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-}Pz)]_2$. The reversible conformation change is seen in the reaction of a closely-related compound, $[Rh(\eta^5\text{-}C_5H_5)(\mu\text{-}Pz)]_2$, with iodine.[62a]

Application of the anion-bridged binuclear complexes to catalysis has also received attention.[86-89] The binuclear precursor $[Rh(CO)L(\mu\text{-}S^tBu)]_2$ (L=tertiary phosphines) has been found to be active and selective in the hydroformylation of alkenes to give aldehydes,[88] while the related species $[RhL_2(\mu\text{-}H)]_2$ uniquely produces trans-alkenes in the catalytic hydrogenation of alkynes. This latter observation is in sharp contrast to that observed for mononuclear metal complexes, in which cis-alkenes are typically obtained.[89] In both processes, experiments suggest that the binuclear metal frameworks remain intact during the reactions, and cooperative effects are occurring between the metal centers.[87,89]

Clearly, the two classes of compounds bridged by anions or dppm ligands share many similarities. For the typical open-book compounds such as $[Ir(CO)(PPh_3)(\mu\text{-}Pz)]_2$[62i] and the typical A-frame compounds like $[Ir_2(CO)_2(\mu\text{-}S)(dppm)_2]$,[90] both are composed of square-planar d^8 ML_4 fragments held in close proximity in the absence of Ir-Ir bonds, and are expected to have analogous valence orbitals.[91] In addition, both classes are found to display analogous reactivity patterns, and both are observed to undergo two-center oxidative-addition reactions, frequently accompanied by metal-metal-bond breaking and making. There are, however, some notable differences in their chemistry. While small molecules such as CO, RNC and SO_2 are frequently incorporated as bridging groups in dppm-bridged compounds, analogous species are rarely observed in the open-book complexes. Although it is well known that metal-phosphorus bonds are strong, cleavage of the anion-metal bonds is not unusual.[65b,67f,74c,75,] In fact, the halide-bridged compounds are often used in metathesis reactions for the preparation of other anion-bridged species mentioned above.

This thesis is divided into two parts. In the first part, the goal is to develop chemistry of complexes bridged by the anionic ligand, 2-mercaptothiazolinate (mtz), in the presence of diphosphine ligands. At the time when this work was undertaken, no complex with such mixed bridging ligands had been reported, although subsequent reports have appeared.[92] Previous studies had shown that 2-mercaptothiazolinate coordinated to metals through the mercapto sulfur and the nitrogen atoms,[77] thus it has the desired bifunctionality. It had also been found that the mtz-bridged complexes having tertiary phosphine ligands, such as $[Rh(CO)(PPh_3)(\mu\text{-mtz})]_2$, adopted a normal open-book structure with the two phosphorus groups being mutually trans.[77a] It was therefore of interest to determine the structure of species involving both mtz and diphosphine ligands. Furthermore, since the dppm- and the anion-bridged complexes represent two major classes of binuclear compounds of the group VIII metals, and both display a very rich chemistry, incorporation of both the dppm and the mtz ligands into a binuclear framework was of special interest. In addition, the bifunctionality of the mtz ligand could also provide the species having such mixed bridges with distinct reactivity patterns. These studies are presented in Chapter 2.



In the second part of this thesis, a continuation of ongoing chemistry of the dppm-bridged binuclear complex, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ will be described. It had already been shown that reaction of this complex with molecular oxygen gave the novel dioxygen adduct, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$, as described earlier. We set out to investigate the chemistry of this species, in order to obtain a better understanding of oxygen-transfer reactions. In addition, the chemistry of the unusual diiodo precursor with unsaturated organic substrates such as ethylene and terminal alkynes was also investigated in order to determine if the electronic or steric properties of the iodo ligand would lend unusual reactivity to this diiridium complex. This part of the study is described in Chapters 3 and 4.

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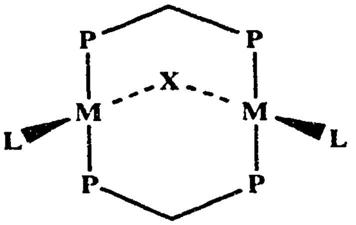
Chapter 2

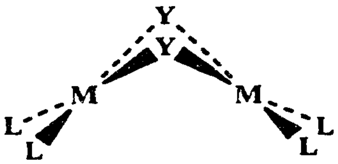
"A-Frame" *vs.* "Open-Book" Geometries in Binuclear Complexes Bridged by Diphosphines and Mercaptothiazolinate Ligands. Unusual Examples Involving a Bridging Bis(diphenylphosphino)ethane Group.

Introduction

Binuclear complexes, in which the metals are held in close proximity, are of interest because of the possibility that the two metals may interact in a cooperative manner and in so doing may display chemistry unique from that displayed at a complex containing a single metal.[1] Two common classes of binuclear complexes involving Rh and Ir are those of the "A-frame"[2] or "open-book"[3] complexes. In the former class the metals are bridged by two neutral diphosphine or related groups (most often dppm ($Ph_2PCH_2PPh_2$)), occupying a trans orientation at each metal, whereas in the latter class the bridging groups are anionic and occupy cis positions at both metals, as shown below for **A** and **B**, respectively.



A



B

In an effort to combine some of the features of both classes of binuclear species we set out to prepare open-book complexes that also contained bridging dppm groups. As a starting point we chose species related to the 2-mercaptothiazolinate-bridged complexes, $[M(CO)L(\mu\text{-mtz})]_2$ (M = Rh, Ir), since the dirhodium species, in which L = PMe_3, was shown to have a short metal-metal separation (3.05 Å),[3m] comparable to the bite of dppm, suggesting that this group could be incorporated as an additional bridge in these complexes. Previous work had also shown that the mtz-bridged binuclear frameworks readily undergo fragmentation in reactions involving molecules such as H_2S and H_2.[4] It seemed likely that the incorporation of a bridging diphosphine group into these complexes would offer greater stability and may allow the isolation of open-book complexes in which one, or even both, bridging mercaptothiazolinate groups were terminally bound. Such "bridge-opened" species had been proposed as key intermediates in the activation of substrates by "open-book" binuclear complexes.[5] We were also interested in the possibility of incorporating dppe ($Ph_2PCH_2CH_2PPh_2$) as a bridging group by utilizing an open-book complex, in which the metals are constrained to be in close proximity. Complexes having this diphosphine as a bridging group are extremely rare[6] owing to the well established propensity of this group to chelate.[7] These and related studies are reported in this chapter.

Experimental Section

All solvents, including deuterated solvents used for NMR experiments, were dried (using the appropriate drying agents listed in the Appendix) and distilled before use and were stored under dinitrogen.

Reactions were carried out at room temperature by using standard Schlenk procedures. 2-Mercaptothiazoline (Hmtz) and bis(diphenylphosphino)-methane (dppm) were purchased from Aldrich, bis(diphenylphosphino)-ethane (dppe) was obtained from Strem Chemicals, hydrated iridium(III) chloride was obtained from Johnson-Matthey, and ^{13}CO (99%) was supplied by Isotec Inc. These and all other reagents were used as received. The compounds *trans*-$[MCl(CO)(dppm)]_2$ (M = Rh,[8] Ir[9]), $[M(COD)(\mu\text{-mtz})]_2$ (M = Rh, Ir)[2n], $[Rh(CO)_2(\mu\text{-mtz})]_2$[2m] and sodium-2-Mercaptothiazolinate[2n] (Na^+mtz^-) were prepared by the previously reported procedures. Sodium hydride, which was used to prepare Na^+mtz^-, was obtained as a 60% oil emulsion from Aldrich and was stored under dinitrogen; before use it was washed with toluene and hexane to remove the oil.[2n]

The NMR spectra were recorded on a Bruker AM400 spectrometer at 400.1 MHz for ^1H, at 161.9 MHz for $^{31}P\{^1H\}$, and at 100.6 MHz for $^{13}C\{^1H\}$ spectra. The $^{13}C\{^1H, ^{31}P\}$ NMR spectra were obtained on a Bruker WH200 spectrometer operating at 50.32 MHz. Infrared spectra were performed on Nicolet 7199 or Mattson Polaris Fourier transform interferometers with use of Nujol mulls on KBr plates, or in solution in KCl cells with 0.5 mm window path lengths. Spectroscopic parameters for the compounds prepared are found in Tables 2.1 and 2.2. Elemental analyses were performed by the microanalytical service within the department. Conductivity measurements were made on 1.0 x 10^{-3} M solutions with use of a Yellow Springs Instrument Co., Model 31 conductivity bridge.

Preparation of Compounds. (a) **$[Rh_2(CO)_2(\mu\text{-mtz})_2(dppm)]$ (1).** To a

Table 2.1. Infrared Spectroscopic Data [a]

Compd	solid [b]	solution [c]
$[\mathrm{Rh_2(CO)_2(dppm)(\mu\text{-}mtz)_2}]$ **(1)**	1995 (vs)	
	1948 (vs)	
$[\mathrm{Ir_2(CO)_2(dppm)(\mu\text{-}mtz)_2}]$ **(2)**	1962 (vs, br)	
$[\mathrm{Rh_2(CO)_2(dppe)(\mu\text{-}mtz)_2}]$ **(3)**		1980 (st)
		1960 (med)
$[\mathrm{Rh_2I_2(CO)_2(dppm)(\mu\text{-}mtz)_2}]$ **(4)**	2059 (st)	2062 (st)
	2037 (med)	2020 (med)
$[\mathrm{Ir_2I_2(CO)_2(dppm)(\mu\text{-}mtz)_2}]$ **(5)**	2039 (vs)	2034 (vs, br)
	2018 (med).	
$[\mathrm{Rh_2I_2(CO)_2(dppe)(\mu\text{-}mtz)_2}]$ **(6)**	2062 (st)	2062 (st)
	2025 (med)	2020 (med)
$[\mathrm{Rh_2(CO)_2(\eta^1\text{-}mtz)(\mu\text{-}mtz)(dppm)_2}]$ **(7)** [d]	1926 (st)	2000 (vs)
	1825 (w, br)	1973 (st)
		1936 (vs, br)
		1820 (w, br)
$[\mathrm{Ir_2(CO)_2(\eta^1\text{-}mtz)(\mu\text{-}mtz)(dppm)_2}]$ **(8)**	1946 (w)	1952 (st, br)
	1896 (st)	1893 (vs, br)
$[\mathrm{Rh_2(CO)_2(\mu\text{-}mtz)(dppm)_2}][\mathrm{Cl}]$ **(9b)**	1988 (vs)	2001 (vs)
	1953 (vs)	1970 (st, br)
$[\mathrm{Rh_2(CO)_2(\mu\text{-}mtz)(dppm)_2}][\mathrm{PF_6}]$ **(9c)**	1991 (vs)	2001 (vs)
	1952 (vs)	1977 (st)

Table 2.1. (continued).

$[Ir_2Cl(CO)_2(\mu\text{-mtz})(dppm)_2]$ **(10)**	1944 (st)	1960 (med)
	1893 (vs)	1902 (vs)
$[Rh_2(CO)_2(\mu\text{-CO})(\mu\text{-mtz})(dppm)_2][Cl]$ **(11a)**	1981 (st)	1985 (vs, br)
	1958 (vs)	1812 (st)
	1797 (st)	
$[Rh_2(CO)_2(\mu\text{-CO})(\mu\text{-mtz})(dppm)_2][PF_6]$ **(11b)**	1976 (vs, br)	1987 (vs, br)
	1798 (st)	1813 (st)

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[a] Abbreviations used: w = weak, med = medium, st = strong, vs = very strong, br = broad. ν(CO). [b] Nujol mull. [c] THF solution except compounds **7**, **9**, and **11**, CH_2Cl_2 solution. [d] see text.

Table 2.2. NMR Spectroscopic Data [a]

Compd	δ ($^{31}P\{^1H\}$) [b]	δ ($^{13}C\{^1H\}$) [c]	δ (^1H) [c]
$[Rh_2(CO)_2(dppm)(\mu\text{-mtz})_2]$ (1)	45.9 (dd, $^1J_{Rh\text{-}P}$ = 142.8 Hz, $^2J_{P\text{-}P}$ = 58.2 Hz), 30.8 (dd, $^1J_{Rh\text{-}P}$ = 153.4 Hz)		4.20 (m,1H), 3.70 (m, 1H), 4.28 (m, 2H), 3.80 (m, 1H), 3.41 (m, 1H), 3.33 (m, 1H), 3.06 (m, 1H), 2.94 (m, 2H)
$[Ir_2(CO)_2(dppm)(\mu\text{-mtz})_2]$ (2)	-5.7 (m), -2.8 (m)		5.20 (m, 1H), 4.18 (m, 1H), 4.38 (m, 1H), 3.55 (m, 2H), 3.40 (m, 2H), 3.20 (m, 1H), 2.20 (m, 1H), 2.00 (m, 1H)

Table 2.2. (continued).

$[Rh_2(CO)_2(dppe)(\mu\text{-}mtz)_2]$ (3)	40.2 (dd, $^1J_{Rh\text{-}P}$ = 147.6 Hz, $^3J_{P\text{-}P}$ = 2.6 Hz), 39.1 (dd, $^1J_{Rh\text{-}P}$ = 157.8 Hz)		4.20 (m 1H), 3.73 (m, 1H), 2.37 (m, 1H), 1.80 (m, 1H), 4.16 (m, 1H), 3.34 (m, 1H), 3.23 (m, 1H), 3.10 (m, 2H), 2.98 (m, 1H), 2.70 (m, 1H), 2.32 (m, 1H)
$[Rh_2I_2(CO)_2(dppm)(\mu\text{-}mtz)_2]$ (4)	19.2 (m), 18.6 (m)	189.2 (dd, $^1J_{Rh\text{-}C}$= 55.6 Hz, $^2J_{P\text{-}C}$ = 7.7 Hz), 186.0 (dd, $^1J_{Rh\text{-}C}$ = 56.6 Hz, $^2J_{P\text{-}C}$= 7.7 Hz)	5.20 (m, 1H), 4.15 (m, 1H), 5.06 (m, 1H), 4.08 (m, 2H), 3.90 (m, 1H), 3.32 (m, 1H), 3.20 (m, 1H), 2.94 (m, 1H), 2.10 (m, 1H)

Table 2.2. (continued)

$[Ir_2I_2(CO)_2(dppm)(\mu\text{-mtz})_2]$ (5)	-21.5 (d, $^2J_{P\text{-}P}$ = 37.8 Hz), -26.1 (d)		4.98 (m,1H), 4.01 (m, 1H), 4.52 (m, 1H), 3.89 (m, 2H), 3.80 (m, 1H), 3.34 (m, 1H), 3.10 (m, 1H), 2.87 (m, 1H), 2.02 (m, 1H)
$[Rh_2I_2(CO)_2(dppe)(\mu\text{-mtz})_2]$ (6)	40.9 (d, $^1J_{Rh\text{-}P}$ = 109.2 Hz), 22.3 (d, $^1J_{Rh\text{-}P}$ = 110.0 Hz)		2.42 (m, 1H), 2.30 (m, 1H), 2.20 (m, 1H), 1.97 (m, 1H), 5.32 (m, 1H), 4.32 (m, 1H), 3.96 (m, 1H), 3.69 (m, 1H), 3.37 (m, 1H), 3.32 (m, 1H), 3.25 (m, 1H), 2.85 (m, 1H)
$[Rh_2(CO)_2(\eta^1\text{-mtz})(\mu\text{-mtz})(dppm)_2]$ (7) ^{d}	31.4 (br), 24.5 (br)	205.3 (br), 195.0 (br)	4.93 (m, 2H), 3.78 (m, 2H), 4.32 (t, 2H), 3.15 (t, 2H), 2.70 (t, 2H), 1.83 (t, 2H)

Table 2.2. (continued).

$[Ir_2(CO)_2(\eta^1\text{-mtz})(\mu\text{-mtz})(dppm)_2]$ **(8)**	4.5 (m), -6.9 (m)	186.3 (t, $^2J_{P\text{-}C}$ = 14.6 Hz), 180.6 (br)	4.93 (m, 2H), 4.26 (m, 2H), 4.41 (t, 2H), 3.30 (t, 2H), 2.68 (t, 2H), 1.67 (t, 2H)
$[Rh_2(CO)_2(\mu\text{-mtz})(dppm)_2][Cl]$ **(9b)**	30.1 (m), 20.6 (m)	194.4 (dt, $^1J_{Rh\text{-}C}$ = 67 Hz, $^2J_{P\text{-}C}$=12 Hz), 193.4 (dt, $^1J_{Rh\text{-}C}$ = 75 Hz, $^2J_{P\text{-}C}$=15 Hz)	3.94 (m, 2H), 3.84 (m, 2H), 2.39 (t, 2H), 1.46 (t, 2H)
$[Rh_2(CO)_2(\mu\text{-mtz})(dppm)_2][PF_6]$ **(9c)**	29.0 (m), 20.7 (m)		3.63 (m, 2H), 3.75 (m, 2H), 2.35 (t, 2H), 1.36 (t, 2H)
$[Ir_2Cl(CO)_2(\mu\text{-mtz})(dppm)_2]$ **(10)**	5.4 (m), -5.8 (m)		4.88 (m, 2H), 4.18 (m, 2H), 2.56 (t, 2H), 1.98 (t, 2H)
$[Rh_2(CO)_2(\mu\text{-CO})(\mu\text{-mtz})(dppm)_2][Cl]$ **(11a)**	32.2 (m), 30.8 (m)		4.22 (m, 2H), 4.12 (m, 2H), 3.00 (t, 2H), 1.86 (t, 2H)

Table 2.2. (continued)

$[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}mtz)(dppm)_2][PF_6]$ (**11b**)	32.4 (m), 30.9 (m)	4.25 (m, 2H), 3.95 (m, 2H), 3.02 (t, 2H), 1.88 (t, 2H)

[a] Abbreviations used: d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad. CD_2Cl_2 solution at 25°C, except compound **3**, in d_8-THF, and compounds 9**b**, **c**, at -80°C. [b] vs 85% H_3PO_4. [c] vs TMS. [d] see text.

THF solution of $[Rh(CO)_2(\mu\text{-mtz})]_2$, prepared by the addition of CO to a THF solution of $[Rh(COD)(\mu\text{-mtz})]_2$ (66.0 mg, 0.10 mmol, in 10 mL), was added 38.4 mg (0.10 mmol) of dppm in 5 mL of THF, causing an immediate color change from wine red to dark purple. After stirring for 1 h, the volume was reduced to ca. 5 mL, and 10 mL of hexane was slowly added to the solution, affording the compound as dark purple microcrystals (75% yield). Anal. calcd for $Rh_2S_4P_2O_2N_2C_{33}H_{28}$: C, 44.90; H, 3.43; N, 3.17. Found: C, 44.91; H, 3.98; N, 3.03.

(b) $[Ir_2(CO)_2(\mu\text{-mtz})_2(dppm)]$ (2). The procedure was the same as for 1, except that $[Ir(COD)(\mu\text{-mtz})]_2$ was used to prepare the tetracarbonyl precursor. The dark purple compound was only spectroscopically characterized due to its extreme air sensitivity.

(c) $[Rh_2(CO)_2(\mu\text{-mtz})_2(\mu\text{-dppe})]$ (3). To a THF solution of $[Rh(CO)_2(\mu\text{-mtz})]_2$ (prepared from $[Rh(COD)(\mu\text{-mtz})]_2$ (66.0 mg, 0.10 mmol, in 10 mL of THF)) was slowly added 38.5 mg (0.097 mmol) of dppe in 5 mL of THF, causing an immediate color change to deep red. The mixture was stirred for *ca.* 0.5 h and the volume was then reduced to *ca.* 2 mL followed by addition of hexane to give a red precipitate. This compound was extremely air sensitive, the solid instantly changing color to brown upon exposure to air.

(d) $[Rh_2I_2(CO)_2(\mu\text{-mtz})_2(dppm)]\cdot 0.5THF$ (4). To a THF solution of 1 (prepared from 66.0 mg (0.10 mmol) of $[Rh(COD)(\mu\text{-mtz})]_2$ in 10 mL of THF) was added 24.5 mg (0.097 mmol) of I_2 in 4 mL of THF, causing an immediate color change from intense purple to dark red. After stirring for 1 h, the volume was reduced to ca. 2 mL, and addition of hexane precipitated a dark red solid (70% yield). Anal. calcd for $Rh_2I_2S_4P_2O_{2.5}N_2C_{35}H_{32}$: C, 35.84; H, 2.93; N, 2.39; I, 21.65. Found: C, 35.61; H, 2.85; N, 2.31; I, 21.80.

(e) [$Ir_2I_2(CO)_2$(μ-mtz)$_2$ (dppm)] (5). To a THF solution of **2** (prepared by using [Ir(COD)(μ-mtz)]$_2$ (84.0 mg, 0.10 mmol, in 10 mL of THF)), was added 24.5 mg (0.097 mmol) of I_2 in 4 mL of THF, causing an immediate color change to orange. The mixture was stirred for 0.5 h, after which reduction of the volume followed by addition of hexane precipitated an orange solid.

(f) [$Rh_2I_2(CO)_2$(μ-mtz)$_2$(μ-dppe)] (6). To a THF solution of **3** (prepared from 134.0 mg (0.20 mmol) of [Rh(COD)(μ-mtz)]$_2$) was added 51.0 mg of I_2 in 5 mL of THF, a deep purple solution was immediately formed. Reduction of the volume followed by addition of hexane yielded a dark red solid (70-75% yield). Anal. calcd for $Rh_2I_2S_4P_2O_2N_2C_{34}H_{32}$: C, 35.49; H, 2.81; N, 2.44; I, 22.60. Found: C, 34.17; H, 2.85; N, 2.39; I, 22.66.

(g) [Rh_2(mtz)$(CO)_2$(μ-mtz)(dppm)$_2$]·CH_2Cl_2 (7). Method A. To a THF solution of [Rh$(CO)_2$(μ-mtz)]$_2$ (prepared from [Rh(COD)(μ-mtz)]$_2$ (132.0 mg, 0.2 mmol, in 20 mL)), was added 153.[illegible] mg (0.40 mmol) of dppm, resulting in an immediate color change to deep red. After stirring for 0.5 h, the volume was reduced to ca. 5 mL followed by precipitation with hexane. Compound **7** was crystallized from CH_2Cl_2/hexane. Anal. calcd for $Rh_2Cl_2S_4P_4O_2N_2C_{59}H_{54}$: C, 52.41; H, 4.03; N, 2.07; S, 9.49. Found: C, 52.85; H, 3.95; N, 2.20; S, 9.70.

Method B. A 110.0 mg (0.10 mmol) sample of *trans*-[RhCl(CO)(dppm)]$_2$ was suspended in 10 mL of THF, to which was added

28.4 mg (0.20 mmol) of sodium-2-mercaptothiazolinate in 5 mL of THF, causing a color change to red within several min. After stirring for 5 h, the solvent was removed under vacuum. The red solid was redissolved in 10 mL of CH_2Cl_2. The solution was then filtered and concentrated to ca. 3 mL. Micro-crystals were obtained upon addition of hexane (90% yield).

(h) $[Ir_2(mtz)(CO)_2(\mu\text{-}mtz)(dppm)_2]$ (8). To a slurry of *trans*-$[IrCl(CO)(dppm)]_2$ (220.0 mg, 0.17 mmol) in 10 mL of THF, was added 49.0 mg (0.34 mmol) of sodium-2-mercaptothiazolinate in 5 mL of THF. The mixture was stirred overnight, during which time a red-orange solution was formed. Filtration followed by reduction in the volume of the solution and addition of hexane gave an orange solid (85-90% yield). Anal. calcd for $Ir_2S_4P_4O_2N_2C_{58}H_{52}$: C, 48.18; H, 3.63; N, 1.94. Found: C, 47.83; H, 3.70; N, 2.03.

(i) $[Rh_2(CO)_2(\mu\text{-}mtz)(dppm)_2][Cl]\cdot CH_2Cl_2$ (9b). The procedure was the same as for **7** in method B, except that 1 equiv of sodium-2-mercaptothiazolinate was used. Compound **9b** was crystallized from CH_2Cl_2/hexane (87% yield). Conductivity measurements: $\Lambda = 29.8\ \Omega^{-1}cm^2mol^{-1}$ in CH_2Cl_2; $\Lambda = 71.6\ \Omega^{-1}cm^2mol^{-1}$ in CH_3NO_2. Anal. calcd for $Rh_2Cl_3S_2P_4O_2NC_{56}H_{50}$: C, 52.99; H, 3.99; N, 1.10. Found: C, 52.97; H, 3.95; N, 1.01.

(j) $[Rh_2(CO)_2(\mu\text{-}mtz)(dppm)_2][PF_6]$ (9c). To a CH_2Cl_2 solution of **9b** (118.0 mg, 0.10 mmol, in 10 mL), was added 1 equiv of $AgPF_6$ (25.0 mg, 0.10 mmol, in 5 mL of CH_2Cl_2). After stirring for 0.5 h, the solution was filtered and the volume was then reduced to ca. 3 mL. Micro-crystals were obtained upon addition of hexane (90% yield). Anal. calcd for

$Rh_2ClS_2P_5F_6O_2NC_{55}H_{48}$: C, 49.69; H, 3.65; N, 1.05. Found: C, 49.56; H, 3.64; N, 1.14.

(k) $[Ir_2Cl(CO)_2(\mu\text{-mtz})(dppm)_2]$ (10). The procedure was the same as for 8, except that 1 equiv of sodium-2-mercaptothiazolinate was used. Compound **10** was crystallized from THF/hexane. Anal. calcd for $Ir_2ClS_2P_4O_2NC_{55}H_{48}$: C, 48.47; H, 3.56; N, 1.03. Found: C, 48.63; H, 3.90; N, 0.91.

(l) $[Rh_2(CO)_2(\mu\text{-CO})(\mu\text{-mtz})(dppm)_2][Cl]$ (11a). A stream of CO was passed through a CH_2Cl_2 solution of **9**, causing an immediate color change to orange accompanied by formation of an orange precipitate. Carbonyl loss from **11a** occurred very rapidly under dinitrogen. Compound **11a** was determined to be a 1:1 electrolyte in CH_3NO_2 ($\Lambda = 74.0$ $\Omega^{-1}cm^2mol^{-1}$).

(m) $[Rh_2(CO)_2(\mu\text{-CO})(\mu\text{-mtz})(dppm)_2][PF_6]$ (11b). The procedure was the same as for **11a**, except that **9c** was used. Carbonyl loss from **11b** also occurred very readily.

X-ray Data Collection. (a) $[Rh_2I_2(CO)_2(\mu\text{-mtz})_2(dppe)]\cdot THF$ (6). Dark red crystals of **6** were grown by slow diffusion of hexane into a THF solution of the complex. Suitable crystals were mounted on glass fibers with epoxy. Data were collected on an Enraf-Nonius CAD4 diffractometer using MoKα radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $12.6 \leq 2\theta \leq 33.6°$. The automatic peak search and reflection indexing programs[10] generated a triclinic cell with the possible space groups of *P*1 or

$P\bar{1}$. The space Group $P\bar{1}$ was chosen, and later verified by the successful refinement of the structure.

Intensity data were collected at 22°C by using the $\theta/2\theta$ scan technique to a maximum $2\theta = 50°$. Backgrounds were scanned for 25% of the peak width on either side of the peak scan. Three reflections were chosen as intensity standards, being remeasured after every 120 min of X-ray exposure; no unusual variation in their intensities was evident. The data were processed in the usual manner with a value of 0.04 for p to downweigh intense reflections.[11] Corrections for Lorenz and polarization effects and for absorption by using the method of Walker and Stuart were applied.[10,12]

(b) $[Rh_2(CO)_2(\mu\text{-mtz})(dppm)_2][Cl]\cdot CH_2Cl_2$ (9b). Red crystals of **9b** were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. Crystals were mounted and flame-sealed in glass capillaries under solvent vapor to minimize solvent loss. Data collection and derivation of unit-cell parameters proceeded in a manner similar to that above (the setting angles of 25 reflections were in the range $22.0° \leq 2\theta \leq 25.7°$). The monoclinic diffraction symmetry and systematic absences ($h0l$, $h+l$ = odd; $0k0$, k = odd) were consistent with the space group $P2_1/n$.

Intensity data were collected at 22°C with use of the $\theta/2\theta$ scan technique to a maximum $2\theta = 50.0°$. No unusual variation was found for the intensity standards. See Table 2.3 for pertinent crystal data and details of intensity collection for both **6** and **9b**.

Structure Solution and Refinement. Both structures were solved in

Table 2.3. Summary of Crystal Data and Details of Intensity Collection

compd	$[Rh_2I_2(CO)_2(\mu\text{-mtz})_2\text{-}(dppe)]\cdot THF$ (6)	$[Rh_2(CO)_2(\mu\text{-mtz})\text{-}(dppm)_2][Cl]\cdot CH_2Cl_2$ (9b)
formula	$C_{38}H_{40}I_2N_2O_3P_2Rh_2S_2$	$C_{58}H_{50}Cl_3NO_2P_4Rh_2S_2$
fw	1222.59	1269.22
space group	$P\bar{1}$	$P2_1/n$
temp, °C	22	22
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
cell parameters		
a, Å	9.856(3)	11.400(1)
b, Å	14.078(6)	21.944(2)
c, Å	16.245(5)	22.134(1)
α, deg	103.66(3)	
β, deg	93.21(3)	92.494(7)
γ, deg	92.91(3)	
V, Å^3	2182(1)	5532(1)
Z	2	4
ρ (calcd), g/cm^3	1.751	1.524
no. of unique data collcd	7606 ($h, \pm k, \pm l$)	9932 ($h, k, \pm l$)
no. of unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	5164	6170
final no. of params refined	433	613

Table 2.3.(continued)

R	0.045	0.062
R_w	0.057	0.082

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

the respective space groups ($P\bar{1}$ for **6** and $P2_1/n$ for **9b**) with use of standard Patterson and Fourier techniques. Full-matrix least-squares refinements proceeded so as to minimize the function $\Sigma w(|F_o|-|F_c|)^2$, where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$. Atomic scattering factors and anomalous dispersion terms were taken from the usual tabulations.[13-15] All hydrogen atom positions were generated on the basis of the geometry of their attached carbon atom using C-H distances of 0.95 Å. Thermal parameters were fixed at 1.2 times that of their attached carbon atom. The hydrogen atoms were included as fixed contributions in the least-squares calculations. The solvent atoms of complex **6** were input as a rigid five-carbon ring that most appropriately described the electron density, due to large thermal parameters, and no attempt was made to distinguish between carbon and oxygen atoms. These atoms were not refined in subsequent least-squares cycles, and their hydrogen atoms were not included.

The final model for complex **6**, with 433 parameters varied, refined to $R = 0.045$ and $R_w = 0.057$. In the final difference Fourier map the 10 highest residuals had a density in the range 1.1-0.8 e/Å^3 and were primarily located in the area of the solvent molecule. For compound **9b** the final model, with 613 parameters varied, converged to $R = 0.062$ and $R_w = 0.082$. The 10 highest peaks had a density of 2.5-0.6 e/Å^3 and were again primarily located near the solvent molecule. The positional and thermal parameters for the non-hydrogen atoms of **6** are given in Table 2.4, and selected bond lengths and angles are given in Tables 2.6 and 2.7, respectively. For complex **9b** the pertinent data are found in Tables 2.5, 2.8 and 2.9.

Table 2.4. Positional and Thermal Parameters of the Atoms of $[Rh_2I_2(CO)_2(\mu\text{-mtz})_2(\mu\text{-dppe})]\cdot THF$ (6) [a]

atom	x	y	z	B (Å^2)
I(1)	0.05272(6)	0.27594(5)	0.49247(4)	4.10(2)
I(2)	-0.04596(6)	0.24254(5)	-0.02031(4)	4.23(2)
Rh(1)	0.06825(6)	0.26932(4)	0.32039(4)	2.32(1)
Rh(2)	0.04262(6	0.26163(4	0.14957(4	2.29(1)
S(1)	0.1953(2)	0.4219(1)	0.3365(1)	2.84(5)
S(2)	0.1022(3)	0.5931(2)	0.2780(2)	4.78(7)
S(3)	-0.1984(2)	0.2637(2)	0.1703(2)	3.78(6)
S(4)	-0.3236(2)	0.4296(2)	0.2825(2)	6.28(9)
P(1)	0.2595(2)	0.1801(1)	0.3199(1)	2.66(5)
P(2)	0.2691(2)	0.2727(2)	0.1160(1)	2.57(5)
O(1)	-0.1215(7)	0.0878(5)	0.3003(5)	5.6(2)
O(2)	0.0142(7)	0.0441(4)	0.1132(4)	4.7(2)
N(1)	0.0546(6)	0.4152(4)	0.1872(4)	2.6(2)
N(2)	-0.1046(6)	0.3553(5)	0.3286(4)	2.9(2)
C(1)	-0.0503(9)	0.1557(7)	0.3056(5)	3.7(2)
C(2)	0.0287(8)	0.1269(6)	0.1274(5)	3.2(2)
C(3)	0.3543(7)	0.1630(5)	0.2250(5)	2.9(2)
C(4)	0.3891(7)	0.2584(5)	0.1999(5)	2.7(2)

Table 2.4. (continued).

C(5)	0.1107(8)	0.4653(6)	0.2574(5)	2.8(2)
C(6)	0.028(1)	0.5798(7)	0.1778(7)	6.4(4)
C(7)	-0.0102(9)	0.4758(6)	0.1396(6)	4.3(3)
C(8)	-0.1955(8)	0.3465(7)	0.2674(6)	3.7(2)
C(9)	-0.253(1)	0.4822(8)	0.3870(7)	5.6(3)
C(10)	-0.1238(9)	0.4393(7)	0.3977(6)	4.7(3)
C(11)	0.2233(9)	0.0559(6)	0.3312(5)	3.5(2)
C(12)	0.200(1)	0.0401(7)	0.4104(6)	5.6(3)
C(13)	0.163(1)	-0.0508(7)	0.4197(7)	6.9(4)
C(14)	0.150(1)	-0.1289(8)	0.3537(8)	7.1(4)
C(15)	0.167(1)	-0.1164(7)	0.2746(7)	6.6(4)
C(16)	0.209(1)	-0.0244(7)	0.2638(6)	4.8(3)
C(21)	0.3995(8)	0.2278(6)	0.4001(5)	3.0(2)
C(22)	0.4075(8)	0.3189(6)	0.4549(5)	3.5(2)
C(23)	0.5177(9)	0.3507(7)	0.5095(6)	4.5(3)
C(24)	0.626(1)	0.2980(9)	0.5134(7)	6.3(3)
C(25)	0.618(1)	0.2049(9)	0.4618(7)	7.6(3)
C(26)	0.507(1)	0.1708(8)	0.4054(7)	5.8(3)
C(31)	0.3155(8)	0.3882(6)	0.0916(6)	3.6(2)
C(32)	0.289(1)	0.4003(7)	0.0102(6)	5.2(3)
C(33)	0.313(1)	0.4883(9)	-0.0084(8)	8.1(3)

Table 2.4. (continued).

C(34)	0.366(1)	0.5692(9)	0.0538(9)	9.2(4)
C(35)	0.395(1)	0.5577(8)	0.1320(9)	7.4(4)
C(36)	0.3716(9)	0.4683(6)	0.1522(7)	4.4(3)
C(41)	0.3328(8)	0.1837(6)	0.0291(5)	3.1(2)
C(42)	0.4664(8)	0.1970(7)	0.0102(5)	3.9(2)
C(43)	0.526(1)	0.1322(8)	-0.0501(6)	5.3(3)
C(44)	0.452(1)	0.048(1)	-0.0928(8)	7.5(4)
C(45)	0.322(1)	0.0350(8)	-0.0780(7)	6.7(4)
C(46)	0.2593(9)	0.1001(7)	-0.0172(6)	4.0(3)
C(101)[b]	0.313	0.113	0.668	12
C(102)[b]	0.440	0.178	0.672	12
C(103)[b]	0.389	0.279	0.693	12
C(104)[b]	0.290	0.274	0.759	12
C(105)[b]	0.232	0.167	0.743	12

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. All atoms except those of solvent molecule were refined anisotropically. Thermal parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameters defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Atoms of solvent molecule of crystallization with fixed contribution (see text).

Table 2.5. Positional and Thermal Parameters of the Atoms of $[Rh(CO)_2(\mu\text{-mtz})(dppm)_2][Cl]\cdot CH_2Cl_2$ (9b)[a]

atom	x	y	z	B (Å^2)
Rh(1)	0.11508(6)	0.25121(3)	0.15107(3)	2.51(2)
Rh(2)	0.25220(6)	0.36751(3)	0.16145(3)	2.50(2)
Cl(1)	0.5878(3)	0.1926(2)	0.9490(1)	7.5(1)
S(1)	0.3954(2)	0.2938(1)	0.1995(1)	3.23(6)
S(2)	0.4559(2)	0.1667(1)	0.2336(1)	4.76(8)
P(1)	0.0518(2)	0.2647(1)	0.2493(1)	2.98(6)
P(2)	0.2012(2)	0.3801(1)	0.2610(1)	2.66(5)
P(3)	0.1864(2)	0.2297(1)	0.0556(1)	2.71(6)
P(4)	0.3179(2)	0.3516(1)	0.0648(1)	2.81(6)
O(1)	-0.0506(6)	0.3452(3)	0.1024(3)	4.7(2)
O(2)	0.1887(7)	0.4958(3)	0.1332(4)	6.0(2)
N(1)	0.2497(6)	0.1963(3)	0.1889(3)	2.8(2)
C(1)	0.0109(8)	0.3065(5)	0.1202(4)	3.4(2)
C(2)	0.2069(9)	0.4453(5)	0.1430(4)	3.8(3)
C(3)	0.1582(7)	0.3078(4)	0.2947(4)	2.6(2)
C(4)	0.3241(7)	0.2710(4)	0.0448(3)	2.5(2)
C(5)	0.3502(8)	0.2193(4)	0.2039(4)	3.0(2)

Table 2.5. (continued).

C(6)	0.2485(9)	0.1298(5)	0.1976(4)	4.3(3)
C(7)	0.344(1)	0.1110(6)	0.2395(7)	7.4(4)
Cl(2)[b]	0.3283(6)	0.4049(3)	0.5923(3)	15
Cl(3)[b]	0.1638(6)	0.3165(3)	0.6217(3)	15
C(8)[b]	0.216(2)	0.365(1)	0.575(1)	15
C(11)	-0.0906(8)	0.2966(5)	0.2622(4)	3.4(2)
C(12)	-0.1810(9)	0.2926(6)	0.2183(5)	6.1(4)
C(13)	-0.2890(9)	0.3141(7)	0.2281(6)	6.7(4)
C(14)	-0.3128(9)	0.3401(7)	0.2825(6)	7.0(4)
C(15)	-0.2281(9)	0.3448(6)	0.3255(5)	5.0(3)
C(16)	-0.1184(8)	0.3235(5)	0.3167(4)	3.7(3)
C(21)	0.0425(9)	0.1910(4)	0.2883(4)	4.0(3)
C(22)	-0.029(1)	0.1472(5)	0.2627(5)	6.0(3)
C(23)	-0.042(1)	0.0917(6)	0.2862(7)	8.4(5)
C(24)	0.022(1)	0.0771(6)	0.3372(8)	11.0(5)
C(25)	0.093(1)	0.1196(7)	0.3656(6)	8.7(5)
C(26)	0.102(1)	0.1770(5)	0.3404(5)	6.1(4)
C(31)	0.3237(8)	0.4064(4)	0.3110(4)	2.9(2)
C(32)	0.3482(9)	0.3821(4)	0.3664(5)	4.1(3)
C(33)	0.4467(9)	0.4011(5)	0.4006(5)	4.9(3)
C(34)	0.5159(9)	0.4431(6)	0.3817(5)	5.3(3)

Table 2.5. (continued).

C(35)	0.489(1)	0.4709(6)	0.3261(6)	6.7(4)
C(36)	0.396(1)	0.4510(5)	0.2909(4)	5.2(3)
C(41)	0.0804(8)	0.4315(4)	0.2769(4)	3.1(2)
C(42)	-0.0075(8)	0.4427(5)	0.2347(4)	3.8(3)
C(43)	-0.1026(9)	0.4784(5)	0.2481(5)	4.8(3)
C(44)	-0.111(1)	0.5028(6)	0.3025(6)	6.2(3)
C(45)	-0.025(1)	0.4928(6)	0.3459(5)	6.0(3)
C(46)	0.0685(9)	0.4571(5)	0.3338(4)	4.8(3)
C(51)	0.0901(8)	0.2450(4)	-0.0105(4)	3.1(2)
C(52)	0.1334(8)	0.2537(5)	-0.0675(4)	3.9(3)
C(53)	0.057(1)	0.2653(5)	-0.1154(4)	5.1(3)
C(54)	-0.061(1)	0.2674(5)	-0.1089(5)	5.2(3)
C(55)	-0.1069(8)	0.2567(5)	-0.0546(5)	4.6(3)
C(56)	-0.0300(8)	0.2466(5)	-0.0052(4)	3.8(2)
C(61)	0.2296(8)	0.1503(4)	0.0416(4)	3.3(2)
C(62)	0.1476(9)	0.1058(5)	0.0493(5)	4.5(3)
C(63)	0.177(1)	0.0455(5)	0.0373(6)	6.9(4)
C(64)	0.280(1)	0.0298(5)	0.0193(6)	7.2(4)
C(65)	0.363(1)	0.0743(5)	0.0108(6)	5.8(3)
C(66)	0.3372(9)	0.1335(5)	0.0222(5)	4.5(3)
C(71)	0.4712(8)	0.3765(4)	0.0566(4)	3.6(2)

Table 2.5. (continued).

C(72)	0.559(1)	0.3404(6)	0.0429(7)	6.7(4)
C(73)	0.671(1)	0.3638(7)	0.0395(7)	8.1(5)
C(74)	0.694(1)	0.4205(6)	0.0497(7)	7.5(4)
C(75)	0.608(1)	0.4541(7)	0.061(1)	18.3(8)
C(76)	0.497(1)	0.4337(6)	0.065(1)	15.5(7)
C(81)	0.2369(8)	0.3855(4)	-0.0004(4)	3.2(2)
C(82)	0.2805(9)	0.3842(5)	-0.0570(4)	4.0(3)
C(83)	0.217(1)	0.4061(5)	-0.1059(4)	5.0(3)
C(84)	0.109(1)	0.4274(6)	-0.0997(5)	5.7(3)
C(85)	0.0602(9)	0.4288(5)	-0.0446(5)	5.3(3)
C(86)	0.1277(9)	0.4078(5)	0.0050(4)	3.8(3)

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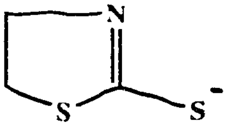
[a] See footnote (a) of Table 2.4. [b] Atoms of CH_2Cl_2 molecule of crystallization

Discussion

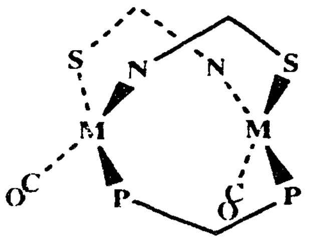
Previous studies[3m,n] have shown that 2-mercaptothiazolinate (mtz) coordinates to two metal centers through the mercapto sulfur and the



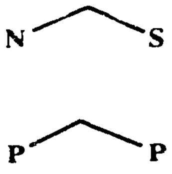
nitrogen atoms, and the complexes so-formed have typical open-book structures. Although a series of mtz-bridged complexes of rhodium, containing monodentate tertiary phosphine ligands such as PPh_3, have been reported,[3m] no complex involving both this anionic bridge and diphosphine ligands such as $PPh_2CH_2PPh_2$ (dppm) has been prepared. In fact, among the numerous open-book compounds reported, none of them contains a diphosphine group. Given the fact that the dppm- and the anion-bridged binuclear complexes represent two major classes of compounds of Rh and Ir, we were interested in the introduction of the dppm group into the mtz-bridged open-book framework.

In the previous study[3m] tetracarbonyl species such as $[Rh(CO)_2(\mu\text{-}mtz)]_2$ were shown to react readily with tertiary phosphines to yield complexes such as $[Rh(CO)(PPh_3)(\mu\text{-}mtz)]_2$. These species were also utilized in this study for the preparation of diphosphine complexes. Although the tetracarbonyl species $[Rh(CO)_2(\mu\text{-}mtz)]_2$ has been described,[3m] the diiridium analogue $[Ir(CO)_2(\mu\text{-}mtz)]_2$ had not previously been reported. Both are prepared by the reaction of their cyclooctadiene precursors, $[M(COD)(\mu\text{-}mtz)]_2$ with CO in THF.[3n] Neither species was isolated but each was reacted in situ with the appropriate diphosphine to obtain the desired product. The IR spectrum of the diiridium tetracarbonyl precursor displays the expected carbonyl bands (2075, 2040, 2005 and 1990 cm^{-1}) typical of these open-book complexes.[3j,l,m]

As was the case for monodentate phosphines, these tetracarbonyl species react readily with the diphosphine, dppm ($Ph_2PCH_2PPh_2$) yielding the dppm-bridged products, $[M_2(CO)_2(\mu\text{-mtz})_2(dppm)]$ (M = Rh (**1**), Ir (**2**)), as shown below. In these complexes the mtz ligand again coordinates through the mercapto sulfur and the nitrogen atoms, as is observed for the monodentate phosphine compounds noted.[3m] For the rhodium species **1** the two carbonyl stretches in the IR spectrum (1995, 1948 cm^{-1}) display a significantly larger separation than those of the PPh_3 analogue (1974, 1966 cm^{-1}). This is probably a consequence of the geometrical difference in these two species. In the PPh_3 adduct the phosphines have a trans disposition at the two metals and both carbonyl groups are opposite the nitrogen ends of the bridging mtz ligands.[3m] In **1** and **2** however the bridging dppm group demands that the ends of the diphosphine group be mutually cis, so assuming a head-to-tail arrangement of mtz ligands, one carbonyl will be



M = Rh (1); Ir (2)



= mtz

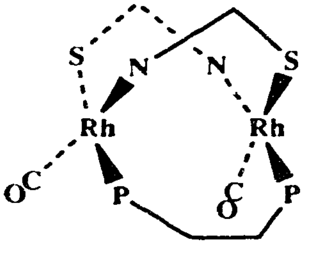
= $PPh_2CH_2PPh_2$

trans to nitrogen while the other is opposite sulfur. A head-to-tail arrangement is most often seen in binuclear complexes containing these anionic three-atom bridges,[3b,g,h,k,l] mentioned in the previous chapter, although the head-to-head arrangement has also been reported.[3j] The head-to-tail arrangement in **1** gives rise to two chemically inequivalent phosphorus nuclei (also opposite either N or S) as shown in the $^{31}P\{^1H\}$ NMR spectrum, which displays two doublets of doublets at δ 30.8 ($^1J_{RhP}$ = 153.4 Hz, $^2J_{PP}$ = 58.2 Hz) and δ 45.9 ($^1J_{RhP}$ = 142.8 Hz). This geometry also leads to the inequivalence of all ten methylene protons associated with the dppm and mtz groups, although owing to overlap of two of these resonances in the ^1H NMR spectrum only nine are resolved (Table 2.2). The proton resonances for the dppm group (δ 4.20, 3.70) were identified by the appropriate ^{31}P-decoupling experiments. The spectroscopic parameters for **2** are comparable to those of **1** suggesting similar structures.

Although these species have been identified as open-book species having a bridging dppm group, they can also be viewed as A-frame complexes having the dppm and one of the mtz groups in mutually trans bridging positions and the other mtz group in the apical position opposite the carbonyls. In these compounds, with three similar bridging groups, the A-frame and open-book formulations are clearly two equivalent ways of categorizing the same structure. In fact, A-frame and open-book structures have several points in common, as noted in Chapter 1; both are composed of two square-planar fragments held in close proximity, and their valence orbitals are very similar.[16]

Reaction of $[Rh(CO)_2(\mu\text{-mtz})]_2$ with 1 equiv of dppe

($PPh_2PCH_2CH_2PPh_2$) yields [$Rh_2(CO)_2(\mu\text{-mtz})_2(\mu\text{-dppe})$] (**3**), an unusual example of a dppe-bridged species, analogous to compounds **1** and **2**. This species is extremely air sensitive and was only characterized spectroscopically. Its IR spectrum shows two carbonyl stretches like those



(3)

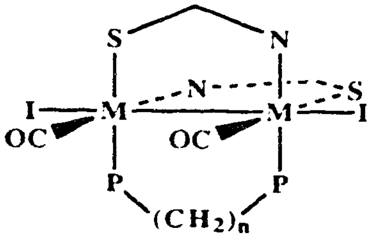
= $PPh_2CH_2CH_2PPh_2$

of the dppm analogue **1**, and its $^{31}P\{^1H\}$ NMR spectrum shows two resonances, at δ 39.1 ($^1J_{RhP}$ = 157.8 Hz, $^3J_{PP}$ = 2.6 Hz) and δ 40.2 ($^1J_{RhP}$ = 147.6 Hz). The positions of these resonances are almost identical with that of the triphenylphosphine analogue, [$Rh(CO)(PPh_3)(\mu\text{-mtz})]_2$ (δ 39.8), consistent with a bridging instead of a chelating dppe. The phosphorus chemical shift of the dppe group, when involved in a five-membered chelate ring, is often found significantly deshielded compared with those seen for nonchelated compounds.[17] A example is seen in the compounds [RhCl(CO)(dppe)] and *trans*-[$RhCl(CO)(PEtPh_2)_2$], the former of which shows a down-field shift of ca. 30 ppm vs. the latter (δ 27) in the $^{31}P\{^1H\}$ NMR spectrum.[18] Although the 3-bond P-P coupling in **3** is much smaller than that observed in some other dppe-bridged complexes such as [$WM(CO)_{10}(\mu\text{-dppe})$] (M = Cr, Mo, W), for which values of *ca.* 35 Hz are observed,[19] it is comparable to the results obtained for [$Ru_4H_4(CO)_{10}(\mu$-

dppe)], for which no P-P coupling was observed.[20] It should be noted that for both free and coordinated diphosphine molecules, the conformation of the molecular backbone as well as the hybridization of the phosphines is crucial in influencing the coupling between the nuclei.[21]

The ^1H NMR spectrum of **3** resembles those of **1** and **2**, suggesting a structure similar to the dppm analogues, as shown. The four resonances (δ 4.20, 3.73, 2.37, 1.80) assigned to the dppe group were identified by broadband ^{31}P decoupling.

One of the unique reactivity patterns of binuclear compounds is the transannular oxidative-addition reaction, which results in a formal one electron oxidation of each metal, and is often accompanied by metal-metal bond forming or breaking.[3a,e,i,l] Although the monophosphine complexes $[M(CO)(PR_3)(\mu\text{-mtz})]_2$ (M=Rh, Ir; R=Ph, Me) each gives mixtures of several species in the reaction with halogens,[4] all three diphosphine-bridged species **1-3** readily undergo transannular oxidative addition of I_2 to cleanly yield the respective products, **4-6**, diagrammed below. In these three products the IR spectra show two carbonyl stretches, the frequencies



M = Rh, n = 1 (4); n = 2 (6)
= Ir, n = 1 (5)

of which have increased by *ca.* 70 cm^{-1} from those of the precursors, as expected for the oxidation of the metals from the +1 to the +2 oxidation state. The $^{31}P\{^1H\}$ NMR spectra for all three compounds are consistent with two chemically different phosphorus environments, one opposite sulfur and the other opposite nitrogen. For **4** the Rh-P and P-P couplings are not immediately obvious owing to the complexity of the spectrum, however for **5** and **6** the $^{31}P\{^1H\}$ spectra are simple, both appearing as two sets of doublets, resulting from two-bond phosphorus-phosphorus coupling in **5** and one-bond rhodium-phosphorus coupling in **6**. No P-P coupling is resolved in the spectrum of **6**. Other spectral parameters, shown in Table 2.2, are in agreement with these structural formulations, which have been verified by the X-ray structure determination of **6**.

The structure of $[Rh_2I_2(CO)_2(\mu\text{-mtz})_2(\mu\text{-dppe})]$ (**6**) is shown in Figure 2.1, and the associated structural parameters are summarized in Tables 2.6 and 2.7. This determination clearly confirms the binuclear, dppe-bridged structure, in which the two cis-oriented mtz ligands bridge in a head-to-tail arrangement. In this geometry the complex can again be viewed as an open-book complex bridged by dppe or it can be thought of as resembling an A-frame complex, except with rather substantial distortions resulting from the small bite of the mtz ligands combined with the wide bite of the dppe group. In this latter formulation the dppe and mtz groups, which are mutually trans, take the positions occupied by dppm groups in the majority of A-frames, while the other mtz ligand occupies the apical site opposite the carbonyls. Both iodo ligands occupy the positions on each metal opposite the Rh-Rh bond, giving the metals octahedral geometries.

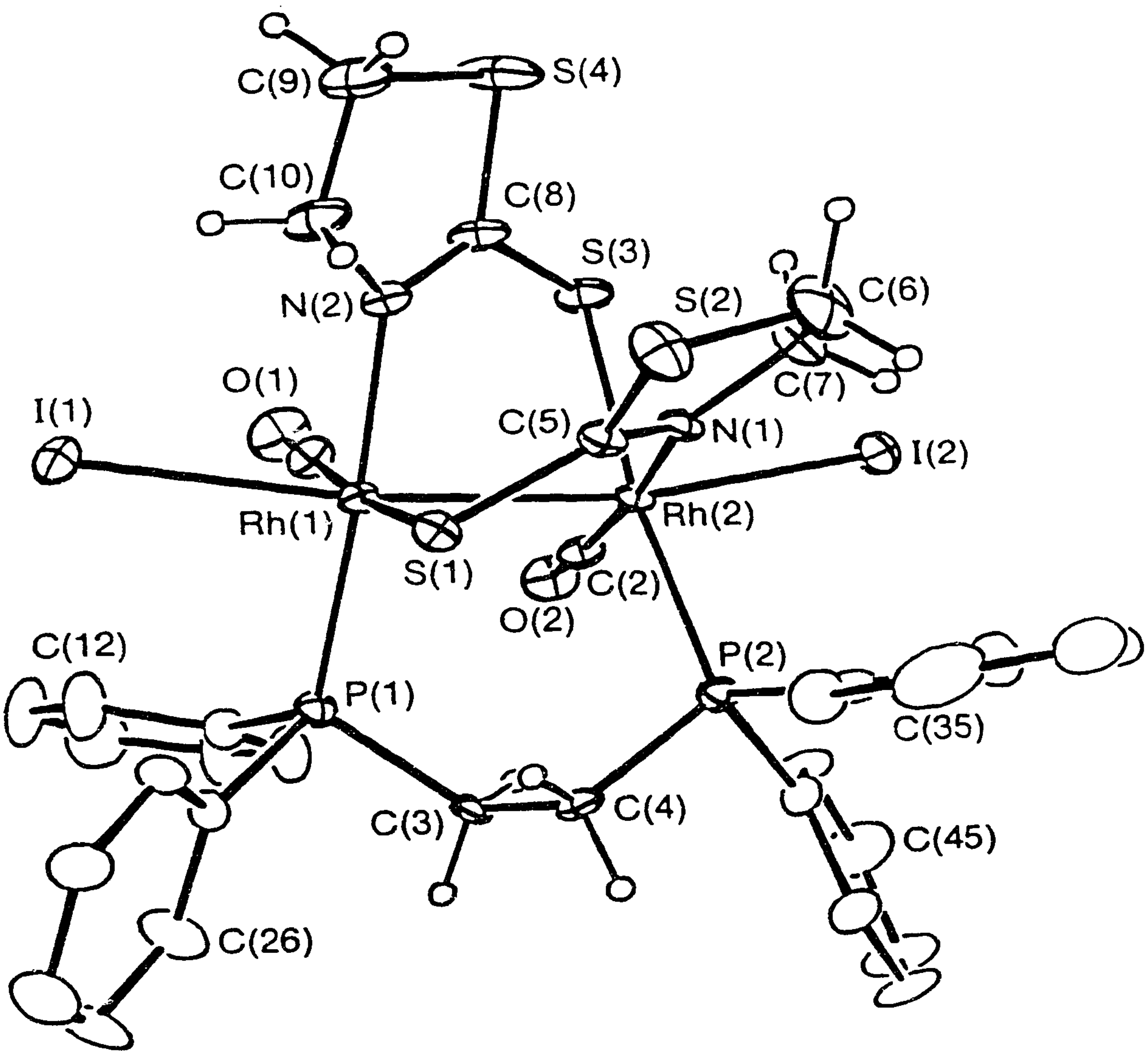


Figure 2.1. Perspective view of complex 6, showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens, which are shown arbitrarily small. Phenyl hydrogens are omitted.

Table 2.6. Selected Distances (Å) in $[Rh_2I_2(CO)_2(\mu\text{-mtz})_2(\mu\text{-dppe})]\cdot THF$ (6)

Rh(1)-Rh(2)	2.748 (1)	Rh(1)-I(1)	2.788 (1)
Rh(1)-S(1)	2.382 (2)	Rh(1)-P(1)	2.317(2)
Rh(1)-N(2)	2.132 (5)	Rh(1)-C(1)	1.892 (7)
Rh(2)-I(2)	2.794 (1)	Rh(2)-S(3)	2.418 (2)
Rh(2)-P(2)	2.333 (2)	Rh(2)-N(1)	2.099 (5)
Rh(2)-C(2)	1.842 (7)	S(1)-C(5)	1.737 (6)
S(3)-C(8)	1.724 (7)	S(2)-C(5)	1.758 (6)
S(2)-C(6)	1.712 (8)	S(4)-C(8)	1.754 (7)
S(4)-C(9)	1.772 (8)	P(1)-C(3)	1.821 (6)
P(1)-C(11)	1.820 (7)	P(1)-C(21)	1.829 (6)
P(2)-C(4)	1.809 (6)	P(2)-C(31)	1.806 (7)
P(2)-C(41)	1.816 (7)	O(1)-C(1)	1.139 (8)
O(2)-C(2)	1.133 (7)	N(1)-C(5)	1.270 (7)
N(1)-C(7)	1.430 (8)	N(2)- C(8)	1.280 (8)
N(2)-C(10)	1.453 (8)	C(3)-C(4)	1.522 (8)
C(6)-C(7)	1.47 (1)	C(9)-C(10)	1.453 (9)

Table 2.7. Selected Angles (deg) in

[$Rh_2I_2(CO)_2(\mu$-mtz$)_2(\mu$-dppe$)]\cdot$THF (6)

a. Bond angles.

I(1)-Rh(1)-Rh(2)	171.61 (2)	I(1)-Rh(1)-S(1)	97.51 (5)
I(1)-Rh(1)-P(1)	89.21 (5)	I(1)-Rh(1)-N2	87.8 (1)
I(1)-Rh(1)-C(1)	83.6 (2)	Rh(2)-Rh(1)-S(1)	86.73 (5)
Rh(2)-Rh(1)-P(1)	97.72 (5)	Rh(2)-Rh(1)-N(2)	85.4 (1)
Rh(2)-Rh(1)-C(1)	91.4 (2)	S(1)-Rh(1)-P(1)	94.29 (6)
S(1)-Rh(1)-N(2)	84.5 (1)	S(1)-Rh(1)-C(1)	173.5 (2)
P(1)-Rh(1)-N(2)	176.6 (1)	P(1)-Rh(1)-C(1)	92.1 (2)
N(2)-Rh(1)-C(1)	89.2 (3)	I(2)-Rh(2)-Rh(1)	166.88 (2)
I(2)-Rh(2)-S(3)	83.22 (5)	I(2)-Rh(2)-P(2)	90.54 (5)
I(2)-Rh(2)-N(1)	97.6 (1)	I(2)-Rh(2)-C(2)	87.3 (2)
Rh(1)-Rh(2)-S(3)	84.09 (6)	Rh(1)-Rh(2)-P(2)	102.38 (5)
Rh(1)-Rh(2)-N(1)	85.3 (1)	Rh(1)-Rh(2)-C(2)	89.3 (2)
S(3)-Rh(2)-P(2)	172.03 (7)	S(3)-Rh(2)-N(1)	88.3 (1)
S(3)-Rh(2)-C(2)	89.6 (2)	P(2)-Rh(2)-N(1)	87.6 (1)
P(2)-Rh(2)-C(2)	95.0 (2)	N(1)-Rh(2)-C(2)	174.3 (3)
Rh(1)-S(1)-C(5)	99.8 (2)	C(5)-S(2)-C(6)	89.2 (3)
Rh(2)-S(3)-C(8)	100.3 (2)	C(8)-S(4)-C(9)	90.1 (3)
Rh(1)-P(1)-C(3)	116.2 (2)	Rh(1)-P(1)-C(11)	113.8 (2)
Rh(1)-P(1)-C(21)	118.5 (2)	C(3)-P(1)-C(11)	103.7 (3)
C(3)-P(1)-C(21)	99.1 (3)	C(11)-P(1)-C(21)	103.4 (3)
Rh(2)-P(2)-C(4)	113.3 (2)	Rh(2)-P(2)-C31	112.1 (2)

Table 2.7. (continued).

Rh(2)-P(2)-C41	121.3 (2)	C(4)-P(2)-C31	107.3 (3)
C(4)-P(2)-C(41)	98.1 (3)	C(31)-P(2)-C(41)	103.1 (3)
Rh(2)-N(1)-C(5)	124.5 (4)	Rh(2)-N(1)-C(7)	123.6 (4)
C(5)-N(1)-C(7)	111.7 (5)	Rh(1)-N(2)-C(8)	123.0 (4)
Rh(1)-N(2)-C(10)	124.8 (4)	C(8)-N(2)-C(10)	111.6 (5)
Rh(1)-C(1)-O(1)	177.1 (6)	Rh(2)-C(2)-O(2)	177.0 (6)
P(1)-C(3)-C(4)	113.0 (4)	P(2)-C(4)-C(3)	110.1 (4)
S(1)-C(5)-S(2)	115.7 (3)	S(1)-C(5)-N(1)	127.4 (5)
S(2)-C(5)-N(1)	116.9 (5)	S(2)-C(6)-C(7)	109.8 (5)
N(1)-C(7)-C(6)	110.6 (6)	S(3)-C(8)-S(4)	117.5 (4)
S(3)-C(8)-N(2)	125.7 (5)	S(4)-C(8)-N(2)	116.8 (5)
S(4)-C(9)-C(10)	108.0 (5)	N(2)-C(10)-C(9)	112.5 (6)

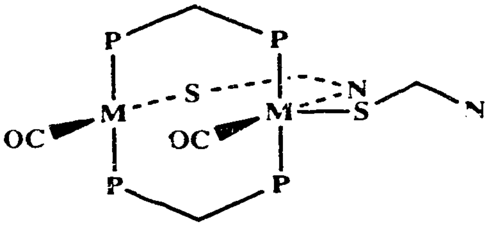
b. Torsion angles.

S(1)-Rh(1)-Rh(2)-N(1)	29.3 (2)
N(2)-Rh(1)-Rh(2)-S(3)	33.3 (2)
P(1)-Rh(1)-Rh(2)-P(2)	36.69(8)
P(1)-C(3)-C(4)-P(2)	99.0 (5)

The Rh-Rh separation of 2.748(1) Å is consistent with a single bond, as expected between the two Rh(II) centers. The octahedra are offset from each other in two ways. First they are inclined about the axial directions by a dihedral angle of 16.4° owing to the differing bites of the mtz and dppe groups, as noted. These different bites are clearly seen in the N(2)-S(3) and P(1)-P(2) non-bonded separations of 2.685(6) and 3.841(3) Å, respectively. Second, the octahedra are staggered about the Rh-Rh bond by an average torsion angle of *ca.* 33°. Although this skewing may be required to minimize non-bonded contacts between the carbonyl groups, it is more likely necessary in order to accommodate the bridging dppe ligand. A similar twisting of the metal framework has been observed in dppe-bridged complexes of rhenium in which torsion angles up to 50° have been noted.[22]

Most parameters within the complex are normal, therefore the Rh-P distances (2.317(2), 2.333(2)Å) are in good agreement, and resemble the analogous distances in dppm-bridged complexes. The Rh-S and Rh-N distances are also normal, except that the distances for groups opposite dppe are longer than those opposite the carbonyls (Rh-S = 2.418(2), 2.382(2)Å; Rh-N = 2.132(5), 2.099(5)Å). This is the opposite of that observed in the related species $[Rh(CO)(PPh_3)(\mu\text{-}SPh)]_2$, in which the Rh-S bonds opposite phosphorus were found to be shorter than those opposite CO.[23]

Unlike diphosphine bridges which are generally rather inert, the mercaptothiazolinate bridges are quite labile and are readily broken.[4] It was therefore of interest to determine whether both mtz bridges would remain intact upon reaction with two equivalents of dppm. Given the overwhelming preference of dppm to bridge metals, and the unlikelihood that both dppm *and* both mtz ligands would simultaneously bridge, it was anticipated that one or both mtz ligands might move from their bridging sites. Treatment of $[M(CO)_2(\mu\text{-mtz})]_2$ (M = Rh, Ir) with two equiv of dppm yields $[M_2(CO)_2(\eta^1\text{-mtz})(\mu\text{-mtz})(dppm)_2]$ (M = Rh (7), Ir (8)) as diagrammed below. The diiridium species **8** displays two signals in the $^{31}P\{^1H\}$ NMR

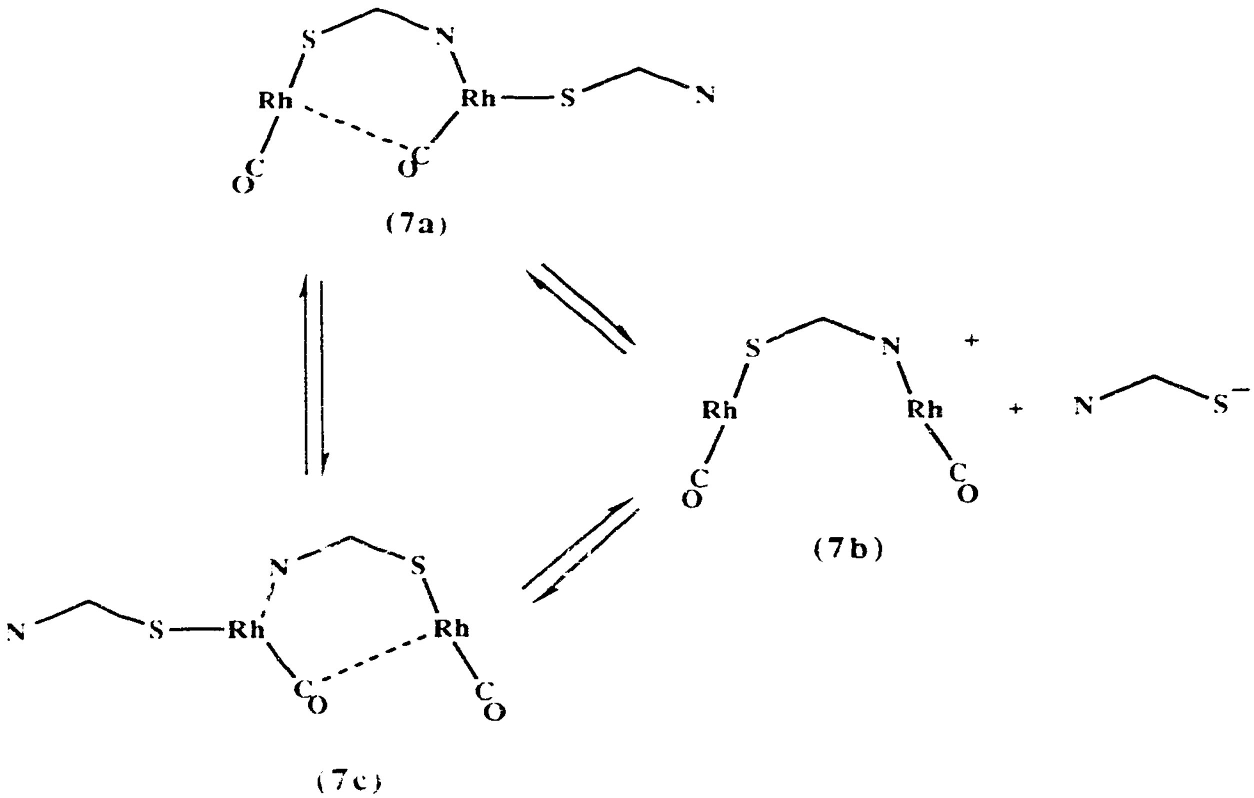


M = Rh (7); Ir (8)

spectrum, characteristic of an AA'BB' spin system and shows four resonances in the ^1H NMR spectrum for the mtz methylene hydrogens at δ 4.41, 3.30, 2.68 and 1.67, in addition to the dppm resonances. Based on a comparison with the resonances for the free mtz anion, at δ 4.0 and 3.6, the low-field resonances above are attributed to the dangling group, while the high-field pair are identified as those of the bridging group. The dangling mtz ligand, as shown above, is proposed to coordinate through the sulfur end, as often suggested for closely-related ligands in other complexes.[3h,24] In the IR spectrum of **8** the two carbonyl bands (1946, 1896 cm^{-1}) are consistent with terminally bound carbonyls, although the lower frequency stretch suggests that this may result from a weak semi-bridging interaction with the second metal, as is demonstrated for 7 (*vide infra*). The $^{13}C\{^1H\}$

NMR spectrum of **8** displays two sharp triplets at -70°C, the high-field one of which becomes broad and featureless at room temperature, without changing significantly in position. The reason for the broadening is not obvious, since the ^1H and $^{31}P\{^1H\}$ NMR spectra remain invariant over the same temperature range.

In contrast to **8**, compound **7** shows strong temperature dependence in the ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra, and its solution IR spectra are more complicated than expected for a dicarbonyl. In the solid the IR spectrum of **7** displays the two bands expected at 1926 and 1825 cm^{-1}; again the low-frequency band is suggestive of a semibridging mode as shown for structure **7a** in Scheme I. However in solution four carbonyl stretches are observed. The lower frequency pair (1936, 1820 cm^{-1}), which are close to those of the solid, appear to correspond to **7a** while those at 2000 and 1973 cm^{-1} appear to arise from the cationic species **7b**, which results from mercaptothiazolinate ion dissociation. Addition of excess mtz$^-$ (as the sodium salt) supports this proposed equilibrium, causing a decrease in the intensity of the two high-frequency bands and an increase in those ascribed to **7a**. This equilibrium is also apparent in the NMR spectra. Although at ambient temperature the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra each displays two broad resonances, lowering the temperature to -80°C gives rise to four resonances in each case, and these can be grouped into pairs corresponding to a major and a minor species in an 1.5 : 1 approximate ratio. In the ^1H NMR spectrum of **7** at ambient temperature the methylene protons of the mtz groups appear as four triplets at δ 4.32, 3.15, 2.70 and 1.83. Addition of free mtz$^-$ to a solution of **7** results in an



Scheme I

increase in the intensity of the two low-field resonances, which also shift towards the resonances for free mtz⁻ (δ 4.0, 3.6) as additional ligand is added. This clearly demonstrates the equilibrium between the species containing the dangling mtz group (**7a**) and the cationic species **7b**. At -80°C, the two high-field triplets (δ 2.70, 1.83), due to the bridging mtz ligand, split to two pairs of triplets (δ 2.72, 1.18 and δ 2.39, 1.43) with a ratio similar to that noted above, corresponding to **7a** and **7b**. Analogous splitting is also observed for the dppm methylene hydrogens. At the same temperature the $^{31}P\{^{1}H\}$ NMR spectrum displays two pairs of multiplets for **7a** (δ 32.5, 26.5) and **7b** (δ 30.0, 20.6) having a AA'BB'XY spin pattern as expected. The assignment of **7a** and **7b** is based on the close resemblance of the spectral parameters for the minor species (**7b**) to those of the cationic species, $[Rh_2(CO)_2(\mu\text{-mtz})(dppm)_2][X]$ (X = Cl (**9b**), PF_6 (**9c**)) (*vide infra*). In the $^{13}C\{^1H\}$ NMR spectrum of **7** at -80°C the resonance at δ 193.3 ($^1J_{RhC}$ = 74.6 Hz, $^2J_{PC}$ = 16 Hz) is assigned to the terminal carbonyl of **7a** and the broad doublet at δ 211.8 is ascribed to the semibridging carbonyl of this species. Broad-band ^{31}P decoupling experiments clearly show this semibridging interaction, as the low-field ^{13}C resonance transforms from a broad doublet to a doublet of doublets with 67 Hz coupling to one rhodium and 13 Hz coupling to the other. The signals arising from the carbonyls of **7b** are overlapped by the high-field ^{13}C resonance of **7a**, as indicated by the broadness of the bottom part of the latter as well as by its integration. Selective homonuclear decoupling experiments point to an additional fluxionality which occurs slowly on the NMR time scale. Irradiation of one of the methylene resonances of the bridging mtz group causes the other methylene resonance of this group to collapse to a singlet, as expected. However, unexpectedly this also results in a significant decrease in the intensity of the corresponding methylene resonance of the dangling group. This observation of spin saturation transfer indicates a slow exchange of terminal and bridging mtz groups as diagrammed in Scheme I. Attempts to increase the rate of terminal-bridging mtz exchange to achieve rapid interconversion, by raising the temperature, were unsuccessful since the compound decomposed at temperatures above ca. 45°C.

Complexes containing two bridging dppm groups and a bridging mtz ligand can also be obtained by the reactions of *trans*-[MCl(CO)(dppm)]$_2$ (M = Rh, Ir) with sodium mercaptothiazolinate. When two equiv of mtz$^-$ are used, compounds **7** and **8** are obtained, as seen in the reactions of [M(CO)$_2$(μ-mtz)]$_2$ with two equiv of dppm. When the above dppm-bridged dichloro complexes are reacted with only one equiv of mtz$^-$, replacement of only one chloride ligand occurs yielding [M$_2$Cl(CO)$_2$(μ-mtz)(dppm)$_2$] (M = Rh(**9a**), Ir(**10**)). The spectral parameters for **10** (see Tables 2.1 and 2.2) are closely comparable to those of **8**, apart from the absence of resonances for the dangling mtz group in the ^{1}H NMR spectrum, and the compound is not conducting in CH$_2$Cl$_2$ ($\Lambda < 4\ \Omega^{-1}$ cm^{2}mol^{-1}), so is assigned an analogous structure in which the dangling mtz group in **8** is replaced by a terminal chloro ligand in **10**.

Although **9a** is shown earlier as having a coordinated chloro ligand, in solution it, like compound 7, is better represented as an equilibrium mix of the neutral species **9a** together with the species **9b**, resulting from chloride dissociation as shown in eq. 1. This is clearly seen in the IR

$$\underset{(\mathbf{9a})}{[\mathrm{Rh_2Cl(CO)_2(\mu\text{-}mtz)(dppm)_2}]} \rightleftharpoons \underset{(\mathbf{9b})}{[\mathrm{Rh_2(CO)_2(\mu\text{-}mtz)(dppm)_2}][\mathrm{Cl}]} \qquad (1)$$

spectrum in solution which displays three carbonyl stretches at 2001, 1970 and 1933 cm^{-1}. The middle band is broad and apparently results from two overlapping bands, so the stretches due to **9a** appear at 1970 and 1933 cm^{-1} whereas those of **9b** appear at 2001 and 1970 cm^{-1}. Addition of AgBF$_4$ to solutions of **9** results in the disappearance of the 1933 cm^{-1} band and sharpening of the central band, and addition of sodium chloride causes these bands to reappear. In the solid state the two carbonyl bands observed (1988, 1953 cm^{-1}) are consistent with the ionic structure **9b**, and this is confirmed by an X-ray structure determination of this species (*vide infra*).

As was noted for **7a** and **7b**, the exchange between **9a** and **9b** is fast on the NMR time scale. Thus at ambient temperature the $^{31}P\{^1H\}$ NMR spectrum of the equilibrium mixture displays two broad resonances, while the ^1H NMR spectrum shows only two triplets (δ 2.43, 1.85) for the mtz methylene protons. Lowering the temperature sharpens the signals in the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra. However in contrast to the equilibrium involving 7a and **7b**, only one species is revealed at -80°C, the spectroscopic parameters of which closely resemble those of $[Rh_2(CO)_2(\mu\text{-}mtz)(dppm)_2][PF_6]$ (**9c**) obtained by reaction of **9**(**a**, **b**) with $AgPF_6$. Therefore it is clear that lowering the temperature shifts the equilibrium in favor of **9b**. At -80°C, the $^{31}P\{^1H\}$ NMR spectrum of **9b** is as expected for an unsymmetric structure, and the $^{13}C\{^1H\}$ NMR spectrum reveals two doublets of triplets at δ 194.4 and 193.4, reminiscent of those of **7b**. The mtz methylene hydrogens appear as triplets in the ^1H NMR spectrum at δ 2.39 and 1.46.

Among the dppm-bridged binuclear compounds of group VIII metals, complexes **7-10** represent a new type of A-frames, in which the capping ligand is bifunctional, and because of this the two metal centers in these A-frames are electronically different, which could give rise to interesting reactivity patterns. The bifunctional feature of the apical mtz ligand also provides a easy access to coordinative unsaturation through cleavage of one of its ends, which is shown to be feasible by the dynamic behavior of 7. Coordinative unsaturation induced by bridge opening has been proposed to be crucial in substrate activation by open-book compounds,[5] as noted earlier. A-frame complexes of group VIII metals, in which the apical ligands are those typically used as bridges in open-book compounds such as pyrazolyl, have been reported recently.[2b,c,f,g] However none of these apex ligands is bifunctional.

The structure of **9b**, as the methylene chloride solvate, has been determined and a representation of the cation is shown in Figure 2.2, while selected bond distances and angles are given in Tables 2.8 and 2.9, respectively. This compound much more resembles conventional "A-frames" than does **6**, in that the trans-bridging groups are dppm with the anionic group (mtz$^-$) at the apex opposite the carbonyls. In fact the structure quite closely resembles that of $[Rh_2(CO)_2(\mu\text{-dmpz})(dppm)_2]^+$,[2g] (dmpz = 3,5-dimethylpyrazolate). The structure determination clearly shows that the chloride ion is not associated with the complex, and the closest contact between rhodium and this anion is 6.842(2) Å. Similarly the CH_2Cl_2 molecule is isolated from both the anion and the cation. Although the geometries about the Rh centers are essentially square planar, there are significant distortions from the idealized geometry. Therefore the N(1)-Rh(1)-C(1) angle is 172.9(2)° and the S(1)-Rh(2)-C(2) angle is 151.9(2)°, resulting from an apparent movement of C(1)O(1) towards Rh(2) and C(2)O(2) away from Rh(1). We believe that these distortions result from the packing. As can be seen in Figure 2.2, phenyl rings 4 and 8 are aimed between the carbonyls and the short C(2)-H(42) and

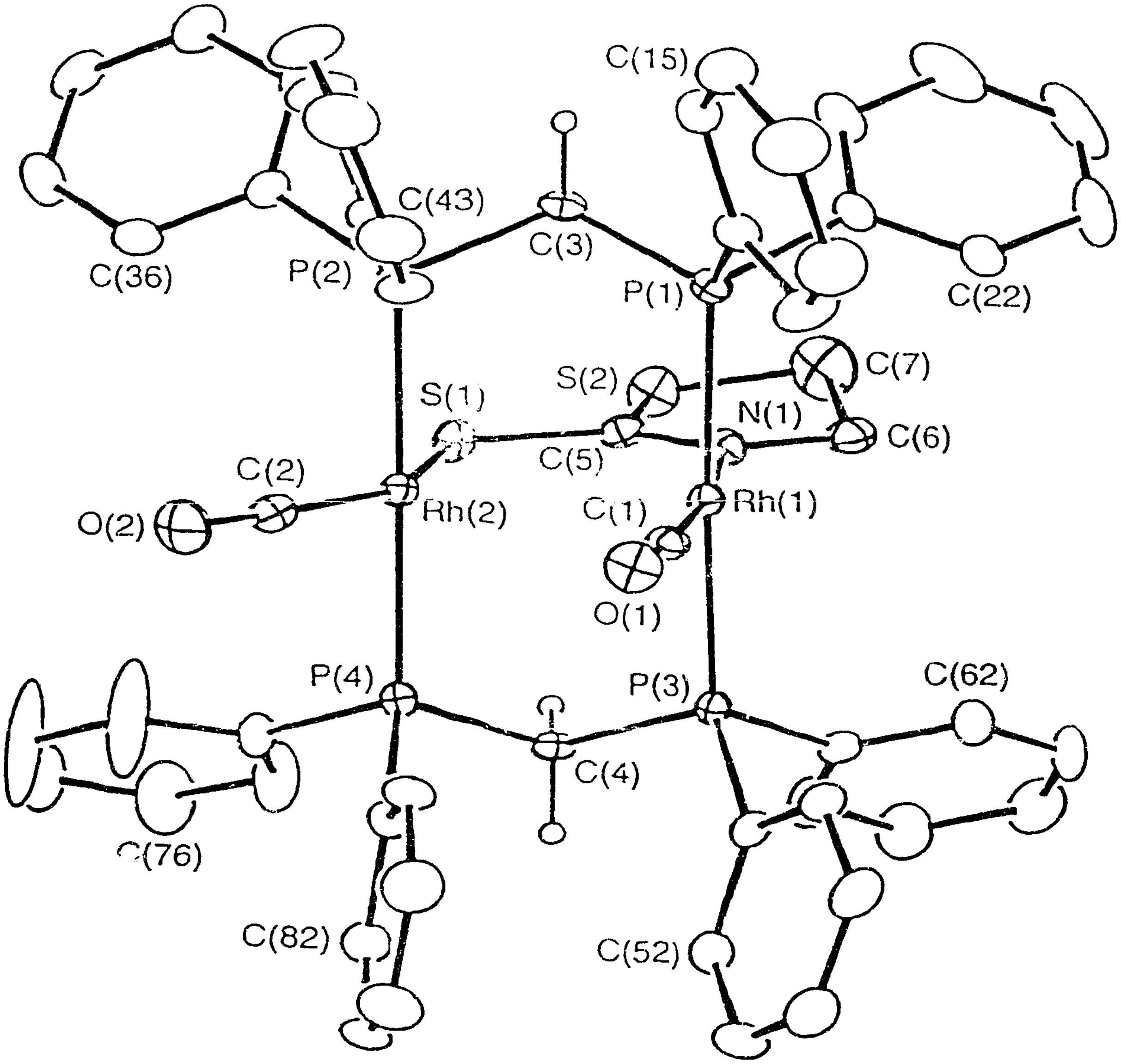


Figure 2.2. Perspective view of the cation of complex **9b**, showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens, which are shown arbitrarily small. Phenyl hydrogens are omitted.

Table 2.8. Selected Distances (Å) in $[Rh_2(CO)_2(\mu\text{-mtz})(dppm)_2][Cl]\cdot CH_2Cl_2$ (9b)

Rh(1)-P(1)	2.339 (2)	Rh(1)-P(3)	2.346 (2)
Rh(2)-P(2)	2.320 (2)	Rh(2)-P(4)	2.324 (2)
Rh(2)-S(1)	2.422 (2)	Rh(1)-N(1)	2.096 (5)
Rh(1)-C(1)	1.811 (7)	Rh(2)-C(2)	1.824 (7)
S(1)-C(5)	1.719 (6)	S(2)-C(5)	1.775 (6)
S(2)-C(7)	1.78 (1)	P(1)-C(3)	1.809 (6)
P(1)-C(11)	1.801 (6)	P(1)-C(21)	1.838 (7)
P(2)-C(3)	1.829 (6)	P(2)-C(31)	1.836 (6)
P(2)-C(41)	1.826 (6)	P(3)-C(4)	1.838 (6)
P(3)-C(51)	1.820 (6)	P(3)-C(61)	1.840 (7)
P(4)-C(4)	1.823 (6)	P(4)-C(71)	1.848 (6)
P(4)-C(81)	1.837 (6)	O(1)-C(1)	1.159 (7)
O(2)-C(2)	1.147 (8)	N(1)-C(5)	1.282 (7)
N(1)-C(6)	1.472 (8)	C(6)-C(7)	1.46 (1)

Table 2.9. Selected Angles (deg) in $[Rh_2(CO)_2(\mu\text{-mtz})(dppm)_2][Cl]\cdot CH_2Cl_2$ (9b)

P(1)-Rh(1)-P(3)	174.96(6)	P(1)-Rh(1)-N(1)	87.3 (1)
P(1)-Rh(1)-C(1)	92.4 (2)	P(3)-Rh(1)-N(1)	88.1 (1)
P(3)-Rh(1)-C(1)	92.4 (2)	N(1)-Rh(1)-C(1)	172.9 (2)
S(1)-Rh(2)-P(2)	86.69 (6)	S(1)-Rh(2)-P(4)	88.86 (6)
S(1)-Rh(2)-C(2)	151.9 (2)	P(2)-Rh(2)-P(4)	175.27 (6)
P(2)-Rh(2)-C(2)	91.2 (2)	P(4)-Rh(2)-C(2)	92.0 (2)
Rh(2)-S(1)-C(5)	117.1 (2)	C(5)-S(2)-C(7)	8[illegible]
Rh(1)-P(1)-C(3)	110.9 (2)	Rh(1)-P(1)-C(11)	120.9 [illegible]
Rh(1)-P(1)-C(21)	110.6 (2)	C(3)-P(1)-C(11)	107.2 (3)
C(3)-P(1)-C(21)	104.5 (3)	C(11)-P(1)-C(21)	101.3 (3)
Rh(2)-P(2)-C(3)	111.5 (2)	Rh(2)-P(2)-C(31)	113.3 (2)
Rh(2)-P(2)-C(41)	118.6 (2)	C(3)-P(2)-C(31)	103.7 (3)
C(3)-P(2)-C(41)	103.8 (3)	C(31)-P(2)-C(41)	104.4 (3)
Rh(1)-P(3)-C(4)	110.4 (2)	Rh(1)-P(3)-C(51)	117.8 (2)
Rh(1)-P(3)-C(61)	116.6 (2)	C(4)-P(3)-C(51)	107.0 (3)
C(4)-P(3)-C(61)	102.1 (3)	C(51)-P(3)-C(61)	101.3 (3)
Rh(2)-P(4)-C(4)	112.7 (2)	Rh(2)-P(4)-C(71)	112.9 (2)
Rh(2)-P(4)-C(81)	119.4 (2)	C(4)-P(4)-C(71)	102.5 (3)
C(4)-P(4)-C(81)	103.1 (3)	C(71)-P(4)-C(81)	104.4 (3)
Rh(1)-N(1)-C(5)	120.5 (4)	Rh(1)-N(1)-C(6)	127.7 (4)
C(5)-N(1)-C(6)	111.7 (5)	Rh(1)-C(1)-O(1)	174.9 (6)
Rh(2)-C(2)-O(2)	173.6 (6)	P(1)-C(3)-P(2)	114.3 (3)

Table 2.9. (continued)

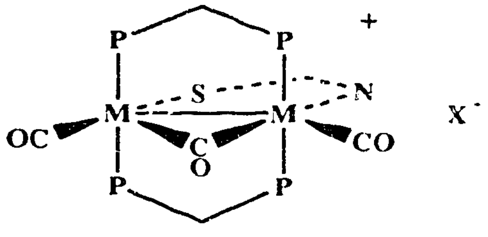
P(3)-C(4)-P(4)	113.9 (3)	S(1)-C(5)-S(2)	116.1 (3)
S(1)-C(5)-N(1)	128.8 (5)	S(2)-C(5)-N(1)	115.1 (5)
N(1)-C(6)-C(7)	110.7 (6)	S(2)-C(7)-C(6)	106.1 (6)

C(2)-H(86) contacts of 2.72 and 2.62 Å appear to distort this carbonyl from its idealized position. Similarly rings 1 and 5 appear to force C(1)O(1) towards Rh(2), giving a C(1)-H(12) contact of 2.56 Å. These distortions appear to force the two metal centers to approach each other and result in a Rh(1)-Rh(2) separation of 2.9957(7) Å which is compressed slightly compared with the intraligand P-P non-bonded contacts of 3.056(2) and 3.068(2) Å, suggesting a possible weak interaction between the metals. The contact between Rh(2) and C(1) (3.158(6) Å) appears to be too long to suggest even a weak semi-bridging interaction, and the IR spectra also do not argue in favor of such an interaction.

All other parameters within the complex are essentially as expected, comparing well with the appropriate parameters in **6**, so deserve no further comment.

The equilibrium mix of **9a** and **9b** react with CO to give $[Rh_2(CO)_2(\mu\text{-}mtz)(\mu\text{-}CO)(dppm)_2][Cl]$ (**11a**), whereas **11b**, having PF_6^{-1} as the counter ion,

ined by the analogous reaction of **9c**. Carbonyl loss from both species to give the starting complexes is very facile, occurring simply upon N_2 purge. The $^{31}P\{^1H\}$ NMR spectra of the two compounds are similar and appear as sharp AA'BB'XY spin patterns, consistent with the structure as



X = Cl (**11a**); PF_6 (**11b**)

shown. The infrared spectrum of **11a** displays two terminal carbonyl stretches (1981, 1958 cm^{-1}), whereas for **11b** only one stretch (1976 cm^{-1}) is revealed for the terminal carbonyls. However the broadness of this stretch suggests that another band is beneath it. Both compounds display bridging carbonyl stretches at *ca.* 1797 cm^{-1} in the IR spectra. The CO stretches of **11a, b** appear to have significantly lower wavenumbers than those (2005-1860 cm^{-1}) observed for the closely-related compounds, $[Rh_2(CO)_2(\mu\text{-}X)(\mu\text{-}CO)(dppm)_2][X]$ (X = Cl, Br, I),[25] suggesting that mtz ligand is more electron-releasing than the halides.

Conclusions

A series of binuclear complexes of Rh and Ir has been synthesized, in which the metals are bridged by both neutral diphosphine ligands (dppm and dppe) and anionic mercaptothiazolinate (mtz) groups. In the first class of compounds, $[M_2(CO)_2(\mu\text{-}mtz)_2(\mu\text{-}L)]$ (L = diphosphine), containing two anionic bridging groups, the complexes can be classified as having either "open-book" or "A-frame" geometries, and both descriptions appear to be equally valid. Two of these species, $[Rh_2(CO)_2(\mu\text{-}mtz)_2(\mu\text{-}dppe)]$ and $[Rh_2I_2(CO)_2(\mu\text{-}mtz)_2(\mu\text{-}dppe)]$, are unusual examples in which dppe functions as a *bridging* group. In the second class of compounds, $[M_2X(CO)_2(\mu\text{-}mtz)(dppm)_2]$ (M = Rh, Ir; X = Cl, mtz), containing two bridging dppm groups, the ease of displacement of the anionic groups from a bridging site has been demonstrated. These species have only one mtz group bridging the metals and are best viewed as classical "A-frame" complexes. The additional anionic ligand (Cl^- or mtz^-)

is terminally bound to one metal, and for M = Rh these terminal groups readily dissociate yielding cationic complexes.

Although numerous open-book complexes containing phosphine ligands are known, the complexes [$M_2(CO)_2(\mu\text{-mtz})_2(\mu\text{-L})$] are the first examples in which diphosphines have been incorporated as ligands. It will be of interest to further explore the chemistry of these species. The complexes of the second class are interesting in that they contain a bifunctional apical ligand, the possible effects of which has been noted in Chapter 1. It may be the bifunctionality of the mtz ligand that gives rise to the unusual dynamic behavior for the complex [$Rh_2(\eta^1\text{-mtz})(CO)_2(\mu\text{-mtz})(dppm)_2$], as shown in Scheme I.

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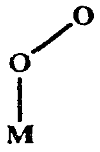
Chapter 3

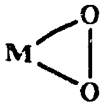
Reactivity Studies of the Unusual Peroxo-Bridged Complex, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$

Introduction

The enormous interest in transition-metal dioxygen complexes over the past half-century[1-3] has stemmed in a large part from the importance of dioxygen complexation to biological systems,[2] and from the involvement of such complexes in the catalytic oxidation of organic substrates.[3] In the large number of dioxygen complexes known, the O_2 ligand has demonstrated a variety of coordination modes (a - f). Although most species fit into the first four types, as classified by Vaska in 1976,[1d] a few examples of structural types e[4] and f[5] are also known.



(a)



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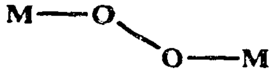

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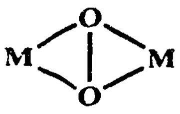

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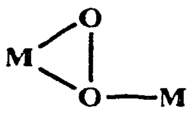
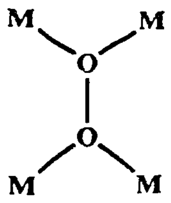
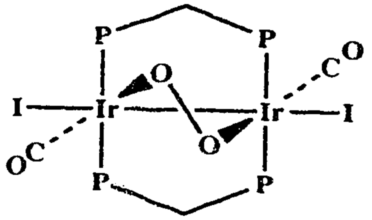


(e)

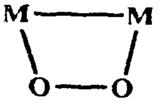


(f)

With the exception of cobalt, for which a large number of binuclear complexes is known,[2b,6] most studies have dealt with mononuclear O_2 species. Recently[7a] the electron-rich complex, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$), as mentioned in Chapter 1, was found to form a novel dioxygen adduct, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**1**), having a structure as shown, in which the dioxygen coordination mode did not belong to one of those previously noted (**a** - **f**). Instead a new type of mode (**g**) was observed,



(**1**)



(**g**)

in which the bridging peroxo moiety was accompanied by a metal-metal bond. It was therefore of interest to investigate the reactivity of this new structural class. In this chapter we present a description of its chemistry.

Experimental Section

General experimental conditions were as described in Chapter 2. $NOBF_4$, $NOPF_6$ and $CH_3SO_3CF_3$ were obtained from Aldrich, and i-propylisocyanide and t-butylisocyanide from Strem. The 99% carbon-13-enriched carbon monoxide was obtained from Isotec Inc. The compound $[Ir_2I_2(CO)_2(\mu-O_2)(dppm)_2]$ (**1**) was prepared as previously reported.[7a] Spectroscopic parameters for the compounds prepared are found in Table 3.1.

(a) Reaction of 1 with H_2SO_4. To a CH_2Cl_2 suspension of **1** (60.0 mg, 0.040 mmol, in 10 mL) was added 1 equiv of H_2SO_4 (1.1 μL in 3 mL of CH_3OH), causing an immediate color change to yellow orange. The solution was stirred for 0.5 h, and the solvents were then removed under vacuum. The resultant product was spectroscopically identified as the previously reported complex, $[Ir_2I_2(CO)_2(\mu-SO_4)(dppm)_2]$ (**2**) (90% yield), initially prepared from the reaction of **1** with SO_2.[7a]

(b) Reaction of 1 with $CuSO_4$. The procedure was the same as in (a), except 1 equiv of $CuSO_4$ was used. Compound **2** was isolated in 85% yield.

(c) Reaction of 1 with NO_2. To a CH_2Cl_2 suspension of **1** (60 mg, 0.04 mmol, in 10 mL) was added 2 equiv of NO_2 , causing an immediate color change from dark purple to orange. After stirring for an additional 0.5 h, the solution was concentrated to ca. 2 mL followed by addition of 10 mL of diethyl ether. The product $[Ir_2I_2(CO)_2(\mu-NO_3)(dppm)_2][NO_3]\cdot CH_2Cl_2$ (**3a**) was precipitated as yellow microcrystals in 70% yield, and was determined to be a 1:1 electrolyte in CH_3NO_2 ($\Lambda = 81.1\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. calcd for $Ir_2I_2Cl_2P_4O_8N_2C_{53}H_{46}$: C, 37.35; H, 2.66; N, 1.68. Found: C, 37.67; H, 2.78; N, 1.67.

(d) Preparation of $[Ir_2I_2(CO)_2(\mu-NO_3)(dppm)_2][BF_4]$ (3b). To a CH_2Cl_2 solution of **3a** (79.0 mg, 0.050 mmol, in 10 mL) was added 55.0 mg of $NaBF_4$

Table 3.1. Spectroscopic Data [a]

compd	Ir, cm^{-1} [b]	NMR δ ($^{31}P\{^1H\}$) [c]	 δ (^1H) [d]
$[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][NO_3]$ (3a)	2049 (st, br); 1518 (med), 1259 (w), 1040 (w), 780 (w);[e] 1340 (vs), 1023 (w), 700 (w) [f]	-20.0 (m) -26.1 (m)	5.91 (m, 2H), 4.40 (m,2H)
$[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][BF_4]$ (3b)	2048 (vs); 1519 (med) 1260 (w), 780 (w) [e]	-20.0 (m) -26.2 (m)	5.86 (m, 2H), 4.32 (m, 2H)
$[Ir_2I_2(CO)_2(\mu\text{-}NO)(dppm)_2][NO_3]$ (4)	2051(vs), 2025 (w); 1518(med);[g] 1340 (vs), 1028 (w), 700 (w) [f]	-14.3 (s)	5.32 (m, 2H), 4.44 (m, 2H)
$[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]$ (5)	2048 (st), 2038 (st) 1645 (med)	-28.2	3.94 (m, 2H), 2.80 (m, 2H)

Table 3.1. (continued)

$[Ir_2(CO_2CH_3)(CN^iPr)_3(\mu\text{-}CO)(\mu\text{-}OH)\text{-}(dppm)_2][I]_2$ (6)	3190 (med);[h] 2193 (vs) 2180 (vs);[j] 1653 (st) 1625 (st); 1036 (med) [k]	-8.1 (br) -11.8 (br)	4.42 (br), 3.58 (br) [i] 3.31 (spt), 3.23 (spt) 3.18 (spt), 2.60 (s, 3H) 0.82 (d, 6H),0.78 (d, 6H) 0.72 (d, 6H)
$[Ir_2(CO_2CH_3)(CN^tBu)_3(\mu\text{-}CO)(\mu\text{-}OH)\text{-}(dppm)_2][I]_2$ (7)	3188 (med);[h] 2181(vs), 2174 (vs);[j] 1655 (vs), 1625 (vs); 1070 (med) [k]	-9.1 (br) -12.1 (br)	3.50 (br),2.58 (s, 3H) 0.83 (s, 9H), 0.78 (s, 9H) 0.75 (s, 9H)
$[Ir_2Cl_2I_2(CO)_2(dppm)_2]$ **(8a)**	2066 (st), 2031 (st)	-13.9 (s)	4.97 (m, 2H), 4.50 (m, 2H)
$[Ir_2Cl_2I_2(CO)_2(dppm)_2]$ **(8b)**	2025 (vs)	-23.0 (s)	5.70 (m, 2H), 5.03 (m, 2H)
$[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$ **(9a)**	3550 (w);[h] 2064 (st) 2032 (vs)	-13.8 (s)	5.20 (m, 2H), 4.17 (m, 2H) 3.06 (q, 1H)

Table 3.1. (continued)

$[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][SO_3CF_3]$ (**9b**)	3550 (w);^{h} 2063 (st) 2031 (st)	-13.7 (s)	5.22 (m, 2H), 4.21 (m, 2H) 3.07 (q, 1H)
$[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][PF_6]$ (**9c**)	3550 (w);^{h} 2062 (st) 2037 (st)	-13.8 (s)	5.20 (m, 2H), 4.05 (m, 2H) 3.00 (q, 1H)

[a] Abbreviations used: vs = *very strong, st = strong, med =- medium, w = weak, m = multiplet, q = quintet, d =* doublet, s = singlet. [b] Nujol mull except compounds **9a-c**, CH_2Cl_2 cast. ν(CO) unless otherwise noted. [c] versus 85% H_3PO_4, 25°C, in CD_2Cl_2. [d] versus TMS, 25°C, in CD_2Cl_2. [e] ν(μ-NO_3). [f] ν(NO_3). [g] ν(NO). [h] ν(OH). [i] see *text.* [j] *ν(CN).* [k] *ν(C-O).*

(0.50 mmol, in 3 mL of CH_3OH). The mixture was stirred for 0.5 h followed by filtration. Concentration of the solution followed by washing with distilled water and addition of diethyl ether resulted in the isolation of **3b** in ca. 90% yield. Anal. calcd for $Ir_2I_2P_4F_4O_5NC_{52}BH_{44}$: C, 38.75; H, 2.75; N, 0.87; I, 15.75. Found: C, 39.09; H, 2.67; N, 0.99; I, 16.07.

(e) Reaction of 1 with NO. Nitric oxide was placed over a CH_2Cl_2 suspension of **1** (60.0 mg, 0.040 mmol, in 10 mL), causing the formation of a deep orange solution in ca. 15 min. The solution was stirred for an additional 0.5 h, the volume was then reduced to ca. 2 mL, and a yellow-orange solid was precipitated upon addition of diethyl ether (75% yield). The product, $[Ir_2I_2(CO)_2(\mu\text{-}NO)(dppm)_2][NO_3]$ (**4**), was determined to be weakly conducting in CH_2Cl_2 ($\Lambda = 29.6\ \Omega^{-1}\ cm^2\ mol^{-1}$), but a normal 1:1 electrolyte in CH_3NO_2 ($\Lambda = 78.7\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. calcd for $Ir_2I_2P_4O_6N_2C_{52}H_{44}$: C, 40.16; H, 2.86; N, 1.80; I, 16.32. Found: C, 39.79; H, 3.08; N, 1.82; I, 16.81.

(f) Reaction of 1 with CO. A stream of CO was passed through a CH_2Cl_2/CH_3OH (30 mL, 5:1) suspension of **1** (100.0 mg, 0.067 mmol) for 4 h, during which time a yellow solution was formed. The solvents were then removed under vacuum. Crystallization from CH_2Cl_2/diethyl ether afforded two distinctive crystalline solids. The yellow microcrystals were spectroscopically identified as $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ by comparision with the authentic sample,[8] and the pale yellow crystals as $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]$ (**5**). The two compounds were the only products observed by NMR spectroscopy; the relative yields between them varied from 1:1 to 1:3. Elemental analysis was not attempted for compound 5, because the fluffy microcrystals of the iodide-bridged compound appeared to coat most of 5.

(g) Reaction of 1 with ^{i}PrNC. In a typical experiment, 36 μL (0.40 mmol) of ^{i}PrNC was added to compound 1 (60.0 mg, 0.040 mmol) in 25 mL of CH_2Cl_2 /CH_3OH (5:1, by volume). A yellow solution was formed in ca. 5 h. Concentration of the solution followed by addition of diethyl ether precipitated $[Ir_2(CO_2CH_3)(CN^{i}Pr)_3(\mu\text{-}CO)(\mu\text{-}OH)(dppm)_2][I]_2$ (6) as a yellow crystalline solid (50% yield). Anal. calcd for $Ir_2I_2P_4O_4N_3C_{65}H_{69}$: C, 45.43; H, 4.06; N, 2.45. Found: C, 44.88; H, 4.27; N, 2.57.

(h) Reaction of 1 with ^{t}BuNC. The procedure was the same as for 6, except ^{t}BuNC was used. The product, $[Ir_2(CO_2CH_3)(CN^{t}Bu)_3(\mu\text{-}CO)(\mu\text{-}OH)(dppm)_2][I]_2$ (7), was isolated from CH_2Cl_2 /diethyl ether as yellow crystals (70-75% yield). Anal. calcd for $Ir_2I_2P_4O_4N_3C_{68}H_{75}$: C, 46.39; H, 4.30; N, 2.39. Found: C, 46.68; H, 4.42; N, 2.49.

(i) Reaction of 1 with excess HCl. Gaseous HCl was bubbled (ca. 0.2 mL/sec) through a CH_2Cl_2 suspension of 1 (60.0 mg, 0.040 mmol, in 10 mL) for 1 min, causing the immediate formation of a yellow solution. After stirring for an additional 0.5 h, the solution was concentrated to ca. 3 mL followed by addition of diethyl ether, resulting in the precipitation of $[Ir_2Cl_2I_2(CO)_2(dppm)_2]\cdot CH_2Cl_2$ (8a) as a microcrystalline solid (80% yield). The presence of one CH_2Cl_2 molecule per dimer unit was indicated by the ^1H NMR spectrum carried out in d_6-acetone. Compound **8a** was determined to be a nonelectrolyte in CH_2Cl_2 solutions ($\Lambda < 2\ \Omega^{-1}cm^2mol^{-1}$). Anal. calcd for $Ir_2I_2Cl_4P_4O_2C_{53}H_{46}$: C, 36.60; H, 2.67; Cl, 8.16; I, 14.59. Found: C, 36.53; H, 2.84; Cl, 8.09; I, 15.56.

Compound **8a** was also produced by reacting a solid sample of **1** with HCl. The dark purple solid immediately turned to orange upon purge with HCl.

(j) Reaction of 1 with 2 equiv of HCl. The procedure was the same as for **8a**, except that only 2 equiv of HCl (2.0 mL, 0.04 mmol) was syringed into a CH_2Cl_2 solution of **1** (60.0 mg, 0.040 mmol, in 20 mL). Isomer **8b**, $[Ir_2Cl_2I_2(CO)_2(dppm)_2]$, was obtained as yellow solid in 75-80% yield. Anal. calcd for $Ir_2I_2Cl_2P_4O_2C_{52}H_{44}$: C, 40.71; H, 2.90; Cl, 4.62. Found: C, 40.51; H, 2.95; Cl, 4.59.

(k) Reaction of 1 with $HBF_4 \cdot OEt_2$. To a benzene suspension of **1** (60.0 mg, 0.040 mmol, in 10 mL), was added 1 equiv of $HBF_4 \cdot OEt_2$ (5.7 μL). The mixture was stirred overnight, during which time the suspension turned to orange. Concentration followed by addition of diethyl ether afforded $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$ (**9a**) as a yellow solid.

(l) Attempted reaction of 1 with $CH_3SO_3CF_3$. The procedure was the same as for **9a**, except that 2 equiv of $CH_3SO_3CF_3$ (ca. 9 μL) was used, yielding $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][SO_3CF_3]$ (**9b**).

(m) Attempted reaction of 1 with $NOBF_4$. To a mixture of **1** (100.0 mg, 0.67 mmol) and $NOBF_4$ (7.8 mg, 0.67 mmol) was added 10 mL of CH_2Cl_2. The mixture was stirred for ca. 3 h, during which time an orange solution was formed. Compound **9a** was obtained as a yellow solid in 85% yield.

The same compound was also produced in the presence of water. The procedure was the same as above except that following addition of CH_2Cl_2, ca. 4 μL of H_2O was added to the mixture. A color change to orange was observed in ca. 10 min.

(n) Reaction of 1 with $NOPF_6$. The procedure was the same as in part (m), except that 1 equiv of $NOPF_6$ was used, and compound **9c** was obtained as the PF_6^- salt.

(o) Reaction of 1 with PPh_3. To a mixture of **1** (60.0 mg, 0.04 mmol) and PPh_3 (5.5 mg, 0.021 mmol) in 10 mL CH_2Cl_2 , was syringed ca. 0.5 mL (ca. 0.02 mmoL) of gaseous HCl. After stirring for 1 h, the solvent was removed under vacuum. A mixture of several species was formed, but the appearance of $OPPh_3$ (ca. 30% yield) was confirmed by $^{31}P\{^1H\}$ NMR (δ 27.5) and IR spectrum ($\nu(P=O)$ = 1187 cm^{-1}).

In the reactions involving H_2SO_4 and HCl, H_2O_2 was formed, which was identified iodimetrically. H_2O_2 was abstracted, by using distilled water, from the CH_2Cl_2 solution in which it was formed. KI was then added to the aqueous solution, followed by the addition of a few drops of starch solution, causing an immediate color change to blue.

X-ray Data Collection. $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2CH_2Cl_2$ (5). Yellow crystals of **5** were obtained by slow diffusion of ether into a CH_2Cl_2 solution of the compound. A suitable crystal was mounted on a glass fiber with epoxy cement and optically centered in the X-ray beam of an Enraf-Nonius CAD4 automated diffractometer. The crystal was cooled to approximately -85°C, using a cold-air stream apparatus (Air Jet Model XR-85-1, FTS Systems, Inc.), and all measurements were made at this temperature using $MoK\alpha$ radiation. The unit cell parameters were obtained at -85°C from a least-squares refinement of the setting angles of 25 reflections in the range $13.5° \leq 2\theta \leq 20.6°$. The automatic peak-search and reflection-indexing programs generated an orthorhombic cell. The systematic absences ($0kl$, $k + l$ = odd; $h0l$, h = odd) led to the choice of space group as $Pna2_1$ or $Pnam$ (a non-standard setting of $Pnma$). $Pna2_1$ was established as the probable one based on the successful refinement of the structure.

Intensity data were collected using the $\theta/2\theta$ scan technique to a maximum $2\theta = 50°$. Backgrounds were measured by extending the scan by 25% on each side of the calculated range. One reflection was chosen as a standard reflection, being remeasured at 120 min intervals of X-ray exposure time. The intensity of this reflection was found to fluctuate about its mean suggesting movement of the crystal in the cold stream, but otherwise no decrease was noted, therefore no decay correction was applied. The data were processed in the usual way with a value of 0.04 used for p to downweigh intense reflections.[9] Corrections for Lorentz and polarization effects and for absorption, using the method of Walker and Stuart, were applied to the data.[10,11] Data collection was carried out by Bernie Santarsiero of the department's X-ray Service Laboratory.

Structure Solution and Refinement. The structure was solved in the space group $Pna2_1$ by using direct methods.[12] The remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Full-matrix least-squares refinements proceeded, minimizing the function $\Sigma w(|Fo| - |Fc|)^2$, where $w = 4\, Fo^2/\sigma^2(Fo^2)$. Atomic scattering factors and anomalous dispersion terms were taken from the usual tabulations.[13-15] Positional parameters for the hydrogen atoms were calculated from the geometries of their attached carbon, using C-H distances of 0.95 Å. All hydrogen atoms were included in the calculations with fixed thermal parameters 1.2 times those of the attached atoms and were constrained to ride on these atoms.

The final model for complex 5, with 328 parameters varied, converged to values of $R = 0.056$ and $R_w = 0.064$. The 10 highest peaks in the final difference Fourier map had a density in the range 2.48-1.37 e/Å^3 and were primarily located near the iridium atoms. See Table 3.2 for a summary of crystal data and X-ray collection information. The positional and thermal parameters for the atoms of **5** are given in Table 3.3.

Results and Discussion

The peroxo-bridged complex $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**1**), as previously reported,[7a,b] is readily obtained by exposing solutions of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ to air or pure oxygen. An X-ray crystallographic study has confirmed the unprecedented structure of this complex, diagrammed in the Introduction section, in which the bridging peroxo unit is accompanied by a metal-metal bond.[7a,b] Although complexes contining a bridging peroxo unit are well known,[2b] these were all shown *not* to possess a metal-metal bond. Complex **1** is therefore the first example having such a bonding mode for the dioxygen ligand. The previous study[7a,b] also showed that the O-O separation in **1** was extremely long, at 1.58(2) Å, in comparison with the values of 1.40 to 1.50 Å found for other peroxo compounds.[1e,2b] Furthermore the skewing about the O-O bond was much less than normally observed in peroxo-bridged compounds,

Table 3.2. Crystallographic Data for $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2\ CH_2Cl_2$ (5)

formula	$C_{55}H_{48}Cl_4O_5P_4I_2Ir_2$
fw	1692.91
space group	$Pna2_1$
temp, °C	-85
radiation (λ, Å)	Mo Kα (0.71069)
cell parameters	
a, Å	30.110 (8)
b, Å	15.678 (6)
c, Å	12.020 (6)
V, Å^3	5674 (1)
Z	4
ρ (calcd), g cm^{-3}	1.982
no. of unique data collcd	5407 (h, k, l)
no. of unique data used $(F_o^2 \geq 3\sigma(F_o^2))$	2598
final no. of params refined	328
R	0.056
R_w	0.064

Table 3.3. Positional (x 10^4) and Thermal Parameters for the Atoms of $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2CH_2Cl_2$ (5)[a]

Ir(1)	4357.3(5)	1957.6(9)	2500	2.04(3)*
Ir(2)	3475.3(4)	2603.8(8)	966(2)	1.78(3)*
I(1)	4843.5(9)	2156(2)	4490(3)	3.55(7)*
I(2)	2683.3(8)	3565(1)	958(3)	3.16(6)*
P(1)	4678(4)	3227(6)	1809(8)	2.3(3)*
P(2)	3906(3)	3693(6)	173(8)	1.8(2)*
P(3)	3961(3)	747(6)	3090(9)	2.0(3)*
P(4)	3114(3)	1438(6)	1852(9)	1.7(2)*
O(1)	5108(9)	828(17)	1725(25)	4.2(7)
O(2)	4184(8)	1532(15)	228(21)	2.5(5)
O(3)	3222(9)	1941(16)	-1263(24)	3.9(6)
O(4)	3817(8)	2578(16)	3143(22)	3.1(5)
O(5)	3659(8)	3203(14)	2370(23)	3.2(6)
C(1)	4813(13)	1256(24)	2002(34)	3.2(9)
C(2)	4084(11)	1923(21)	960(40)	3.0(7)
C(3)	3336(12)	2183(23)	-381(38)	3.4(9)
C(4)	4523(10)	3545(22)	449(28)	1.7(7)
C(5)	3513(11)	541(20)	2124(29)	2.2(8)
Cl(1)[2]	5943(5)	186(8)	4090(13)	6.4(3)

Table 3.3. (continued).

Cl(2)[2]	6492(5)	1668(9)	4021(13)	6.8(4)
Cl(3)[2]	3331(5)	7697(9)	3595(14)	7.6(4)
Cl(4)[2]	2784(5)	8625(10)	2071(14)	7.9(4)
C(11)	5264(10)	3104(19)	1620(27)	1.2(6)
C(12)	5403(12)	2540(23)	757(33)	3.4(9)
C(13)	5873(12)	2362(25)	663(34)	4(1)
C(14)	6191(12)	2789(21)	1346(30)	2.9(9)
C(15)	6027(16)	3311(30)	2122(41)	6(1)
C(16)	5593(11)	3500(21)	2368(34)	2.7(8)
C(21)	4630(12)	4232(22)	2578(41)	3.1(8)
C(22)	4377(13)	4294(25)	3523(35)	3.6(9)
C(23)	4326(13)	5074(22)	4075(37)	3.3(9)
C(24)	4496(15)	5776(29)	3708(44)	6(1)
C(25)	4720(13)	5731(26)	2735(39)	4(1)
C(26)	4813(14)	4976(28)	2178(40)	5(1)
C(31)	3830(11)	4814(21)	601(28)	1.9(8)
C(32)	3615(12)	5006(22)	1532(30)	2.3(8)
C(33)	3575(14)	5865(27)	1855(40)	5(1)
C(34)	3805(11)	6488(22)	1102(38)	3.1(8)
C(35)	4003(12)	6291(23)	243(32)	2.7(8)
C(36)	4059(12)	5450(22)	-45(33)	2.7(8)

Table 3.3. (continued).

C(41)	3840(10)	3709(19)	-1326(26)	0.9(6)
C(42)	3534(13)	4163(24)	-1735(35)	3.4(9)
C(43)	3416(17)	4175(31)	-2915(44)	7(1)
C(44)	3706(13)	3768(25)	-3585(41)	5(1)
C(45)	4018(15)	3293(28)	-3188(41)	5(1)
C(46)	4102(15)	3306(27)	-2085(38)	5(1)
C(51)	4284(12)	-235(23)	2968(32)	2.8(9)
C(52)	4600(16)	-302(28)	3662(45)	5(1)
C(53)	4914(16)	-1077(28)	3558(44)	6(1)
C(54)	4884(14)	-1610(26)	2830(36)	4(1)
C(55)	4504(15)	-1534(29)	2109(40)	5(1)
C(56)	4197(12)	-824(21)	2192(31)	2.6(8)
C(61)	3721(12)	686(22)	4481(35)	2.7(8)
C(62)	3667(12)	1404(25)	5181(33)	3.1(9)
C(63)	3456(12)	1263(23)	6176(40)	4.0(9)
C(64)	3355(14)	490(25)	6576(39)	5(1)
C(65)	3411(12)	-169(23)	5919(45)	4.1(9)
C(66)	3573(12)	-87(23)	4834(33)	3.0(9)
C(71)	2733(11)	887(21)	912(40)	3.1(8)
C(72)	2284(11)	1154(20)	907(38)	2.5(7)

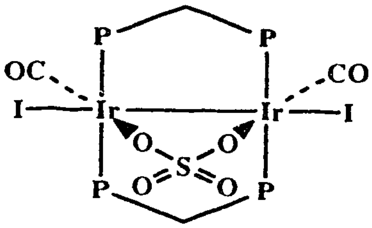
Table 3.3. (continued).

C(73)	1977(14)	781(24)	262(36)	4(1)
C(74)	2144(14)	203(25)	-501(42)	5(1)
C(75)	2562(11)	-75(21)	-590(32)	1.9(7)
C(76)	2874(12)	287(21)	151(31)	2.3(8)
C(81)	2817(13)	1608(24)	3123(35)	3.2(9)
C(82)	2799(11)	2364(23)	3635(31)	2.5(8)
C(83)	2598(14)	2551(29)	4683(41)	5(1)
C(84)	2357(12)	1874(23)	5066(33)	2.9(8)
C(85)	2362(12)	1076(23)	4600(35)	3.1(9)
C(86)	2576(11)	980(22)	3653(31)	2.3(8)
C(98)[b]	6014(14)	1178(25)	3475(39)	5(1)
C(99)[b]	2790(18)	7857(34)	3156(54)	9(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. Starred atoms were refined anisotropically. Thermal parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameters defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Atoms of CH_2Cl_2 molecules of crystallization.

probably due to the constraint imposed by the metal-metal bond. It was of obvious interest to investigate the reactivity of this unusual peroxo moiety on the assumption that the long O-O separation and the inherent strain associated with this unit might give rise to unusual reactivity, either at the O_2 moiety or at the metal-metal bond.[7b] Subsequent to the original study it has been assumed that the long O-O separation in **1** may be an artifact arising from systematic errors in the data,[7c] nevertheless, the reactivity of this group remains of interest.

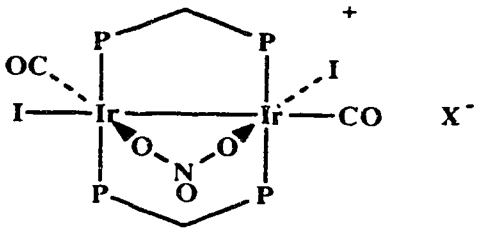
Typical reactions observed for peroxo compounds are those involving SO_2 and NO_2,[1b,e] leading to sulfate and nitrate species, such as $[IrX(SO_4)(CO)(PPh_3)_2]$ (X = Cl, Br, I), obtained in the reaction of $[IrX(O_2)(CO)(PPh_3)_2]$ with SO_2.[16] Previously it was shown that the reaction of **1** with SO_2 yielded $[Ir_2I_2(CO)_2(\mu\text{-}SO_4)(dppm)_2]$ (**2**), in which the $\mu\text{-}O_2$ unit was replaced by $\mu\text{-}SO_4$.[7a,b] Compound **2**, as shown by the $^{31}P\{^1H\}$ NMR spectrum, is a symmetric species in which all phosphorus nuclei are



(**2**)

chemically equivalent. Its IR spectrum, which shows three sulfate bands at 1245, 1140 and 952 cm^{-1} besides the two carbonyl stretches at 2037 and 2026 cm^{-1}, supports the presence of a bridging sulfate group.[17] By comparison, the mononuclear sulfate complexes above showed sulfate bands at ca. 1300,1170, 890, 860 and 670.[16] Compound **2** is also obtained by reaction of **1** with H_2SO_4, with release of H_2O_2, or by reaction of **1** with $CuSO_4$, as shown by the ^1H NMR, $^{31}P\{^1H\}$ NMR and IR spectra. The formation of H_2O_2 was verified iodimetrically.

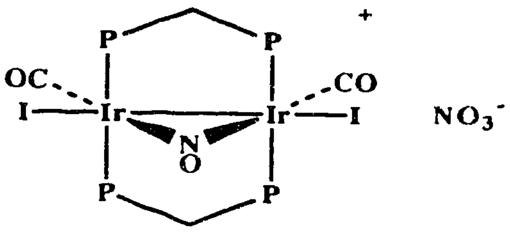
The peroxo complex also reacts readily with 2 equiv of NO_2 to give the nitrate-bridged product $[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][NO_3]$ (**3a**), quite analogous to the reaction of the mononuclear iridium dioxygen compounds noted above with NO_2, which also yielded nitrate species, $[IrX(NO_3)_2(CO)(PPh_3)_2]$.[16] The IR spectrum of **3a** shows bands at 1518, 1259, 1040 and 780 cm^{-1} associated with the coordinated nitrate group and bands at 1340, 1023 and 700 cm^{-1} associated with the free nitrate anion. These latter three bands disappear upon replacement of the nitrate ion by tetrafluoroborate anion resulting from reaction of **3a** with $NaBF_4$, yielding **3b**. The bands for the coordinated nitrate group are comparable to those



X=NO$_3$ (3a); BF$_4$ (3b)

reported for a variety of related species,[16,18] such as the mononuclear iridium compounds noted.[16] Although compounds **2** and **3** are rather analogous, the $^{31}P\{^1H\}$ NMR spectra of **3(a,b)** show an AA'BB' pattern, indicating that the two metal centers are inequivalent. The inequivalence of the phosphorus environments in **3** most likely results from the arrangement of iodo and carbonyl ligands as shown in the sketch. This arrangement is as observed in the alkyne adducts of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$,[8] and differs from the arrangement in **2**, in which the two iodo ligands and the two carbonyl groups are mutually cis. The change in arrangement of carbonyl and iodo ligands from a symmetrical disposition in **1** to an unsymmetrical one in **3** suggests that iodide dissociation occurs at some stage of the reaction. Although it is not clear why **2** and **3** should have different arrangement of ligands, it should be noted that nothing is known about the mechanisms of these reactions.

Although the O_2 adducts of closely-related mononuclear dioxygen compounds are reported to be inert to reaction with nitric oxide or carbon monoxide,[16] the binuclear analogue **1** reacts with both of these diatomics. Reaction of **1** with excess NO takes about 15 min for completion, yielding the nitrosyl-bridged product $[Ir_2I_2(CO)_2(\mu\text{-}NO)(dppm)_2][NO_3]$ (**4**), again having a nitrate counter-ion. Compound **4** is a normal 1:1 electrolyte in



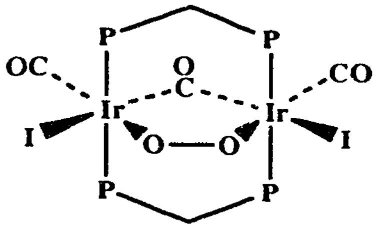
(4)

CH_3NO_2 (Λ = 78.7 Ω^{-1} cm^2 mol^{-1}), although it is only weakly conducting in

CH_2Cl_2 (Λ = 29.6 Ω^{-1} cm^2 mol^{-1}). The IR spectrum shows two carbonyl bands at 2051 and 2025 cm^{-1}, and a strong band at 1518 cm^{-1}, due to the bridging nitrosyl group, as well as bands typical of the nitrate anion. This nitrosyl stretch falls in the range (1400-1600 cm^{-1}) typical of bridged nitrosyls.[19] The $^{31}P\{^1H\}$ NMR spectrum is again typical of a symmetrical species. Dppm-bridged diiridium or dirhodium nitrosyls have not previously been reported, but the above reaction is not without precedent. Treatment of $[Ni(O_2)(^tBuNC)_2]$ with NO in the presence of ^tBuNC produces the nitrosyl complex, $[Ni(NO)(^tBuNC)_3][NO_3]$, also as a nitrate salt,[18a] although in the related Pd and Pt species, $[M(O_2)(PPh_3)_2]$ (M = Pd, Pt), formation of dinitro compounds was suggested instead.[16,18b]

The oxidation of carbon monoxide by mononuclear dioxygen complexes generally yields carbonates.[1e] A typical example is seen in the reaction of $[Pt(O_2)(PPh_3)_2]$ with CO, yielding the carbonate-chelated compound $[Pt(CO_3)(PPh_3)_2]$.[20] However, the nickel complex noted above affords a dicarbonyl species and carbon dioxide.[18a] Compound **1** also reacts with CO, although in CH_2Cl_2 the reaction is slow, requiring more than 100 h. The same reaction in either a CH_2Cl_2/CH_3OH or a CH_2Cl_2/CH_3CN solvent mix is complete within 4 h. In all cases the same two products are obtained, together with carbon dioxide, which can be detected by using a aqueous sodium carbonate/phenolphthalein solution which turns from pink to colorless in the presence of **1** and CO.[21] One of the complexes is readily identified as the previously characterized $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)\text{-}(dppm)_2][I]$.[8] The other product displays a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ -28.2 and shows bands in the IR spectrum at 2048, 2038 and

1645 cm^{-1}. Although it originally appeared that the low-frequency stretch arose from a carbonate group, subsequent studies have shown that it results from a carbonyl w has inserted into the Ir-Ir bond of **1** to give $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(\mu\text{-}CO)(dppm)_2]$ (**5**). This is the only product in this study which results from ligand insertion into the metal-metal bond, while leaving the peroxo moiety intact. It can also be shown by ^{13}CO labelling that it is one of the originally bound carbonyls that moves to the bridging position and that direct insertion of free CO into the Ir-Ir bond does not occur. The reaction of **1** with ^{13}CO gives IR bands at 2040, 1993 and 1643 cm^{-1}, in which only one of the terminal carbonyl bands has shifted significantly. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum of this product shows only one carbonyl resonance at δ 164.6, in the region typical of terminal carbonyls. Although the chemical shift of this resonance also falls in the region seen for other carbonate complexes,[22] the IR result above, which shows that only one of the terminal carbonyls is ^{13}C-enriched, rules out the possibility that it might arise from a carbonate group. In addition, when the totally ^{13}CO-enriched **5** is prepared, the two resonances at δ 224.5 and 164.4, integrating as 1:2, confirm that the high-



(5)

field resonance results from the terminal carbonyl.

The reaction of **1** with CO appears to proceed via two pathways. One involves the oxidation of the substrate by the peroxo moiety to give CO_2 and the iodide-bridged complex, reminiscent of the reaction of the nickel species noted, while the other one involves the insertion of CO into the metal-metal bond of **1**, a reaction that is not surprising considering the strain imposed by the Ir-Ir bond in this precursor. The significant increase in the reaction rate, when polar solvents are utilized, indicates that a polar intermediate may be involved at some stage of the reaction. Such an intermediate could be formed by cleavage of one of the oxygen-iridium bonds, as suggested for a similar reaction involving mononuclear iridium complexes,[22a] or by iodide dissociation.

The structural formulation of **5** has been confirmed by an X-ray structure determination. A representation of the compound is given in Figure 3.1, and relevant bond lengths and angles are shown in Tables 3.4 and 3.5. Compound **5** has the expected geometry in which both dppm groups bridge the metals in a trans arrangement. The most obvious difference in the geometry of **5** and its precursor results from cleavage of the metal-metal bond and increase of the Ir-Ir separation from 2.705(1)Å in **1** to 3.388(2)Å in **5**. The geometries at the metals are distorted octahedral, characteristic of an Ir(III)/Ir(III) system. Such a description requires formulation of the bridging carbonyl as a formally dianionic group, which is consistent with formulating **5** as a dimetalloketone. Although this is not the normal formulation for a bridging carbonyl, it has previously been suggested,[23] and is consistent with the geometry at this

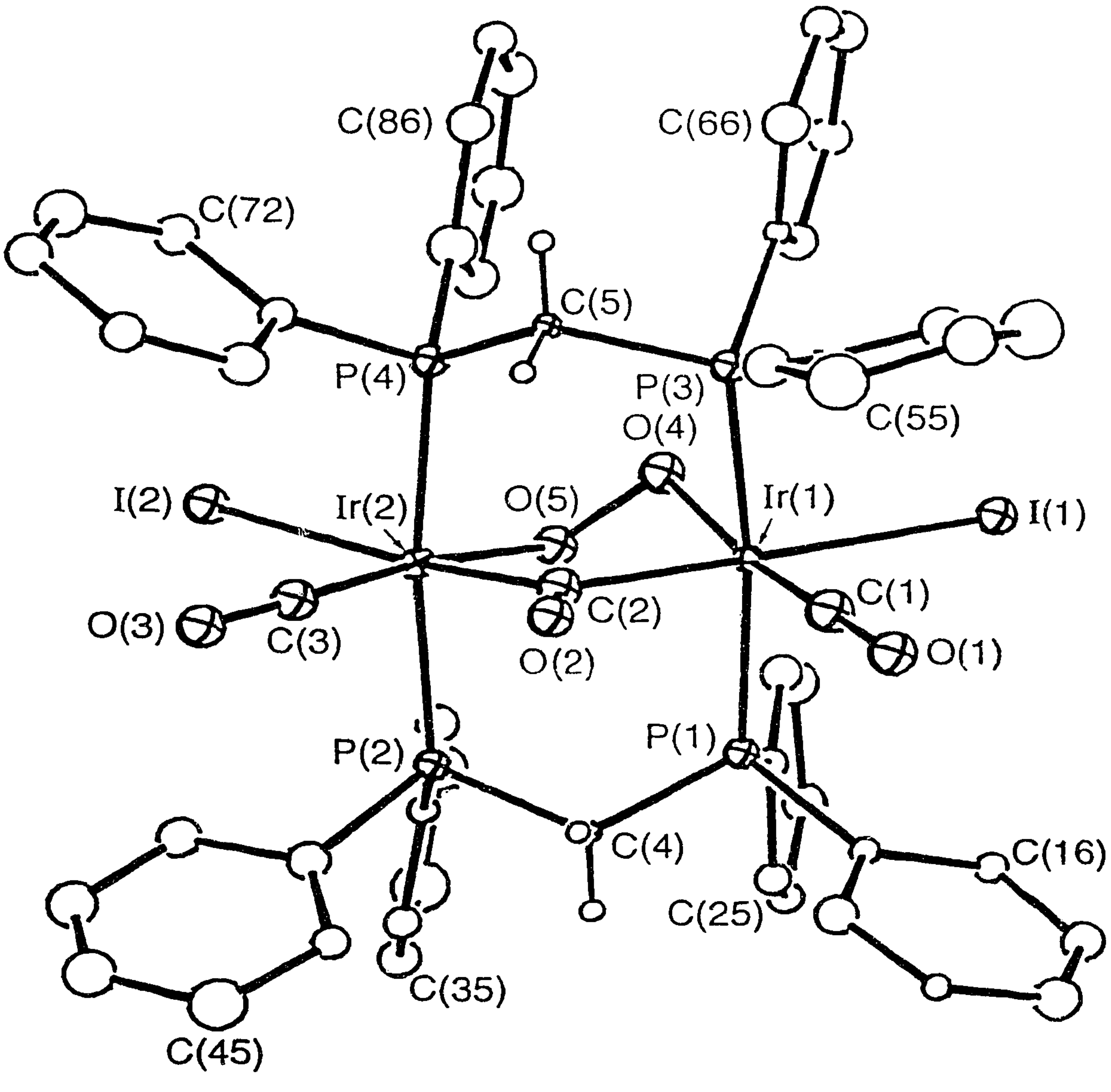


Figure 3.1. Perspective view of complex 5, showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens, which are shown arbitrarily small. Phenyl hydrogens are omitted.

Table 3.4. Selected Distances (Å) in
$[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot CH_2Cl_2$ (5)

Ir(1)-I(1)	2.822 (3)	Ir(1)-P(1)	2.363 (9)
Ir(1)-P(3)	2.350 (9)	Ir(1)-O(4)	2.05 (2)
Ir(1)-C(1)	1.86 (4)	Ir(1)-C(2)	2.03 (4)
Ir(2)-I(2)	2.821 (2)	Ir(2)-P(2)	2.347 (9)
Ir(2)-P(4)	2.378 (9)	Ir(2)-O(5)	2.01 (2)
Ir(2)-C(2)	2.12 (3)	Ir(2)-C(3)	1.80 (4)
P(1)-C(4)	1.77 (3)	P(1)-C(11)	1.79 (3)
P(1)-C(21)	1.83 (4)	P(2)-C(4)	1.90 (3)
P(2)-C(31)	1.85 (3)	P(2)-C(41)	1.81 (3)
P(3)-C(5)	1.81 (3)	P(3)-C(51)	1.83 (3)
P(3)-C(61)	1.82 (4)	P(4)-C(5)	1.88 (3)
P(4)-C(71)	1.83 (4)	P(4)-C(81)	1.79 (4)
O(1)-C(1)	1.16 (4)	O(2)-C(2)	1.11 (4)
O(3)-C(3)	1.18 (4)	O(4)-O(5)	1.43 (3)

Table 3.5. Selected Angles (deg) in $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2CH_2Cl_2$ (5)

Ir(2)-Ir(1)-I(1)	146.61 (7)	Ir(2)-Ir(1)-P(1)	82.9 (2)
Ir(2)-Ir(1)-P(3)	90.5 (2)	Ir(2)-Ir(1)-O(4)	56.0 (7)
Ir(2)-Ir(1)-C(1)	126 (1)	I(1)-Ir(1)-P(1)	89.6 (2)
I(1)-Ir(1)-P(3)	95.5 (2)	I(1)-Ir(1)-O(4)	92.3 (6)
I(1)-Ir(1)-C(1)	87 (1)	I(1)-Ir(1)-C(2)	171.1 (9)
P(1)-Ir(1)-P(3)	173.4 (3)	P(1)-Ir(1)-O(4)	93.3 (7)
P(1)-Ir(1)-C(1)	95 (1)	P(1)-Ir(1)-C(2)	82.4 (9)
P(3)-Ir(1)-O(4)	82.4 (7)	P(3)-Ir(1) -C(1)	90 (1)
P(3)-Ir(1)-C(2)	92.8 (9)	O(4)-Ir(1)-C(1)	172 (1)
O(4)-Ir(1)-C(2)	92 (1)	C(1)-Ir(1)-C(2)	89 (1)
Ir(1)-Ir(2)-I(2)	145.5 (1)	Ir(1)-Ir(2)-P(2)	90.3 (2)
Ir(1)-Ir(2)-P(4)	83.4 (2)	Ir(1)-Ir(2)-O(5)	57.8 (6)
Ir(1)-Ir(2)-C(3)	124 (1)	I(2)-Ir(2)-P(2)	94.4 (2)
I(2)-Ir(2)-P(4)	91.5 (2)	I(2)-Ir(2)-O(5)	89.2 (6)
I(2)-Ir(2)-C(2)	177.9 (8)	I(2)-Ir(2)-C(3)	90 (1)
P(2)-Ir(2)-P(4)	173.6 (3)	P(2)-Ir(2)-O(5)	81.3 (7)
P(2)-Ir(2)-C(2)	83.5 (9)	P(2)-Ir(2)-C(3)	92 (1)
P(4)-Ir(2)-O(5)	96.3 (7)	P(4)-Ir(2)-C(2)	90.6 (9)
P(4)-Ir(2)-C(3)	91 (1)	O(5)-Ir(2)-C(2)	90 (1)
O(5)-Ir(2)-C(3)	173 (1)	C(2)-Ir(2)-C(3)	91 (2)
Ir(1)-P(1)-C(4)	117 (1)	Ir(1)-P(1)-C(11)	111 (1)

Table 3.5. (continued)

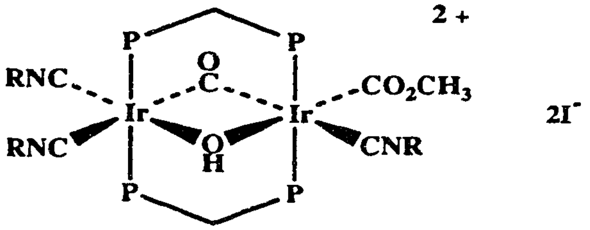
Ir(1)-P(1)-C(21)	121 (1)	C(4)-P(1)-C(11)	100 (1)
C(4)-P(1)-C(21)	102 (2)	C(11)-P(1)-C(21)	104 (1)
Ir(2)-P(2)-C(4)	112 (1)	Ir(2)-P(2)-C(31)	121 (1)
Ir(2)-P(2)-C(41)	111 (1)	C(4)-P(2)-C(31)	101 (1)
C(4)-P(2)-C(41)	106 (1)	C(31)-P(2)-C(41)	104 (1)
Ir(1)-P(3)-C(5)	109 (1)	Ir(1)-P(3)-C(51)	113 (1)
Ir(1)-P(3)-C(61)	121 (1)	C(5)-P(3)-C(51)	101 (2)
C(5)-P(3)-C(61)	106 (2)	C(51)-P(3)-C(61)	104 (2)
Ir(2)-P(4)-C(5)	111 (1)	Ir(2)-P(4)-C(71)	112 (1)
Ir(2)-P(4)-C(81)	120 (1)	C(5)-P(4)-C(71)	99 (1)
C(5)-P(4)-C(81)	106 (2)	C(71)-P(4)-C(81)	107 (2)
Ir(1)-O(4)-O(5)	110 (2)	Ir(2)-O(5)-O(4)	108 (2)
Ir(1)-C(1)-O(1)	177 (3)	Ir(1)-C(2)-Ir(2)	110 (2)
Ir(1)-C(2)-O(2)	129 (3)	Ir(2)-C(2)-O(2)	121 (3)
Ir(2)-C(3)-O(3)	176 (3)	P(1)-C(4)-P(2)	117 (2)
P(3)-C(5)-P(4)	117 (2)		

group, which suggests sp^2 hybridization of carbon, as indicated by the wide Ir(1)-C(2)-Ir(2) angle of 110(2)°. This formulation is also consistent with the low IR stretch for this group. This class of bridging carbonyl, not accompanied by a metal-metal bond, is uncommon, but is found in several examples in which the metals are also bridged by dppm groups.[23b,24] Cleavage of the Ir-Ir bond in **1** to give **5** has resulted in a relaxation of the strain at the peroxo bridge. Therefore the angles at the oxygens (Ir(1)-O(4)-O(5) = 110(2)° and Ir(2)-O(5)-O(4) = 108(2)°) have opened up slightly from the value of 102.0(4)° in **1**. Similarly the Ir(1)-O(4)-O(5)-Ir(2) torsion angle of 62(2)° is also closer to the values observed in other peroxo-bridged species, compared with the analogous one found in **1** (34.6°). The widening of the Ir-Ir separation in **5** has also resulted in less repulsion between the substituents on both metals, so although the two metal-centered octahedra are staggered slightly about the Ir-Ir vector, the associated torsion angles (av. 7.9°) are about half of the values in **1**.[7]

The O(4)-O(5) separation in **5** (1.43(3)Å) is normal for an O-O single bond, and is shorter than the exceptionally long distance found in **1** (1.58(2)Å). Whether this shortening is of chemical significance is of doubt, since the thermal ellipsoids associated with the oxygen atoms and the relatively poor diffraction quality of the crystal of **1**[7a] suggested, as mentioned above, that the abnormally long O-O separation may be an artifact arising from systematic errors in the data.[7c]

Compound **5** is one of several examples of peroxo-bridged complexes in which the O_2 unit forms part of a 5-membered metallocycle.[1e,2b-d,2g] However this appears to be the first such metallocycle in which a carbonyl is a bridging group together with O_2.

Examples involving the oxidation of isocyanides by dioxygen compounds, as in the reaction of $[Ni(O_2)(^tBuNC)_2]$ with ^tBuNC to give $[Ni(^tBuNC)_4]$ and ^tBuNCO,[18a] are rare. In CH_2Cl_2/CH_3OH (5:1, by volume), compound **1** reacts with excess (5-10 equiv) ^iPrNC yielding a product containing three isocyanide ligands. However no evidence for oxidation of the isocyanide is observed and all of the added isocyanide is accounted for in the ^1H NMR spectrum by the three coordinated groups and that remaining unreacted. The product is formulated as the hydroxide-bridged methoxycarbonyl complex $[Ir_2(C(O)OCH_3)(^iPrNC)_3(\mu\text{-}OH)(\mu\text{-}CO)(dppm)_2][I]_2$ (**6**). The IR spectrum of **6** displays two strong



R=^{i}Pr (6); ^{t}Bu (7)

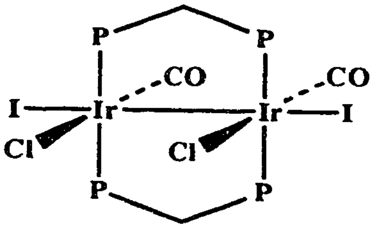
absorptions at 2193 and 2180 cm^{-1}, assignable to the coordinated isocyanide ligands. Two low-frequency bands at 1653 and 1625 cm^{-1} can be assigned to the bridging carbonyl and to the carbonyl group of the methoxycarbonyl ligand, although because of the proximity of these bands it has not been possible to identify which is which. Bridging carbonyls in the absence of metal-metal bonds have been shown to display stretches in this region, as shown by compound 5, and this range is also common for alkoxycarbonyl ligands.[25] The ^{13}CO-enriched compound displays the expected shift of these two bands (to 1614 and 1592 cm^{-1}) in the IR spectrum, ruling out the possibility that they may arise from an isocyanide group. An additional band at 1036 cm^{-1} can also be assigned to ν(C-O) of the methoxycarbonyl group.[25] The O-H stretch of the hydroxy group appears as a broad band at 3190 cm^{-1}. This is at slightly lower wavenumber than expected, possibly due to hydrogen bonding involving the iodide ion, as has been observed in other hydroxy-halide compounds.[26] The conductivity of **6** (120.0 Ω^{-1} cm^2 mol^{-1} in CH_3NO_2) is also lower than expected for a 1:2 electrolyte,[27] and may result from the proposed hydrogen bonding. The hydroxide group of **6** readily undergoes proton exchange with H_2O, even in the solid state, as evidenced by the appearance of O-H and O-D bands (3190, 2360 cm^{-1}) when the compound is prepared in the presence of D_2O.

The presence of the methoxycarbonyl group is further supported by the $^{13}C\{^1H\}$ and ^1H NMR spectra of **6**. In the $^{13}C\{^1H\}$ NMR spectrum the bridging carbonyl appears as a broad singlet at δ 228.1 and the methoxycarbonyl appears as a triplet at δ 150.6 ($^2J_{PC}$ = 7.1 Hz). This latter resonance falls at the high-field end of the range typically found (δ 158-215)[25] for alkoxycarbonyls and related groups. The methoxy protons appear as a singlet at δ 2.60 in the ^1H NMR spectrum, changing to a doublet in the ^{13}CO-enriched compound ($^3J_{HC}$ = 3.8 Hz). When CD_3OD is used as solvent no methyl signal is observed for the methoxycarbonyl protons, confirming that methanol is the origin of the methoxy moiety. The ^1H NMR spectrum also shows the expected pattern of doublets and septets ($^3J_{HH}$ = 6 Hz) for the ^iPrNC groups in the expected regions. One of the septets appears to mask the hydroxide resonance as judged by the absence of a clear signal for this group and by integration of the isocyanide resonances.

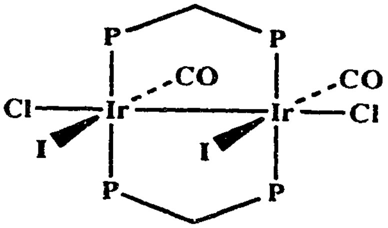
The analogous compound [$Ir_2(CO_2Me)(^tBuNC)_3(\mu$-OH)($\mu$-CO)-$(dppm)_2][I]_2$ (**7**), shown above, is obtained in a similar manner by the reaction of **1** with ^{t}BuNC, and is characterized in the same way. Again the hydroxide proton can not be unambiguouly assigned in the ^{1}H NMR spectrum due to the broadness of the spectrum even at -80°C. Both compounds **6** and **7** appear to be fluxional as shown by their ^{1}H and $^{31}P\{^1H\}$ NMR spectra. However the nature of this fluxionality was not elucidated.

Alkoxycarbonyl complexes are commonly prepared by the reaction of carbonyl complexes with the nucleophilic alkoxide anions.[25] However their generation from weak nucleophiles such as alcohols is less common.[28] Significantly compound **1** itself does not react with methanol, even after several days. It may be that iodide substitution by the isocyanide ligands renders the carbonyls more electrophilic because of the resulting dipositive charge on the complex, leading to nucleophilic attack by methanol. However it should be pointed out that we have no mechanistic information on this reaction, and although we assume that protonation of the dioxygen moiety by methanol occurs, we are unable to comment on the stage at which this occurs, on the fate of the oxygen atom which is lost, or on the possible role of adventitious water.

Protonation of a peroxo compound with acids to give H_2O_2 is well established, and if the anion of the acid is coordinating, the reaction can be a useful route for the preparation of the anion-substituted compound.[1e] As with other dioxygen complexes,[1e] compound **1** reacts rapidly with protic acids, yielding H_2O_2, as detected iodimetrically. An example is already seen in the reaction of **1** with H_2SO_4, affording the sulfate-bridged **2**. Treatment of **1**, either in solution or the solid state, with excess gaseous HCl yields $[Ir_2I_2Cl_2(CO)_2(dppm)_2]$ (**8a**) immediately. This species is shown by $^{31}P\{^1H\}$ NMR spectroscopy to be a symmetric species (singlet δ -13.9), and has two carbonyl bands at 2066 and 2031 cm^{-1} in the IR spectrum. Conductivity measurements show that **8a** is not conducting in CH_2Cl_2 solutions ($\Lambda < 2\ \Omega^{-1}cm^2mol^{-1}$). If **1** is instead treated with only 2 equiv of HCl, a different species, **8b**, is obtained, having a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ -23.0 and a carbonyl band in the IR spectrum at 2025 cm^{-1}. Compound **8b** is also produced as the major species in the reaction of *trans*-$[IrCl(CO)(dppm)]_2$ with one equiv of iodine. Surprisingly no **8a** is formed in this reaction, as shown by the NMR spectra. Elemental analyses indicate that both **8a** and **8b** are dichloro diiodo complexes, so they are formulated as the isomers shown. The isomer with the good π-donor iodo



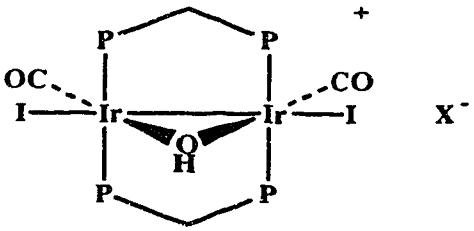
(8a)



(8b)

ligands trans to the carbonyls is formulated as **8b** based on the lower carbonyl stretch for this isomer.

Protonation of **1** with 1 equiv of $HBF_4 \cdot Et_2O$ yields a symmetric species having two carbonyl bands at 2064 and 2032 cm^{-1} in the IR spectrum and a weak absorption at 3550 cm^{-1} attributed to the OH stretch of a hydroxide group. The ^1H NMR spectrum displays a quintet for the hydroxy proton at δ 3.06 ($^2J_{PH}$ = 2.8 Hz) which simplifies to a singlet upon ^{31}P decoupling. This product is formulated as $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$ (**9a**) and apparently results from adventitious water as has been previously observed in protonation reactions involving O_2 complexes.[29] Attempts to obtain this product more directly, by the oxidative addition of I_2 to the known hydroxy-bridged $[Ir_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$,[26a] *did* yield **9a** in about 30% yield together with other unidentified products, adding support to its formulation.



X=BF₄ (9a); PF₆ (9b); SO₃CF₃ (9c)

Initial attempts to prepare the nitrate-bridged complex **3** (as either the BF_4^- or PF_6^- salts) by reaction of **1** with $NOBF_4$ or $NOPF_6$ in CH_2Cl_2 instead gave rise to the hydroxy-bridged compounds **9a** and **9c**. Similar results have previously been obtained, even when precautions were taken to dry solvents and glassware.[30] The above reaction proceeds more readily in the presence of added H_2O and yields significant quantities of the OD-bridged product when D_2O is added, as judged by the decrease in the OH resonance in the ^1H NMR spectrum. When the reaction of **1** with $NOBF_4$ is carried out in carefully dried THF, the major product *is* the nitrate-bridged species **3b**, although **9a** is still observed in varying amounts.

Although peroxo compounds of group VIII metals are known to catalyze the oxidation of organic phosphines,[3a,31] no reaction was observed between **1** and PPh_3, even after several days. However in the presence of 1 equiv of protic acid (eg. HCl, CH_3CO_2H), PPh_3 is readily oxidized to $OPPh_3$, along with the formation of other unidentified species. The $OPPh_3$ was identified by the $^{31}P\{^1H\}$ NMR (δ 27.5) and IR spectra ($\nu(P{=}O) = 1187\ cm^{-1}$). The amount of oxidation depends directly on the amount of acid added and is therefore not catalytic in acid. It appears therefore that protonation of the peroxo group to yield the hydrogen peroxide anion occurs and it is this anion which performs the oxidation. Such a mechanism has previously been proposed for the catalytic oxidation of PPh_3 by $Pt(PPh_3)_3$.[32]

Dioxygen complexes are known to react with olefins and ketones.[1c] However compound **1** was found to be unreactive with the few substrates that we investigated; no reaction was observed with ethylene, tetrafluoroethylene, tetrachloroethylene, *cis*-1,2-dichloroethylene or acetone. The inertness of **1** towards ethylene as well as acetylene may not be surprising, since studies of the dioxygen compounds of the group VIII metals have showed that these compounds only react with the carbon-carbon multiple bonds rendered electrophilic by the introduction of electron-withdrawing substituents.[1e] Its inertness towards species such as tetrafluoroethylene, on the other hand, may indicate that its peroxo moiety is less nucleophilic than those in compounds such as $Pt(O_2)(PR_3)_2$,[1e] or may result from steric effects arising from the dppm ligands, which render the attack of the substrates at the O_2 group difficult. Although **1** did react with hexafluoroacetone, several species were obtained under a variety of conditions, and this has not been pursued.

Conclusions

The dioxygen compounds of iridium were shown to be generally less reactive than those of the nickel triads,[1b,e] as manifested by their reactivity towards substrates such as CO and NO. However the peroxo-bridged complex, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**1**), reacts with a variety of inorganic or organic species, although it does not react with species such as olefins. It should be noted that under normal conditions, molecular oxygen does not react with SO_2, NO_2 and CO. The oxidation of these molecules clearly shows the activation of the dioxygen group upon coordination to metal centres.

For the most part, the chemistry of **1** with small molecules is as expected. Therefore reactions with NO_2 and SO_2 yield the nitrate- and sulfate-bridged products, respectively, and protonation of the dioxygen moiety releases H_2O_2. However compound **1** does exhibit a significant variety of unusual reactivities with other small molecules. With nitric oxide, oxidation occurs to give the unusual nitrosyl-bridged species as the nitrate salt, $[Ir_2I_2(CO)_2(\mu\text{-}NO)(dppm)_2][NO_3]$. Reaction with carbon monoxide results in both oxidation of the substrate to give carbon dioxide and $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$, and CO-addition to yield the unusual carbonyl- and peroxo-bridged species $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(\mu\text{-}CO)(dppm)_2]$. Compound 1 in methanol reacts with isocyanides to give $[Ir_2(C(O)OMe)(CNR)_3(\mu\text{-}OH)(\mu\text{-}CO)(dppm)_2][I]_2$, in which the methoxycarbonyl group has come from methanol through nucleophilic attack on a coordinated carbonyl. The bridging hydroxide group has originated through protonation of the peroxy group either by methanol or adventitious water. Adventitious water was found to play a role in a number of reactions, so although 1 reacted with $NOBF_4$ to give $[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][BF_4]$ in carefully dried solvents, the hydroxide-bridged species, $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$, was also obtained, sometimes as the major or sole product depending on the wetness of the solvent.

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Chapter 4

Alkyne-to-Vinylidene Tautomerism Mediated by Two Adjacent Metal Centers, and Rare Examples of Ethylene Coordination in "A-Frame" Compounds

Introduction

Transition-metal vinylidene complexes are key species in the chemistry of two-carbon ligands,[1] and continue to attract considerable current interest.[1,2] It has been suggested that vinylidene species play an important role in Fischer-Tropsch chemistry,[3] in alkyne polymerization[4] and in C-C bond formation in the condensation of alkynes with other substrates.[5] Vinylidene complexes have also proven useful in the synthesis of novel organic compounds.[6]

Although the majority of vinylidene complexes involve only a single metal center,[1] binuclear vinylidene-bridged complexes are attracting recent interest. One of the routes to such species, involving the tautomerism of alkynes, is demonstrated in the treatment of a dirhodium complex with phenylacetylene,[7] and in related reactions involving dihaloacetylenes.[8] Unlike the tautomerism mediated by a single metal center, which is generally accepted as proceeding via a 1,2-hydrogen shift of an η^2-alkyne group,[1,9] the mechanism involving binuclear species is not well understood. On the model alkyne-bridged compound, $[Pt_2H_4(\mu\text{-}C_2H_2)]^{4-}$, calculations by Silvestre and Hoffmann, showed that direct isomerization of the bridging alkyne to a bridging vinylidene moiety was energetically unlikely.[9]

In previous studies,[10,11] the binuclear iodo complex, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**), was found to display unusual reactivity towards dioxygen.[11] The reactivity of its oxygen adduct, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ has been described in Chapter 3. An extension of the chemistry of complex **1** to terminal alkynes has again shown atypical chemistry; rather than the conventional μ,η^2-alkynes usually obtained, as in the reactions of **1** with internal alkynes[10] or in reactions of the dichloro analogue, $[Ir_2Cl_2\text{-}(CO)_2(dppm)_2]$, with internal or terminal alkynes,[12] complex **1** yielded vinylidene-bridged products with both acetylene and phenylacetylene. In this chapter we report the details of these reactions, in which we have attempted to spectroscopically monitor intermediates in these transformations in hopes of establishing the functions of the adjacent metals in the acetylene-to-vinylidene tautomerization.

In addition, surprisingly perhaps, complex **1** was found to be reactive towards another two-carbon substrate, ethylene. Mononuclear olefin complexes are well-known, and many of these complexes are involved in important reactions such as alkene hydrogenation, polymerization and hydrocarbonylation.[13] In fact, much of our understanding about the interaction between transition metals and unsaturated molecules is derived from studies of these mononuclear olefin species.[13,14] However much less is known about the chemistry of binuclear olefin complexes. This may not be surprising, since the number of olefin-coordinated binuclear complexes is far less than that of the mononuclear counterparts. As a matter of fact, although numerous dppm-bridged binuclear complexes of Rh and Ir have been reported,[15] none of them is known to contain a coordinated ethylene molecule. The reaction of **1** with ethylene is therefore very unusual. It was of interest to determine how the ethylene molecule would interact with the dppm-bridged binuclear framework. This reaction as well as that of $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-dppm})_2][BF_4]$ (**2**) with ethylene is also described in this chapter.

Experimental Section

General experimental conditions were as described in Chapter 2. All solvents were distilled and stored under argon. Reactions were conducted at room temperature unless otherwise noted. Acetylene and phenylacetylene were purchased from Matheson and Aldrich, respectively, and acetylene (98.9% ^{13}C enriched) was obtained from MSD Isotopes. These and all other reagents were used as received. The compounds, $[Ir_2I_2(CO)(\mu\text{-}CO)(\text{dppm})_2]$ (1) and $[Ir_2(CO)_2(\mu\text{-}I)(\text{dppm})][BF_4]$ (2), were prepared as previously reported.[10] Spectroscopic data for the compounds prepared are found in Tables 4.1 and 4.2.

Preparation of Compounds. (a) $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\text{dppm})_2]$ (5). To a CH_2Cl_2 solution of $[Ir_2I_2(CO)(\mu\text{-}CO)(\text{dppm})_2]$ (1) (200.0 mg, 0.14 mmol, in 15 mL) was added 3.6 mL of acetylene (0.14 mmol), by a gas-tight syringe, resulting in an immediate color change from *dark* to light orange. After stirring for ca. 20 h, the solvent was removed in vacuum. The yellow residue was recrystallized from CH_2Cl_2/Et_2O to give **5** as dark orange

Table 4.1. Spectroscopic Data [a]

compd	IR, cm^{-1} [b]	δ ($^{31}P\{^{1}H\}$) [c]	δ (^{1}H) [d]
[$Ir_2(CO)_2(\mu$-I)(μ-HC_2H)(dppm)$_2$][I] (3)	1998 (vs)	-32.1 (s)	8.48 (br, 2H), 5.52 (m, 2H)
			4.01 (m, 2H)
[$Ir_2I(CO)_2(\mu$-HC_2H)(dppm)$_2$][I] (4)	2000 (st)	-28.2 (m)	8.52 (m, 1H, H^2), 8.06 (m, 1H,
	1968 (vs)	-36.3 (m)	H^1, $J_{H^1H^2}$ = 3.3 Hz), 5.79 (m,
			2H), 4.91 (m, 2H)
[$Ir_2I_2(CO)_2(\mu$-CCH_2)(dppm)$_2$] (5)	1985 (med)	-20.2 (m)	5.34 (m, 2H), 4.62 (m, 2H)
	1960 (vs)	-38.0 (m)	
[Ir_2(H)I$(CO)_2(\mu$-CCPh)(dppm)$_2$][I] (6)	2028 (w)	-9.0 (m)	4.55 (m, 2H), 3.46 (m, 2H)
	1996 (w)	-25.3 (m)	-11.55 (t, 1H, $^{2}J_{PH}$ = 12.4 Hz)
[$Ir_2I_2(CO)_2(\mu$-CC(H)Ph)(dppm)$_2$] (7)	1998 (med)	-23.3 (m)	8.48 (br, 1H), 5.50 (m, 1H)
	1984 (vs)	-24.1 (m)	5.02 (m, 1H), 3.60 (m, 1H)
		-32.5 (m)	3.34 (m, 1H)
		-33.0 (m)	

Table 4.1. (continued).

$[Ir_2I(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]$ **(8)**	2018 (st)	-18.3 (m)	9.18 (dt, 1H, $^1J_{HH}$ = 6 Hz, $^3J_{PH}$ =
	2009 (med)	-29.2 (m)	3 Hz), 8.84 (br, s, 1H),
			8.02 (dm, 1H), 7.96 (br, s, 1H),
			4.46 (m, 2H),3.00 (m, 2H)
$[Ir_2(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]_2$	2027 (med)	-33.5 (s)	9.34 (br, s, 2H), 5.16 (m, 2H)
(9a)			2.62 (m, 2H)
$[Ir_2(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][BF_4]_2$	2028 (st)	-33.4 (s)	9.32 (br, s, 2H), 5.18 (m, 2H)
(9b)			2.62 (m, 2H)
$[Ir_2I(CO)(C_2H_4)(\mu\text{-}CO)(dppm)_2][I]$ **(10a)**	1964 (vs, br)	-5.67 (m)	4.22 (m, 2H), 4.04 (m, 2H),
	1804 (med)	-6,94 (m)	2.68 (m, 2H), 1.58 (m, 2H)
$[Ir_2I(CO)(C_2H_4)(\mu\text{-}CO)(dppm)_2][BF_4]$ **(10b)**	1959(vs, br)	-5.69 (m)	4.21 (m, 2H), 3.96 (m, 2H),
	1803 (med)	-6.92(m)	2.69 (m, 2H), 1.59 (m, 2H)

[a] Abbreviations used: w = weak, med = medium, st = strong, vs = very strong, s = singlet, m = multiplet, dt = doublet of triplets, dm = doublet of multiplet, br = broad. $^{13}C\{^1H\}$ NMR spectroscopic data are given in Table 4.2. [b] Nujol mull, ν(CO). [c] vs 85% H_3PO_4, in CD_2Cl_2, at 25°C except compounds 6 and 7 (-80°C). [d] vs TMS.

Table 4.2. ^{13}C NMR Spectroscopic Data^a

compd	δ (^{13}C{^{1}H})
[Ir$_2$(CO)$_2$(μ-I)(μ-HC$_2$H)(dppm)$_2$][I] (3)	180.5 (m, CO); 113.9 (dt, HC$_2$H, $^2J_{CC}$ = 14 Hz, $^2J_{CP}$ = 6 Hz)
[Ir$_2$I(CO)$_2$(μ-HC$_2$H)(dppm)$_2$][I] (4)	181.8 (dt, $^2J_{CC}$ = 25 Hz, $^2J_{CP}$ = 9 Hz, C^4), 159.2 (t, $^2J_{CP}$ = 10 Hz, C^3); 106.6 (m, C^1, $^2J_{CP^1}$ = 3.3 Hz, J_{CP^2} = 2.5 Hz, $^1J_{CC}$ = 59 Hz), 105.6 (m, C^2, $^3J_{CP^1}$ = 2.5Hz, $^2J_{CP^2}$ = 6.5Hz)
[Ir$_2$I$_2$(CO)$_2$(μ-CCH$_2$)(dppm)$_2$] (5)	194.3 (dm, C$_\alpha$) 129.8 (d, C$_\beta$, $^1J_{C\alpha C\beta}$ = 67 Hz); 181.9 (t, $^2J_{CP}$ = 13 Hz), 169.5 (t, CO, $^2J_{CP}$ = 12 Hz)
[Ir$_2$I$_2$(CO)$_2$(μ-CCHPh)(dppm)$_2$] (7)	192.6 (q, $^2J_{CP}$ = 5 Hz, Cα), 135.6 (s, C$_\beta$); 184.8 (CO), 166.6 (CO)
[Ir$_2$I(CO)$_2$(μ-HC$_2$H)(μ-CCH$_2$)(dppm)$_2$][I] (8)	174.1 (t, $^2J_{CP}$ = 7 Hz, CO), 172.9 (t, CO); 154.7 (dm, C$_\alpha$), 139.5 (d, C$_\beta$, $^1J_{C\alpha C\beta}$ = 57 Hz); 141.2 (dm), 133.0 (dq, HC$_2$H, $^1J_{CC}$= 57 Hz)

Table 4.2. (continued).

$[Ir_2(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]_2$ **(9a)**	172.8 (s, CO); 152.0 (dq, $^1J_{CC}$ = 57 Hz, C_α, $^2J_{CP}$ = 8 Hz), 147.3 (s), 128.6 (d, $^1J_{CC}$ = 57 Hz, C_β)

[a] Abbreviations used: s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet, dt = doublet of triplets, dq = doublet of quintets, dm = doublets of multiplets; in CD_2Cl_2 vs TMS, at 25°C.

crystals in 50% yield. Anal. calcd for $Ir_2I_2O_2P_4C_{54}H_{46}$: C, 43.55; H, 3.12. Found: C, 43.52; H, 3.22.

(b) [$Ir_2(CO)_2(\mu$-I)(μ-HC_2H)(dppm)$_2$][I] (3) and [$Ir_2I(CO)_2(\mu$-HC_2H)-(dppm)$_2$][I] (4). These compounds were characterized spectroscopically. Their formation was monitored by using NMR and IR spectroscopy. Compound **3** appeared immediately after addition of either excess or 1 equiv of acetylene to **1**, and was stable at -40°C. At room temperature, it transformed to **4** in ca. 20 min. Compound **5** was the only product after the solution was stirred for ca. 20 h at 20°C.

(c) [$Ir_2I_2(CO)_2(\mu$-CC(H)Ph)(dppm)$_2$] (7). To a CH_2Cl_2 solution of **1** (200.0 mg, 0.14 mmol, in 15 mL) was added 15.0 μL of phenylacetylene (0.14 mmol), causing a color change to light orange almost immediately. After stirring for ca. 2 h, the solvent was removed. Redissolution of the residue in 2 mL of CH_2Cl_2 followed by addition of 15 mL of Et_2O precipitated a yellow orange solid, which was washed with Et_2O and dried to give **7** in ca. 80% yield. The same compound was also obtained when excess phenylacetylene was used. Anal. Calcd for $Ir_2I_2O_2P_4C_{60}H_{50}$: C, 46.03; H, 3.32. Found: C, 46.01; H, 3.22.

(d) [$Ir_2I(H)(CO)_2(\mu$-CCPh)(dppm)$_2$][I] (6). Compound **6** was characterized spectroscopically at temperatures below -40°C. In a typical experiment, 1 or several equiv of phenylacetylene was syringed into an NMR tube containing 30.0 mg of compound **1** (0.020 mmol, in 0.50 mL of CD_2Cl_2) at -78°C. NMR spectra, recorded at temperatures below -40°C, showed only one product, identified as **6**. At temperatures from 0 to 25°C, **7** was the only product. To obtain an IR spectrum of **6**, the reaction was conducted at -78°C, and after stirring for 0.5 h, Et_2O was added at the same temperature to the solution. The precipitated solid contained both **6** and **7**.

(e) $[Ir_2I(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]$ (8) and $[Ir_2(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]_2$ (9a). Acetylene was passed through a CH_2Cl_2 solution of **5** (60.0 mg, 0.040 mmol, in 10 mL), at a rate of ca. 0.3 mL sec^{-1} causing an immediate color change to yellow. The solution was stirred for 0.5 h followed by concentration to ca. 2 mL and addition of Et_2O. The precipitated yellow solid contained two products, identified as complexes **8** and **9a** in a typical ratio of ca. 1.8:1.

Complexes **8** and **9a** were also obtained by reacting **1** with excess acetylene for ca. 20 h, and the same cationic complexes were also spectroscopically (^1H NMR, $^{31}P\{^1H\}$ NMR and IR spectra) identified in the reaction of $[Ir_2(CO)_2(\mu\text{-}I)(dppm)][BF_4]$ (**2**) with excess acetylene. This latter reaction was carried out in THF and completed within 0.5 h.

Addition of 2 equiv of $AgBF_4$ to the mix of **8** and **9a** in CH_2Cl_2 afforded $[Ir_2(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][BF_4]_2$ (**9b**), characterized only spectroscopically due to its instability.

(f) $[Ir_2(CO)(C_2H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (10a). Ethylene gas (1 atm) was placed over a 5-mL CH_2Cl_2 solution of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**) (30 mg, 0.02 mmol), causing a slight color change from orange to light orange within 1-2 min; the reaction was reversible upon flushing with dinitrogen. To obtain NMR spectra, the reaction was carried out in CD_2Cl_2 solution under an ethylene atmosphere. Compound **10a** was determined to be a 1:1 electrolyte in ethylene-saturated CH_2Cl_2 solution ($\Lambda = 47.3$ Ω^{-1} cm^2 mol^{-1}).

(g) $[Ir_2(CO)(C_2H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]\cdot CH_2Cl_2$ (10b). Ethylene gas (1 atm) was placed over a 5-mL solution of $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (2), resulting in an immmediate color change from red to orange with accompanying precipitation of the product. After the mixture was stirred for 0.5 h, the solvent was removed under vacuum. Compound **10b** is soluble in CH_2Cl_2 and was recrystallized from this solvent. Anal. Calcd for $Ir_2I_2Cl_2P_4F_4O_2C_{55}BH_{50}$: C, 43.00; H, 3.29; I, 8.26. Found: C, 42.85; H, 3.16; I 8.41.

X-ray Data Collection. Suitable crystals of $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)\text{-}(dppm)_2]$ (R = H (5), Ph (7)) were grown from CH_2Cl_2/ether at 22°C. Data for both compounds were collected on an Enraf-Nonius CAD4 diffractometer with use of MoKα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $21.3° \leq 2\theta \leq 23.6°$ (5) and $20.0° \leq 2\theta \leq 23.9°$ (7). The diffraction symmetry and the systematic absences $0kl$, k = odd; $h0l$, l = odd; $hk0$, h = odd for **5** and $h00$, h = odd; $0k0$, k = odd; $00l$, l = odd for **7**, are consistent with the space groups *P*bca and $P2_12_12_1$, respectively. Data were collected to a maximum $2\theta = 50°$ and background counts were obtained by extending the scan 25% on each side of the peaks. Three reflections were chosen as intensity standards and were remeasured at 120 min intervals of X-ray exposure. There was no significant variation in the intensities of either set of standards so no correction was applied. The data were processed in the usual way with a value of 0.04 used for p to downweigh intense reflections[16], and absorption corrections were applied by the method of Walker and Stuart.[17] See Table 4.3 for a summary of crystal data and X-ray collection information.

Structure Solution and Refinement. Both structures were solved by direct methods, using MULTAN[18] to locate the Ir, I and P atoms. All other atoms were located after subsequent least-squares cycles and difference fourier syntheses. Atomic scattering factors[19,20] and anomalous dispersion terms[21] were taken form the usual sources. All hydrogen atoms of the complexes were included as fixed contributions; their idealized positions were generated from the geometries of the attached carbon atoms and their thermal parameters set at 20% greater than the isotropic thermal parameters of these carbons. In compound **5** a CH_2Cl_2 molecule was located and refined to 75% occupancy. Several other regions of electron density, remote from the complex, were located in the cell but could not unambiguously be assigned as solvent. This unassigned electron density, and the poorer quality of the crystals of **5** prevented a better refinement. The final model for **5** with 319 parameters varied refined to R = 0.064 and Rw = 0.086, and on the final Fourier map the maximum electron density (3.60 e/Å^3) was associated with the assumed disordered solvent in **5**. For compound **7** the final model with 331 parameters varied refined to R = 0.046 and Rw = 0.050, and the final difference Fouier map had the maximum residual density of 1.06 e/Å^3, located in the vicinity of the iridium atoms. Refinement of the other enantiomer of **7** resulted in significantly poorer values for R and R_w so the original choice was assumed correct.

Table 4.3. Crystallographic Data for $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2]\cdot 0.75\ CH_2Cl_2$ (5) and $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(dppm)_2]$ (7)

compd	5	7
formula	$C_{54}H_{46}I_2Ir_2O_2P_4\cdot 0.75\ CH_2Cl_2$	$C_{60}H_{50}I_2Ir_2O_2P_4$
fw	1552.84	1565.24
space group	*P*bca	$P2_12_12_1$
temp, °C	22	22
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
cell parameters		
a, Å	16.474 (3)	13.093 (3)
b, Å	18.289 (3)	18.177 (3)
c, Å	37.642 (9)	22.784 (4)
ρ (calcd), g cm^{-3}	1.849	1.902
V, Å^3	11306 (1)	5423 (1)
Z	8	4
no. of unique data collcd	10856	4457
no. of unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	3766	2985
linear abs coeff (μ) cm^{-1}	60.112	61.689

Table 4.3. (continued).

range of transm factors	0.8597-1.1952	0.8753-1.5266
final no. of params refined	319	331
R	0.064	0.046
R_w	0.086	0.050

For compound 5 the positional and thermal parameters of the non-hydrogen atoms are given in Table 4.4; the equivalent parameters for compound 7 are given in Table 4.5. Selected lengths and angles for the compounds are tabulated in Tables 4.6 to 4.9.

Description of Structures

To a first approximation the structures of both complexes [$Ir_2I_2(CO)_2(\mu$-CC(H)R)(dppm)$_2$] (R = H (5), Ph (7)) are quite similar. These are shown in Figures 4.1 and 4.2. Compound 5 crystallizes with CH_2Cl_2 in the lattice, however there are no unusual contacts involving the solvent molecule, and its parameters are normal. Both compounds have an "A-frame" geometry in which the dppm groups bridge the metals in a trans arrangement, with the vinylidene units also bridging the metals in the equatorial plane perpendicular to the metal phosphine bonds. The parameters within both species are remarkably similar and both resemble the related dichloro tricarbonyl compound, [$Ir_2Cl_2(CO)_2(\mu$–CO)(dppm)$_2$],[22] in which a carbonyl bridges the metals instead of a vinylidene unit. In both vinylidene-bridged compounds the metals have distorted octahedral geometries in which the two Ir(II) centers are joined by an Ir-Ir single bond. Although the Ir-Ir separation in 7 (2.783(1)Å) is very close to that in the carbonyl-bridged analogue (2.779(1)Å),[22] the distance observed in 5 (2.825(1)Å) is somewhat longer; however this difference is not large, and all distances are consistent with normal single bonds. The major distortions from octahedral geometry in both 5 and 7 result from the strain imposed by the bridging vinylidene groups and the accompanying

Table 4.4. Positional and Thermal Parameters of the Atoms of $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2]$ (5).[a]

atom	x	y	z	B(Å^2)
Ir(1)	0.42093(7)	0.07445(7)	0.35945(3)	2.79(2)*
Ir(2)	0.53415(7)	0.17778(7)	0.38531(3)	3.10(3)*
I(1)	0.4513(1)	0.0913(1)	0.28721(6)	5.05(6)*
I(2)	0.6062(2)	0.2444(1)	0.44436(7)	5.81(7)*
P(1)	0.5177(4)	-0.0185(4)	0.3607(2)	3.0(2)*
P(2)	0.6405(5)	0.0928(4)	0.3827(2)	3.3(2)*
P(3)	0.3199(5)	0.1634(5)	0.3542(2)	3.3(2)*
P(4)	0.4395(5)	0.2740(5)	0.3843(2)	3.5(2)*
O(1)	0.292(1)	-0.039(1)	0.3607(5)	3.5(4)
O(2)	0.606(2)	0.245(2)	0.3170(8)	9.4(8)
C(1)	0.340(2)	0.001(2)	0.3633(9)	6.0(9)
C(2)	0.585(2)	0.222(2)	0.3457(9)	5.9(9)
C(3)	0.456(2)	0.103(2)	0.4109(8)	3.0(6)
C(4)	0.427(2)	0.089(2)	0.4410(9)	5.1(8)
C(5)	0.618(2)	0.018(1)	0.3522(7)	2.2(6)
C(6)	0.363(2)	0.252(2)	0.3498(9)	4.7(8)
C(11)	0.525(2)	-0.071(2)	0.3986(8)	3.3(6)
C(12)	0.464(2)	-0.077(2)	0.4233(7)	3.2(6)
C(13)	0.468(2)	-0.127(2)	0.4527(8)	3.8(7)
C(14)	0.538(2)	-0.164(2)	0.4571(9)	4.7(8)
C(15)	0.602(2)	-0.163(2)	0.4366(8)	4.2(7)

Table 4.4. (continued).

C(16)	0.597(2)	-0.114(2)	0.4050(8)	4.0(7)
C(21)	0.506(2)	-0.084(2)	0.3250(8)	4.1(7)
C(22)	0.556(2)	-0.090(2)	0.295(1)	5.7(9)
C(23)	0.542(2)	-0.145(2)	0.271(1)	6(1)
C(24)	0.489(2)	-0.198(2)	0.2759(9)	5.1(8)
C(25)	0.438(2)	-0.197(2)	0.305(1)	6(1)
C(26)	0.449(2)	-0.136(2)	0.332(1)	6(1)
C(31)	0.735(2)	0.126(2)	0.3643(8)	3.8(7)
C(32)	0.788(3)	0.159(2)	0.388(1)	9(1)
C(33)	0.867(3)	0.188(2)	0.373(1)	9(1)
C(34)	0.877(2)	0.183(2)	0.333(1)	7(1)
C(35)	0.828(2)	0.151(2)	0.315(1)	6.0(9)
C(36)	0.757(2)	0.119(2)	0.3314(8)	4.8(8)
C(41)	0.676(2)	0.042(2)	0.4226(8)	3.4(7)
C(42)	0.746(2)	0.004(2)	0.4197(8)	3.7(7)
C(43)	0.768(2)	-0.041(2)	0.449(1)	6.0(9)
C(44)	0.723(2)	-0.042(2)	0.4787(9)	5.0(9)
C(45)	0.655(2)	0.001(2)	0.4812(9)	4.[illegible](8)
C(46)	0.633(2)	0.047(2)	0.4542(9)	4.6(8)
C(51)	0.255(2)	0.156(2)	0.3140(8)	3.8(7)
C(52)	0.267(2)	0.202(2)	0.2844(8)	4.1(8)
C(53)	0.214(2)	0.198(2)	0.2556(9)	5.2(9)
C(54)	0.156(2)	0.148(2)	0.254(1)	6(1)
C(55)	0.143(2)	0.104(2)	0.287(1)	7(1)

Table 4.4. (continued).

C(56)	0.195(2)	0.105(2)	0.317(1)	6(1)
C(61)	0.242(2)	0.164(2)	0.3879(8)	5.4(8)
C(62)	0.236(2)	0.110(2)	0.413(1)	6.0(9)
C(63)	0.171(3)	0.111(3)	0.437(1)	10(1)
C(64)	0.120(3)	0.169(3)	0.438(1)	11(2)
C(65)	0.120(3)	0.218(3)	0.412(1)	10(1)
C(66)	0.190(2)	0.219(2)	0.387(1)	8(1)
C(71)	0.375(2)	0.302(2)	0.4245(8)	4.1(8)
C(72)	0.327(2)	0.368(2)	0.418(1)	6.1(9)
C(73)	0.270(2)	0.381(2)	0.448(1)	7(1)
C(74)	0.267(3)	0.339(3)	0.476(1)	9(1)
C(75)	0.316(2)	0.277(2)	0.481(1)	7(1)
C(76)	0.368(2)	0.261(2)	0.457(1)	7(1)
C(81)	0.480(2)	0.367(2)	0.3697(9)	5.7(9)
C(82)	0.484(2)	0.385(2)	0.3327(9)	4.8(8)
C(83)	0.516(2)	0.455(2)	0.326(1)	7(1)
C(84)	0.537(2)	0.498(2)	0.3525(9)	5.7(9)
C(85)	0.534(3)	0.484(3)	0.386(1)	10(1)
C(86)	0.508(2)	0.414(2)	0.3940(9)	6.0(9)
C(99)[b]	0.212(5)	0.445(4)	0.255(2)	14(2)
Cl(1)[b]	0.277(1)	0.4075(9)	0.2856(5)	11.4(6)*
Cl(2)[b]	0.218(1)	0.427(1)	0.2144(7)	18.0(9)*

Table 4.4. (continued).

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. Starred atoms were refined anisotropically. Thermal parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameters defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Atoms of CH_2Cl_2 molecule of crystallization.

Table 4.5. Positional and Thermal Parameters of the Atoms of $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(dppm)_2]$ (7).[a]

atom	x	y	z	B(Å^2)
Ir(1)	-0.16740(7)	0.05064(6)	0.04302(4)	1.98(2)*
Ir(2)	-0.09097(7)	-0.01468(5)	-0.05833(4)	1.95(2)*
I(1)	-0.3582(1)	0.1097(1)	0.01189(8)	3.53(4)*
I(2)	0.0341(1)	-0.1160(1)	-0.11805(8)	4.24(4)*
P(1)	-0.0931(5)	0.1603(3)	0.0132(3)	2.1(1)*
P(2)	0.0383(5)	0.0776(3)	-0.0692(3)	2.2(1)*
P(3)	-0.2633(5)	-0.0521(4)	0.0724(3)	2.5(1)*
P(4)	-0.2012(4)	-0.1145(4)	-0.0443(3)	2.5(1)*
O(1)	-0.155(2)	0.101(1)	0.1674(7)	6.3(5)*
O(2)	-0.213(1)	0.024(1)	-0.1666(7)	4.8(5)*
C(1)	-0.167(2)	0.086(1)	0.120(1)	3.9(6)
C(2)	-0.164(2)	0.010(1)	-0.1273(9)	2.9(5)
C(3)	-0.040(2)	-0.009(1)	0.027(1)	3.4(5)
C(4)	0.049(1)	-0.030(1)	0.0520(9)	2.1(4)
C(5)	0.037(2)	0.143(1)	-0.012(1)	3.6(6)
C(6)	-0.307(2)	-0.097(1)	0.0066(9)	2.5(5)
C(11)	-0.085(2)	0.226(1)	0.0717(9)	2.3(5)
C(12)	-0.173(2)	0.252(1)	0.0963(9)	2.4(5)
C(13)	-0.168(2)	0.303(1)	0.146(1)	3.1(5)
C(14)	-0.076(2)	0.324(1)	0.165(1)	3.1(5)
C(15)	0.014(2)	0.302(2)	0.145(1)	4.3(6)
C(16)	0.010(2)	0.253(1)	0.097(1)	2.9(5)

Table 4.5. (continued).

C(21)	-0.145(2)	0.216(1)	-0.048(1)	3.0(5)
C(22)	-0.192(2)	0.184(1)	-0.094(1)	2.9(5)
C(23)	-0.216(2)	0.224(1)	-0.144(1)	2.5(5)
C(24)	-0.197(2)	0.296(1)	-0.144(1)	3.3(6)
C(25)	-0.147(2)	0.330(2)	-0.098(1)	5.1(7)
C(26)	-0.125(2)	0.293(1)	-0.048(1)	3.3(5)
C(31)	0.173(2)	0.048(1)	-0.0707(9)	2.5(4)
C(32)	0.235(2)	0.053(1)	-0.020(1)	3.3(5)
C(33)	0.340(2)	0.038(1)	-0.0239(9)	3.1(5)
C(34)	0.382(2)	0.012(1)	-0.073(1)	3.7(6)
C(35)	0.323(2)	0.00[illegible](2)	-0.122(1)	4.8(6)
C(36)	0.217(2)	0.028(1)	-0.122(1)	2.6(5)
C(41)	0.039(2)	0.135(1)	-0.1364(9)	1.9(4)
C(42)	0.010(2)	0.101(2)	-0.190(1)	3.7(6)
C(43)	0.003(2)	0.148(2)	-0.240(1)	4.3(6)
C(44)	0.027(2)	0.220(1)	-0.240(1)	3.9(6)
C(45)	0.060(2)	0.256(2)	-0.184(1)	4.5(7)
C(46)	0.061(2)	0.209(1)	-0.1351(9)	2.4(5)
C(51)	-0.378(2)	-0.032(1)	0.1138(9)	2.8(5)
C(52)	-0.475(2)	-0.046(1)	0.094(1)	3.2(5)
C(53)	-0.560(2)	-0.022(2)	0.129(1)	4.6(7)
C(54)	-0.545(2)	0.016(2)	0.180(1)	5.9(8)
C(55)	-0.450(2)	0.029(2)	0.199(1)	4.2(6)
C(56)	-0.363(2)	0.003(1)	0.169(1)	3.9(6)
C(61)	-0.213(2)	-0.126(1)	0.120(1)	3.6(6)

Table 4.5. (continued).

C(62)	-0.123(2)	-0.107(1)	0.151(1)	3.6(6)
C(63)	-0.091(2)	-0.163(2)	0.191(1)	4.8(7)
C(64)	-0.139(2)	-0.228(2)	0.196(1)	5.1(7)
C(65)	-0.229(2)	-0.245(2)	0.169(1)	4.7(7)
C(66)	-0.260(2)	-0.190(2)	0.128(1)	4.7(7)
C(71)	-0.151(2)	-0.199(1)	-0.0162(9)	2.4(5)
C(72)	-0.210(2)	-0.264(2)	-0.015(1)	4.0(6)
C(73)	-0.180(2)	-0.326(2)	0.016(1)	5.9(8)
C(74)	-0.086(2)	-0.328(2)	0.045(1)	4.7(6)
C(75)	-0.030(2)	-0.262(1)	0.045(1)	3.9(6)
C(76)	-0.059(2)	-0.199(1)	0.015(1)	2.7(5)
C(81)	-0.273(2)	-0.142(1)	-0.111(1)	3.9(6)
C(82)	-0.232(2)	-0.196(2)	-0.147(1)	6.0(8)
C(83)	-0.288(2)	-0.219(2)	-0.196(1)	5.8(8)
C(84)	-0.378(2)	-0.180(2)	-0.213(1)	4.1(6)
C(85)	-0.410(2)	-0.126(2)	-0.179(1)	5.9(7)
C(86)	-0.356(2)	-0.106(1)	-0.127(1)	3.3(5)
C(91)	0.090(2)	-0.017(1)	0.1121(9)	2.7(4)
C(92)	0.152(2)	-0.074(2)	0.135(1)	5.5(7)
C(93)	0.195(3)	-0.056(2)	0.197(2)	7.8(9)
C(94)	0.179(3)	0.005(2)	0.215(1)	7.6(9)
C(95)	0.127(2)	0.063(2)	0.195(1)	6.0(8)
C(96)	0.077(2)	0.048(1)	0.140(1)	3.7(5)

[a]See footnote (a) of Table 4.4.

Table 4.6. Selected Distances (Å) in $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2]$ (5)

Ir(1)-Ir(2)	2.825(1)	Ir(1)-I(1)	2.778(2)
Ir(1)-P(1)	2.329(5)	Ir(1)-P(3)	2.333(6)
Ir(1)-C(1)	1.89(3)	Ir(1)-C(3)	2.09(2)
Ir(2)-I(2)	2.796(2)	Ir(2)-P(2)	2.342(6)
Ir(2)-P(4)	2.350(6)	Ir(2)-C(2)	1.89(3)
Ir(2)-C(3)	2.12(2)	P(1)-C(5)	1.81(2)
P(1)-C(11)	1.73(2)	P(1)-C(21)	1.80(2)
P(2)-C(5)	1.82(2)	P(2)-C(31)	1.81(2)
P(2)-C(41)	1.85(2)	P(3)-C(6)	1.77(2)
P(3)-C(51)	1.86(2)	P(3)-C(61)	1.80(2)
P(4)-C(6)	1.86(2)	P(4)-C(71)	1.91(2)
P(4)-C(81)	1.90(3)	O(1)-C(1)	1.09(3)
O(2)-C(2)	1.21(3)	C(3)-C(4)	1.26(3)

Table 4.7. Selected Angles (deg) in [$Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2$] (5)

Ir(2)-Ir(1)-I(1)	98.27(5)	Ir(2)-Ir(1)-P(1)	91.7(1)
Ir(2)-Ir(1)-P(3)	91.9(1)	I(2)-Ir(1)-C(1)	155.5(8)
Ir(2)-Ir(1)-C(3)	48.3(5)	I(1)-Ir(1)-P(1)	88.7(2)
I(1)-Ir(1)-P(3)	88.2(1)	I(1)-Ir(1)-C(1)	106.2(8)
I(1)-Ir(1)-C(3)	146.2(5)	P(1)-Ir(1)-P(3)	175.5(2)
P(1)-Ir(1)-C(1)	88.0(8)	P(1)-Ir(1)-C(3)	88.4(6)
P(3)-Ir(1)-C(1)	89.8(8)	P(3)-Ir(1)-C(3)	96.0(5)
C(1)-Ir(1)-C(3)	107(1)	Ir(1)-Ir(2)-I(2)	147.56(6)
Ir(1)-Ir(2)-P(2)	92.0(1)	Ir(1)-Ir(2)-P(4)	93.3(1)
Ir(1)-Ir(2)-C(2)	108.0(8)	Ir(1)-Ir(2)-C(3)	47.1(5)
I(2)-Ir(2)-P(2)	90.3(1)	I(2)-Ir(2)-P(4)	88.2(2)
I(2)-Ir(2)-C(2)	104.5(8)	I(2)-Ir(2)-C(3)	100.4(5)
P(2)-Ir(2)-P(4)	172.4(2)	P(2)-Ir(2)-C(2)	85.5(8)
P(2)-Ir(2)-C(3)	92.5(5)	P(4)-Ir(2)-C(2)	87.7(8)
P(4)-Ir(2)-C(3)	95.1(5)	C(2)-Ir(2)-C(3)	155.0(9)
Ir(1)-P(1)-C(5)	110.7(6)	Ir(1)-P(1)-C(11)	118.1(7)
Ir(1)-P(1)-C(21)	113.4(7)	C(5)-P(1)-C(11)	106.8(9)
C(5)-P(1)-C(21)	101.8(9)	C(11)-P(1)-C(21)	105(1)
Ir(2)-P(2)-C(5)	111.8(6)	Ir(2)-P(2)-C(31)	115.7(7)
Ir(2)-P(2)-C(41)	121.9(7)	C(5)-P(2)-C(31)	101.1(9)
C(5)-P(2)-C(41)	101.6(9)	C(31)-P(2)-C(41)	103(1)
Ir(1)-P(3)-C(6)	111.0(7)	Ir(1)-P(3)-C(51)	115.5(7)
Ir(1)-P(3)-C(61)	117.0(9)	C(6)-P(3)-C(51)	103(1)
C(6)-P(3)-C(61)	110(1)	C(51)-P(3)-C(61)	99(1)

Table 4.7. (continued).

Ir(2)-P(4)-C(6)	107.3(7)	Ir(2)-P(4)-C(71)	123.5(8)
Ir(2)-P(4)-C(81)	116.3(8)	C(6)-P(4)-C(71)	104(1)
C(6)-P(4)-C(81)	103(1)	C(71)-P(4)-C(81)	101(1)
Ir(1)-C(1)-O(1)	170(2)	Ir(2)-C(2)-O(2)	168(2)
Ir(1)-C(3)-Ir(2)	84.6(7)	Ir(1)-C(3)-C(4)	134(2)
Ir(2)-C(3)-C(4)	140(2)	P(1)-C(5)-P(2)	111(1)
P(3)-C(6)-P(4)	114(1)		

Table 4.8. Selected Bond Distances (Å) in $[\mathrm{Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(dppm)_2}]$ (7)

Ir(1)-Ir(2)	2.783(1)	Ir(1)-I(1)	2.810(2)
Ir(1)-P(1)	2.320(6)	Ir(1)-P(3)	2.349(6)
Ir(1)-C(1)	1.88(3)	Ir(1)-C(3)	2.03(2)
Ir(2)-I(2)	2.815(2)	Ir(2)-P(2)	2.396(6)
Ir(2)-P(4)	2.341(6)	Ir(2)-C(2)	1.89(2)
Ir(2)-C(3)	2.06(2)	P(1)-C(5)	1.83(2)
P(1)-C(11)	1.79(2)	P(1)-C(21)	1.85(2)
P(2)-C(5)	1.76(2)	P(2)-C(31)	1.84(2)
P(2)-C(41)	1.86(2)	P(3)-C(6)	1.80(2)
P(3)-C(51)	1.81(2)	P(3)-C(61)	1.85(3)
P(4)-C(6)	1.84(2)	P(4)-C(71)	1.79(2)
P(4)-C(81)	1.85(2)	O(1)-C(1)	1.12(3)
O(2)-C(2)	1.13(2)	C(3)-C(4)	1.35(3)
C(4)-C(91)	1.49 (3)		

Table 4.9. Selected Angles (deg) in $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(dppm)_2]$ (7)

Ir(2)-Ir(1)-I(1)	105.86(5)	Ir(2)-Ir(1)-P(1)	88.4(1)
Ir(2)-Ir(1)-P(3)	95.1(1)	Ir(2)-Ir(1)-C(1)	157.7(8)
Ir(2)-Ir(1)-C(3)	47.5(6)	I(1)-Ir(1)-P(1)	88.4(1)
I(1)-Ir(1)-P(3)	84.3(1)	I(1)-Ir(1)-C(1)	96.2(8)
I(1)-Ir(1)-C(3)	153.1(6)	P(1)-Ir(1)-P(3)	172.4(2)
P(1)-Ir(1)-C(1)	88.7(8)	P(1)-Ir(1)-C(3)	93.4(7)
P(3)-Ir(1)-C(1)	90.6(8)	P(3)-Ir(1)-C(3)	94.0(7)
C(1)-Ir(1)-C(3)	111(1)	Ir(1)-Ir(2)-I(2)	152.80(5)
Ir(1)-Ir(2)-P(2)	92.4(1)	Ir(1)-Ir(2)-P(4)	89.7(1)
Ir(1)-Ir(2)-C(2)	114.1(6)	Ir(1)-Ir(2)-C(3)	46.6(6)
I(2)-Ir(2)-P(2)	89.8(1)	I(2)-Ir(2)-P(4)	85.3(1)
I(2)-Ir(2)-C(2)	92.6(6)	I(2)-Ir(2)-C(3)	107.5(7)
P(2)-Ir(2)-P(4)	173.0(2)	P(2)-Ir(2)-C(2)	96.1(7)
P(2)-Ir(2)-C(3)	80.2(7)	P(4)-Ir(2)-C(2)	89.2(7)
P(4)-Ir(2)-C(3)	96.5(7)	C(2)-Ir(2)-C(3)	159.5(9)
Ir(1)-P(1)-C(5)	109.6(8)	Ir(1)-P(1)-C(11)	112.4(7)
Ir(1)-P(1)-C(21)	122.3(7)	C(5)-P(1)-C(11)	107(1)
C(5)-P(1)-C(21)	101(1)	C(11)-P(1)-C(21)	103(1)
Ir(2)-P(2)-C(5)	112.9(8)	Ir(2)-P(2)-C(31)	118.2(8)
Ir(2)-P(2)-C(41)	118.8(7)	C(5)-P(2)-C(31)	103(1)
C(5)-P(2)-C(41)	103(1)	C(31)-P(2)-C(41)	98.3(9)
Ir(1)-P(3)-C(6)	107.1(7)	Ir(1)-P(3)-C(51)	115.6(8)
Ir(1)-P(3)-C(61)	123.5(8)	C(6)-P(3)-C(51)	105.0(9)
C(6)-P(3)-C(61)	106(1)	C(51)-P(3)-C(61)	98(1)

Table 4.9. (continued).

Ir(2)-P(4)-C(6)	114.6(7)	Ir(2)-P(4)-C(71)	119.2(7)
Ir(2)-P(4)-C(81)	114.3(8)	C(6)-P(4)-C(71)	102(1)
C(6)-P(4)-C(81)	100(1)	C(71)-P(4)-C(81)	104(1)
Ir(1)-C(1)-O(1)	170(3)	Ir(2)-C(2)-O(2)	176(2)
Ir(1)-C(3)-Ir(2)	86.0(9)	Ir(1)-C(3)-C(4)	142(2)
Ir(2)-C(3)-C(4)	132(2)	C(3)-C(4)-C(91)	131(2)
P(1)-C(5)-P(2)	111(1)	P(3)-C(6)-P(4)	111(1)

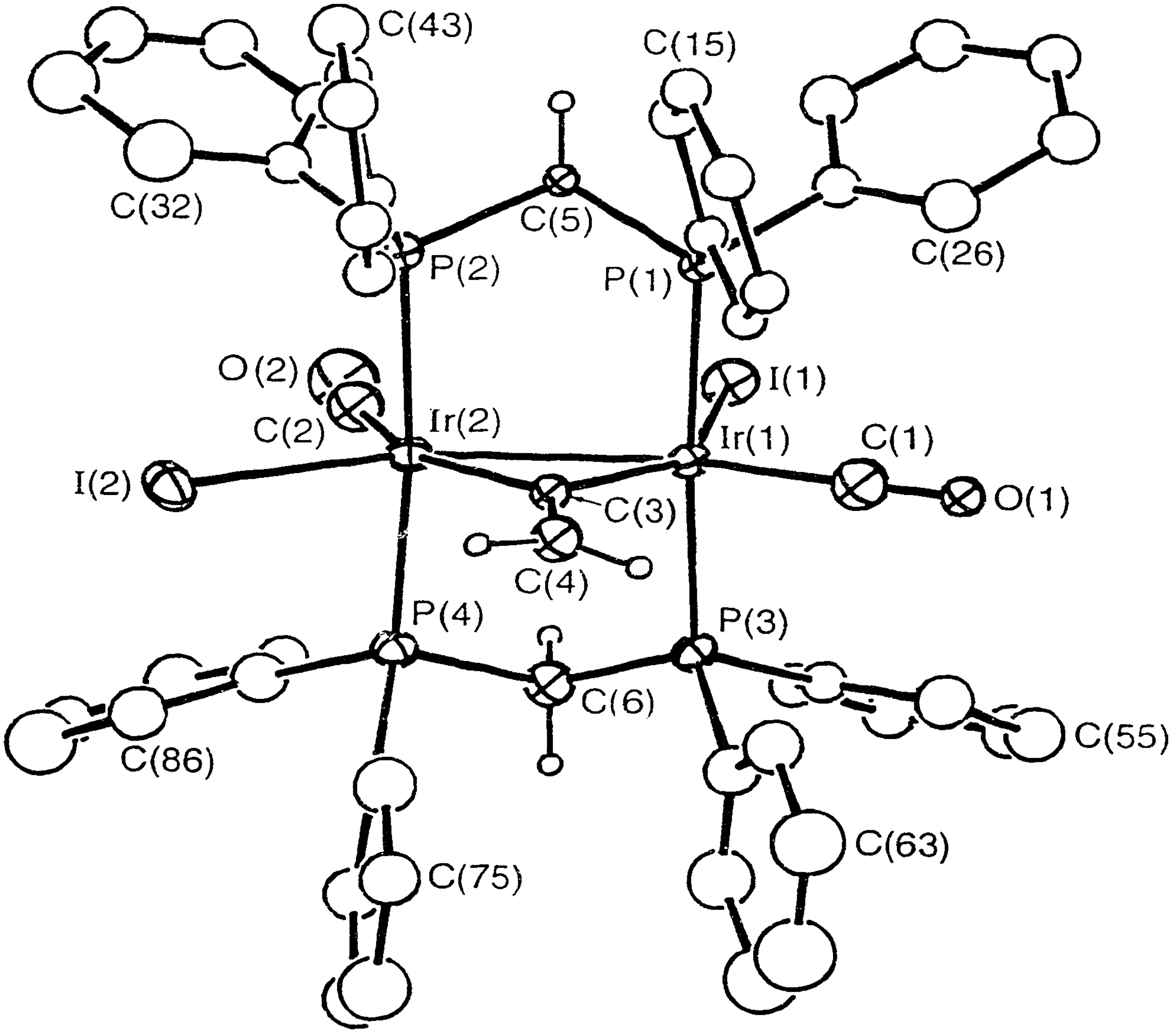


Figure 4.1. Perspective view of complex 5, showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens, which are shown arbitrarily small. Phenyl hydrogens are omitted.

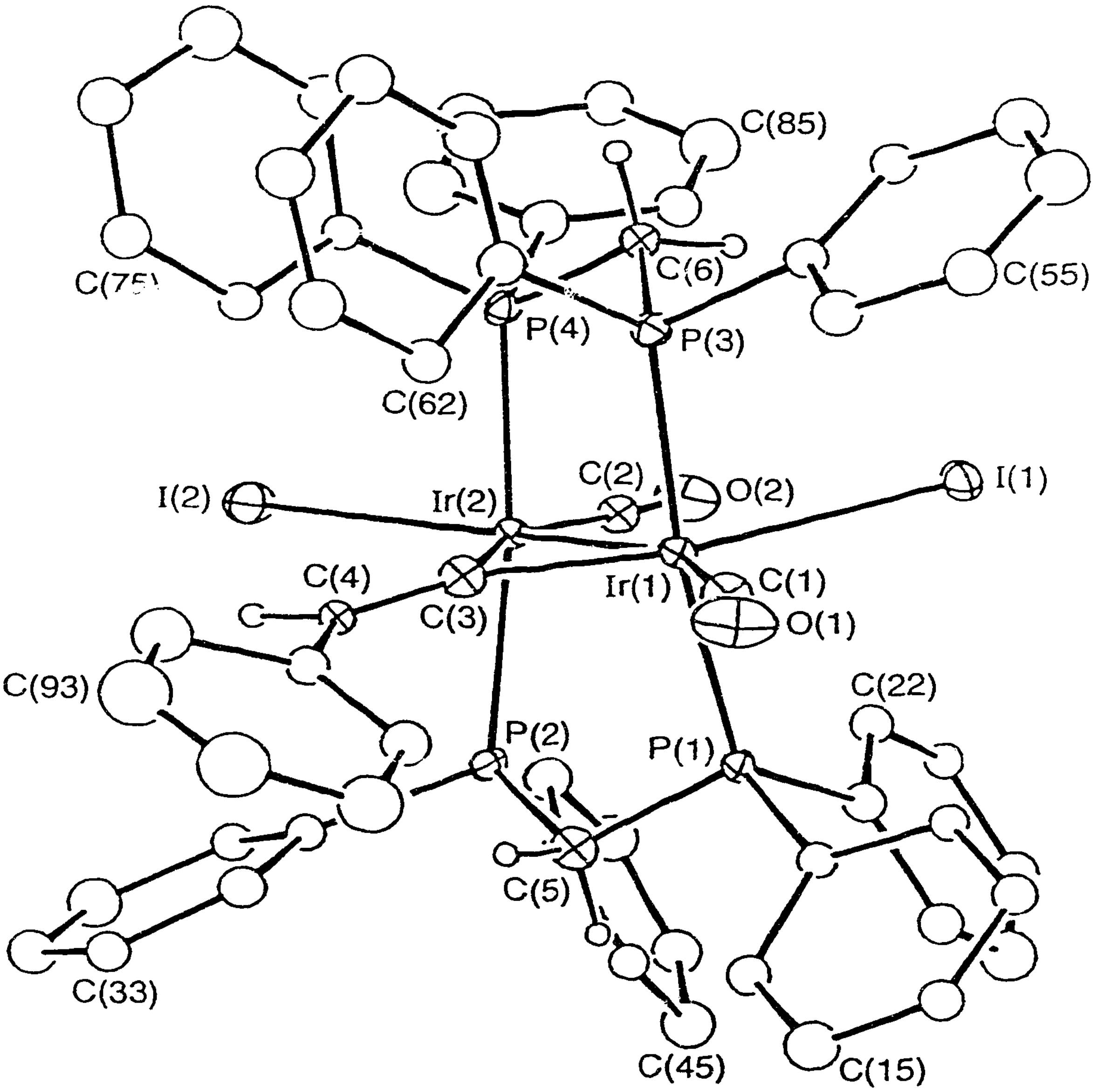


Figure 4.2. Perspective view of complex 7, showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens, which are shown arbitrarily small. Phenyl hydrogens are omitted.

metal-metal bonds. Therefore the angles at each metal subtended by the vinylidene α carbon and the adjacent metal are very acute (near 47°) while all the other angles between adjacent ligands in the equatorial plane are greater than 90°. All parameters involving the iodo and carbonyl ligands compare very closely between **5** and **7** and are also clearly comparable to those in one isomer of the dichlorotricarbonyl compound.[22] In both **5** and **7** the iodo ligand is almost trans to the Ir-Ir bond on one metal while the other is cis to it on the adjacent metal. There are no significant differences in the Ir-I distances opposite the Ir-Ir bonds (2.796(2)Å (**5**), 2.815(2)Å (**7**)) and those opposite the vinylidene unit (2.778(2)Å (**5**), 2.810(2)Å (**7**)).

In both cases the vinylidene groups bridge the metals symmetrically, with the Ir-C(3) distances (*av* 2.08Å) involving these groups, and the Ir(1)-C(3)-Ir(2) angles (84.6(7)° (**5**), 86.0(9)°(**7**)) agreeing surprisingly well with the related parameters involving the bridging carbonyl ligand in $[Ir_2Cl_2(CO)_2(\mu\text{-}CO)(dppm)_2]$.[22] Although the two vinylidene units are symmetrically bound at the α carbon, they are tilted somewhat, in opposite directions. In both cases the tilts appear to result from non-bonded contacts within each complex, although the natures of these contacts differ because of the differing substituents on the vinylidene units of **5** and **7**. In **5** the slightly larger Ir(2)-C(3)-C(4) angle (140(2)°) compared to Ir(1)-C(3)-C(4) (134(2)°) shows that the vinylidene group is tilted slightly towards Ir(1), probably to minimize repulsions with the adjacent iodo ligand I(2). In **7** the respective angles (132(2)°, 142(2)°) show that the phenylvinylidene unit is tipped towards Ir(2) and I(2); in this case it appears that this distortion minimizes the more severe contacts between the phenyl substituent on C(4) and the carbonyl group C(1)O(1). Other subtle differences in angles involving the iodo and carbonyl ligands also appear to result from the above non-bonded contacts in **5** and **7**.

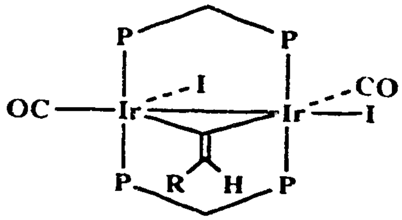
Although the contact between the phenyl substituent (group 9) and the carbonyl C(1)O(1) is potentially severe, the vinylidene unit is not significantly skewed about the olefin bond (the Ir(1)-C(3)-C(4)-C(91) torsion angle is only 2(4)°). Instead, the phenyl substituent twists about the C(4)-C(91) bond, resulting in an average C(3)-C(4)-C(91)-C(ortho) torsion angle of 35°. As a result this phenyl substituent points in the direction of the phenyl groups on P(1) causing a twisting of the ligand framework on Ir(1) compared to that on Ir(2) (see Figure 2). This twisting is most severe for P(1) as seen by the P(1)-Ir(1)-Ir(2)-P(2) torsion angle of 21.8(2)° in **7** compared with only 5.2(3)° in **5**. The other ligands on Ir(1) show a similar trend, so the I(1)-Ir(1)-Ir(2)-C(2) torsion angle is 12.0(8)° in **7**, but only 2(1)° in **5** and the P(3)-Ir(1)-Ir(2)-P(4) angle is 8.5(2)° in **7** compared to 2.3(3)° in **5**.

The C(3)-C(4) bonds of the vinylidene units (1.26(3)Å (**5**), 1.35(3)Å (**7**)) do not differ significantly, and are normal for a double bond in an olefinic unit.[1]

Discussion

The reactions of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**) with one equiv of either acetylene or phenylacetylene at ambient temperature yield the vinylidene complex **5** after *ca.* 20 h or the phenylvinylidene complex **7** after *ca.* 2 h. These products, $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ (R = H (**5**), Ph (**7**)) have the structures shown, as described in the previous section.

For both compounds the bands in the IR spectra indicate terminal carbonyls, with those of 7 (1998, 1984 cm^{-1}) being higher than those of 5 (1985, 1960 cm^{-1}), consistent with the phenyl-substituted vinylidene being a better π-acceptor.[1] The $^{31}P\{^1H\}$ NMR spectrum of 5 displays an AA'BB'



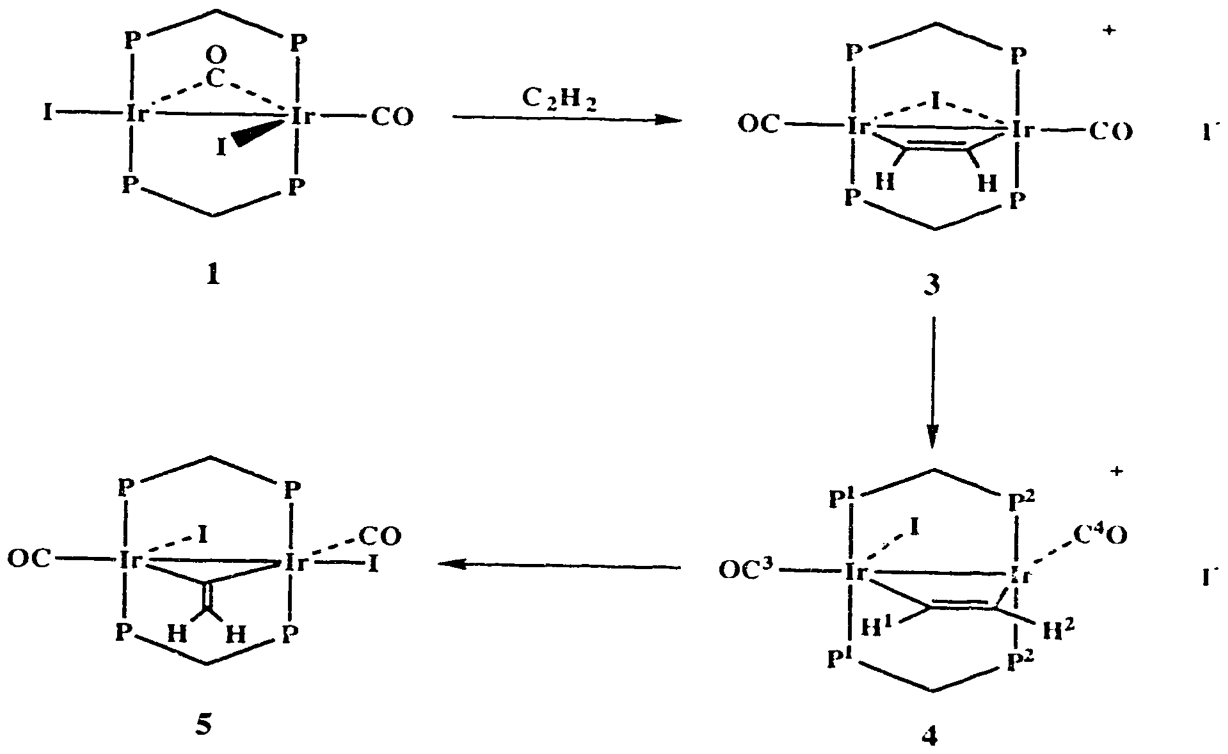
R = H (5); Ph (7)

pattern indicating an unsymmetrical arrangement of ligands, as found in the solid-state structure, in which the iodo ligand is opposite the metal-metal bond on one metal and cis to it on the other. In the ^1H NMR spectrum the vinylic protons of 5 are not obvious, presumably being obscured by the phenyl resonances. In a related dirhodium complex these proton resonances were also not observed,[7] whereas in the phenylvinylidene-bridged product 7 the vinylic proton is observed at -80°C as a broad signal at δ 8.46.

The $^{13}C\{^1H\}$ NMR spectrum of 5, prepared using acetylene which was ^{13}C-enriched at both positions, displays a doublet of multiplets at δ 194.3, assigned to C_α, and a doublet at δ 129.8, attributed to C_β. The apparent multiplet results from coupling to the four phosphorus nuclei and the doublet results from coupling between the C_α and C_β nuclei. This latter coupling of 67 Hz compares well to the value of 67.2 Hz in ethylene, and shows the apparent insensitivity of this coupling to substituents on ethylene.[23] Although the chemical shift for C_β is typical, that for C_α is at unusually high field, since generally these resonances appear in the region δ 250-380.[1]

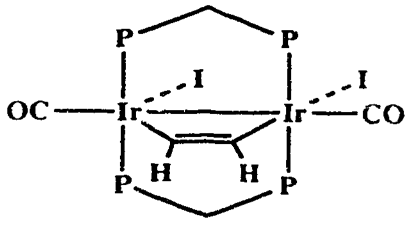
Unlike compound **5**, which has temperature-invariant $^{31}P\{^1H\}$ and ^1H NMR spectra, compound **7** displays temperature-dependent spectra. At ambient temperature the $^{31}P\{^1H\}$ NMR spectrum is typical of an AA'BB' spin system, as observed for **5**, and the ^1H NMR spectrum displays two resonances for the dppm methylene groups. At -80°C however, the spectra become consistent with the solid-state structure, displaying *four* different phosphorus resonances and four resonances for the methylene protons. In the low-temperature limiting structure the molecule has "left-right" asymmetry owing to the arrangement of the I and CO ligands, whereas "top-bottom" asymmetry apparently results from the orientation of the phenyl substituent on the vinylidene unit. We suggest that the temperature dependence results from a fluxional process in which the vinylidene phenyl group twists about the C(4)-C(91) bond, causing an accompanying twist of the ligand framework on Ir(1) in order to minimize non-bonded contacts between the vinylidene phenyl group and those on P(1) and P(3) *(vide supra)*.

Although the reaction of **1** with acetylene is fast, compound **5** is not the first species observed; the first species observed, both at ambient temperature and at -80°C is compound **3** (shown on Scheme I), which transforms readily to **4** at ambient temperature. The $^{31}P\{^1H\}$ NMR spectrum of **3** appears as a singlet, indicating that all phosphorus nuclei

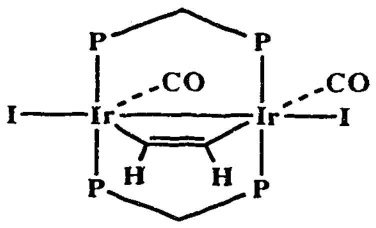


Scheme I

are chemically equivalent, and the ^{1}H NMR spectrum displays a broad signal for the acetylene protons at δ 8.48. In the IR spectrum of a mixture of 3 and 4 the only band attributable to 3 is at 1998 cm^{-1}. A ^{13}C{^{1}H} NMR spectrum of 3 (^{13}C-enriched at the carbonyl and acetylenic carbons) shows two resonances at δ 180.5 and 113.9, for the carbonyl and acetylenic carbons, respectively, displaying coupling of 14 Hz between these nuclei. The resonance for the acetylenic carbons also shows additional coupling to two phosphorus nuclei, consistent with the structure shown for 3. An alternate structure, in which the alkyne is bound perpendicular to the Ir-Ir axis with an accompanying cis-phosphine arrangement seems unlikely, since such a geometry has only previously been observed for complexes having the metals in the zero oxidation state.[7,24] In addition, the perpendicular mode might be expected to show coupling of the acetylenic carbons to all four phosphorus nuclei, which is not observed. Although the ^{13}C chemical shift of the acetylenic carbons has previously been used to establish the alkyne binding mode, the observed value is intermediate between the normal ranges for parallel (δ 120-150) and perpendicular (δ 60-100) binding modes, so is inconclusive in this case. The structure proposed for **3**, in which I$^-$ dissociation from the complex has occurred, is based on the spectral similarities of **3** with those of the DMAD analogue.[10] If the iodide ligand were to remain coordinated, two geometries would be possible, giving rise to a symmetrical product; these would either have both iodo ligands mutually adjacent as in **A**, or opposite the Ir-Ir bond as in **B**. Structure **A** seems unlikely since the cis arrangement of the carbonyls and the acetylene ligand would be expected to give rise to much smaller ^{13}C-^{13}C coupling than the 14 Hz observed. In addition this structure would result in unfavorable contacts between the two iodide groups. Although the almost-trans arrangement of CO's and the acetylene



A



B

ligand in **B** would result in coupling between these groups comparable to that observed, this geometry is not consistent with the geometry proposed for the subsequent species **4**. However it should be noted that since the arrangement of the I and CO ligands in **4** cannot be unambiguously determined (*vide infra*), structure **B** cannot be ruled out. Compound **3** is never present as the only species, therefore its conductivity unfortunately could not be determined.

Conversion of **3** to **4**, shown in Scheme I, is rapid at ambient temperature. The $^{31}P\{^1H\}$ NMR spectrum of **4** is typical of an AA'BB' spin system, having two different chemical environments at each Ir center. Compound **4** shows the acetylenic proton resonances at δ 8.52 and 8.06 as unresolved multiplets in the ^1H NMR spectrum. With broadband ^{31}P decoupling these resonances collapse to a pair of doublets displaying vicinal H-H coupling of only 3.3 Hz. This coupling is unexpectedly smaller than values of between 6 and 12 Hz in substituted ethylenes[25] and in coordinated acetylene.[26] Selective ^{31}P-decoupling experiments indicate that the low-field acetylenic proton resonance (H^2) is coupled to only one set of phosphorus nuclei (labelled P^2 on Scheme I), having a coupling constant of *ca.* 1.5 Hz, whereas the higher-field resonance (H^1) is coupled to *all* four phosphorus nuclei, with a coupling of again *ca.* 1.5 Hz, indicating that H^1 may be at a position quite different from that of H^2. The $^{13}C\{^1H\}$ NMR spectrum of **4** (using ^{13}C-enriched acetylene) displays an AB quartet at *ca.* δ 106 for the two acetylene carbons, with additional coupling to the phosphorus nuclei, as shown in Figure 4.3. It is significant that the higher-field branches of this spectrum are somewhat more complicated

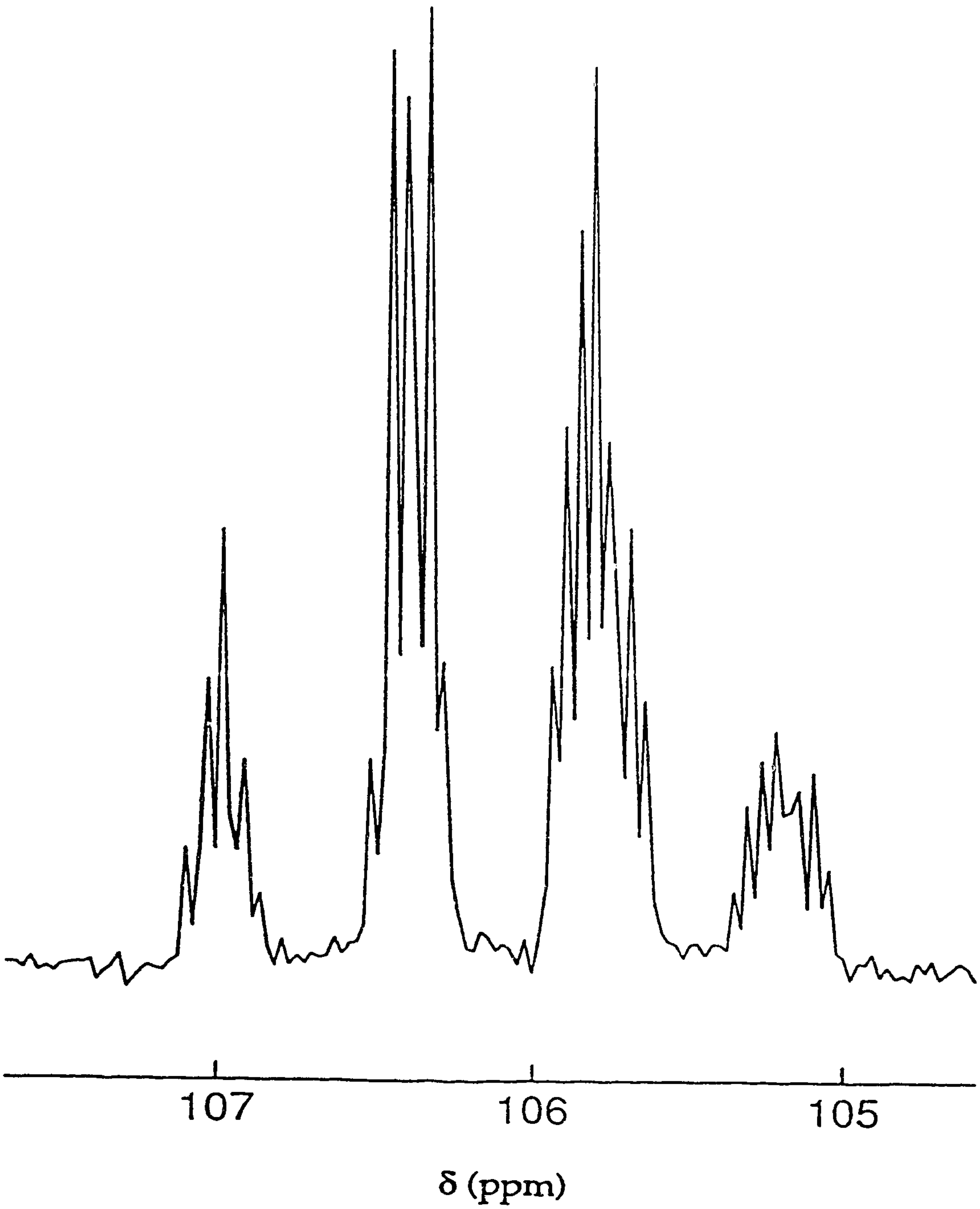


Figure 4.3. The $^{13}C\{^{1}H\}$ NMR spectrum of complex **4** containing ^{13}C-enriched acetylene.

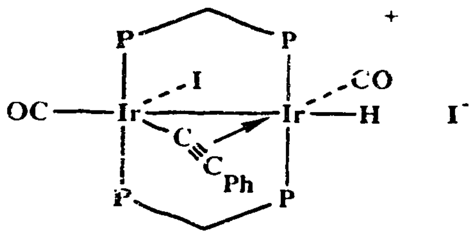
than the lower-field ones, showing additional phosphorus coupling. The selective ^{31}P decoupling experiments show that the high-field carbon (C^2, attached to H^2) couples with two phosphorus nuclei (P^2) more strongly than with the others (6.5 *vs.* 2.5 Hz) whereas the low-field carbon (C^1, attached to H^1) couples to P^2 with a 2.5 Hz coupling constant and to P^1 with a 3.3 Hz constant. This latter observation is reminiscent of the coupling noted between H^1 and the four phosporus nuclei, suggesting that the acetylenic carbon (C^1) may be close to a bridging position. In a sample of **4** in which all the acetylenic and carbonyl carbons were ^{13}C enriched a strong coupling (25 Hz) is observed between C^2 and the carbonyl carbon at δ 181.8 (C^4), suggesting a trans arrangement, whereas no coupling involving C^1 and the carbonyl carbon at δ 159.2 (C^3) is observed. Based on these data we propose the structure shown for **4** on Scheme I. In this formulation the symmetrically-bound acetylene of **3** has slid towards Ir^2 (attached to P^2) to yield an unsymmetrically-bound acetylene in which C^1 is now closer to Ir^2 than in **3**. It is also significant that the chemical shifts of the carbon nuclei (δ 106.6, 105.6) in **4** are at higher field than those of **3** (δ 113.9), and the coupling constant between these carbons (*ca.* 59 Hz) is smaller than noted earlier for **5** and substituted ethylenes (ca. 67 Hz). In the complex $[Rh_2(CO)_2(\mu\text{-}HC_2Ph)(dppm)_2]$, which contains a normal parallel acetylene, such coupling is ca. 70 Hz.[27] Both observations suggest a lowering of the C-C bond order in **4** and a change in hybridization[28,29] towards sp^3. It may also be that this lowering of the C-C bond order may be responsible[30] for the small vicinal H-H coupling noted earlier. These data indicate that in complex **4** the π^* or π orbital of the dimetallo-olefin unit might also interact with Ir^2, although it is not clear which orbital of Ir^2 is involved. The structure shown for **4** is unusual but is not totally without precedent; the structure of $[Rh_2Cl(CNMe)_2(\mu\text{-}CF_3C_2CF_3)(dppm)_2][BF_4]$ showed an unsymmetrical binding mode of the alkyne in which one carbon was shifted significantly towards the other metal, giving rise to nominally non-bonded Rh-C contacts of 2.660(7) and 2.902(7)Å.[31] It was suggested at the time that a weak interaction, of the type proposed here, was involved. Unsymmetrically-coordinated alkynes have also been noted for other dppm-bridged complexes,[12,32] although interaction involving the π bond was not suggested in these studies. Furthermore, it is noted that there are numerous trinuclear complexes in which the alkyne ligand is σ-bonded to two metals, and at the same time, also π-bonded to a third metal.[33]

In the proposed structure for **4**, one of the carbonyl groups (C^4O) is trans to the acetylenic carbon C^2, while the other one (C^3O) is disposed cis to C^1. Although this arrangement is consistent with the carbon-carbon coupling constants noted earlier, an alternate geometry, in which the position of C^3O is exchanged with that of the coordinated iodo ligand, might also result in analogous coupling constants. If **4** adopts this latter geometry dissociation of the coordinated iodo ligand must take place before **5** is produced, as can be seen in Scheme I. The proposal that **4** is a cationic complex having an iodide counterion is based on its conductivity in nitromethane (79.8 $\Omega^{-1}cm^2mol^{-1}$). In addition the transformation from a mutually adjacent arrangement of iodo ligands in **1** to the arrangement in **5**, in which they are no longer adjacent, requires reversible dissociation of I^- or CO; the former seems more likely. In CH_2Cl_2 the low conductivity (12 $\Omega^{-1}cm^2mol^{-1}$) suggests ion pairing in this solvent. In fact the iodide counterion appears to hinder the transformation of 4 to 5, possibly owing to the reversibility of the dissociation (*vide infra*). No other intermediate, in the transformation of 1 to 5, was observed. The hydrogen migration step (or steps) to yield 5 is much slower than the facile transformation of 3 to 4, requiring *ca*. 20 h at room temperature.

The possibility that C-H activation and the 1, 2-hydrogen shift had already taken place in the transformation of 3 to 4, making 4 a vinylidene-bridged species, was considered and rejected. This conclusion is based in part on the facile conversion of 3 to 4 and on the very slow conversion of 4 to 5; it seems reasonable to assume that the C-H activation and H-transfer steps will be rate determining. More importantly, ^{13}C gated decoupling experiments reveal no triplet which would be expected for this hypothetical species. Instead these experiments show that the acetylenic carbons of 4 each bear one hydrogen, being further split into doublets compared to the fully H-decoupled spectrum, consistent with the formulation suggested in Scheme I. The ^{13}C NMR spectra of the gated decoupling experiments also reveal $^1J_{C^1H^1} \approx 160$ Hz and $^1J_{C^2H^2} \approx 175$ Hz, indicating that the C^1-H^1 bond might have been slightly weakened.

As noted earlier, the reaction of 1 with phenylacetylene at ambient temperature yields only 7, with no evidence of intermediates being observed. However, at -40°C an additional species 6 is observed, which transforms slowly to 7 at this temperature or rapidly at temperatures above 0°C. The $^{31}P\{^1H\}$ NMR spectrum of 6 displays a pattern typical of an

AA'BB' spin system and the ^{1}H NMR shows a high-field triplet at δ -11.55 ($^2J_{P-H}$ = 12.4 Hz). The presence of the hydride signal suggests that **6** is an acetylide complex, however confirmation by IR spectroscopy is not possible since **6** is only ever present in small amounts resulting in the clear identification of only two new weak shoulders at 2028 and 1996 cm^{-1}, superimposed on the dominant bands of compounds **1** and **7**. The structure shown for **6**, in which the acetylide is bound in a σ, π fashion is based on analogies with related species.[34] In spite of the uncertainty in the structure of **6**, it is clearly an acetylide-hydride complex, an observation



6

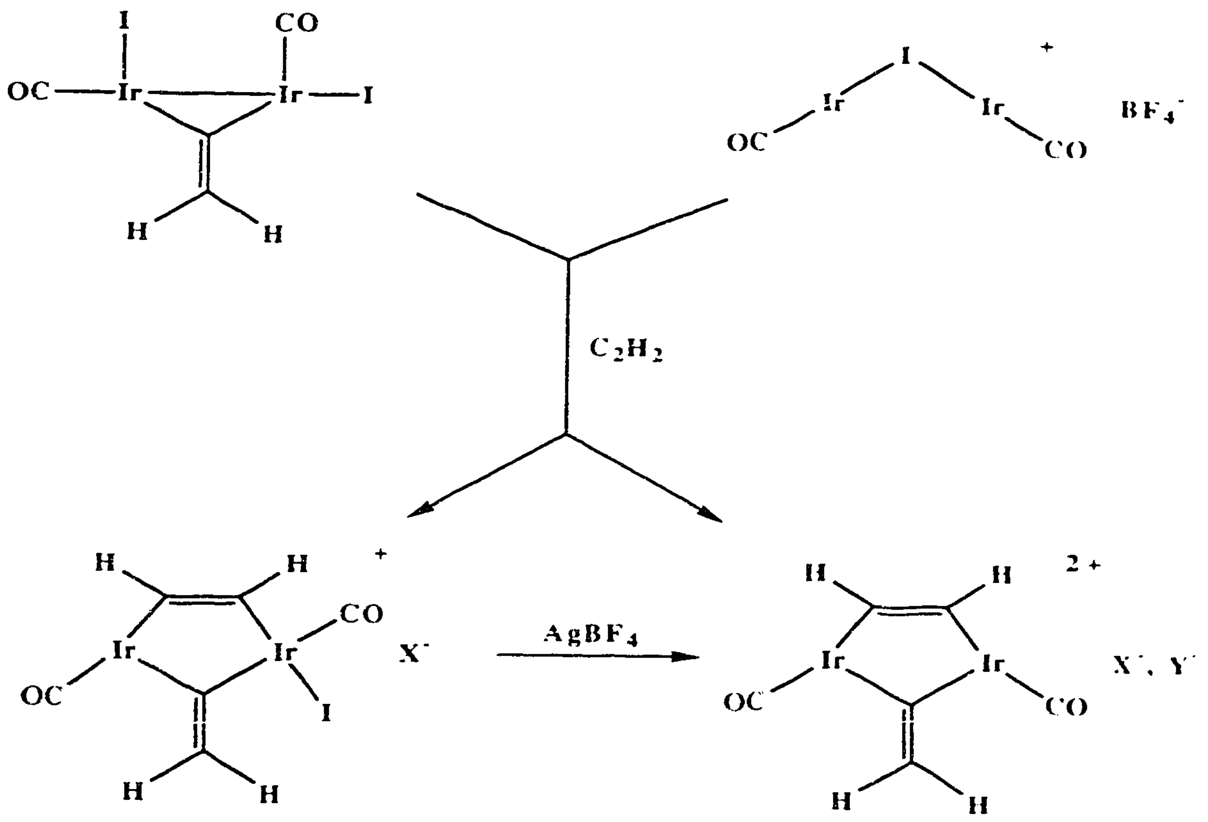
that has significant implications regarding the proposed mechanism of the acetylene-to-vinylidene tautomerism *(vide infra)*. This is of course based on the assumption that both acetylene and phenylacetylene react with **1** by the same mechanism.

The conversion of the acetylene-bridged species **3** to the vinylidene-bridged product **5** is the first such transformation reported. Although both classes of species were obtained for a related dirhodium species, it was shown in that study that the acetylene adduct observed was not a necessary intermediate in the formation of the vinylidene-bridged product.[7] It is also significant that the alkyne adduct observed in the dirhodium complex was bound perpendicular to the metal-metal bond, and *not* parallel to it proposed for our intermediate in the hydrogen-transfer reaction. As n earlier, dihaloacetylenes have been reported to give vinylidene complexes, however no intermediate acetylene complexes were detected in these studies.[8]

Based on the species observed in both the acetylene and phenylacetylene reactions, we propose a scheme for the acetylene-to-vinylidene transformation, much as shown in Scheme I, with the exception that species **4** (and its phenyl analogue) is followed by an acetylide-hydride species such as **6**. We propose that transfer of the hydrogen from the α-to-β-carbons occurs through an acetylide-hydride intermediate analogous to **6**. Although a previous study showed that a bridged acetylene-to-vinylidene transformation was unlikely,[9] it should be noted that the proposed transition state used in the calculations does not resemble any of the structures proposed for our observed intermediates. In particular, it appears that this transformation, via an acetylide-hydride intermediate, is feasible, as was previously suggested.[9]

There are numerous mononuclear complexes, which have been shown to mediate the acetylene-vinylidene rearrangement, and the mechanisms appear well established.[1] The generally-accepted mechanism involves a 1,2 hydrogen shift via initial slippage of the alkyne to give an η^1 geometry. An alternative pathway involving oxidative addition of the acetylene to yield an acetylide-hydrido intermediate, as proposed above, has also been forwarded,[35] although a theoretical study indicates that this latter route is of much higher energy than the former.[9] Interconversion of acetylene to vinylidene also occurs on a trinuclear framework,[1] and the mechanism has also been considered.[9] The mechanism we proposed for the acetylene-vinylidene transformation is the first for a binuclear system.

In an attempt to induce carbon-carbon coupling in the vinylidene products **5** and **7**, these complexes were exposed to additional acetylene and phenylacetylene. While no reaction was detected between phenylacetylene and either **5** or **7**, or between acetylene and **7**, compound **5** *did* react instantly with acetylene to give two products **8** and **9a** in *ca.* 1.8:1 ratio, respectively. These products have been identified spectroscopically as the vinylidene- and acetylene-bridged complexes, $[Ir_2I(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]$ (**8**) and $[Ir_2(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]_2$ (**9a**), as shown in Scheme II (diphosphine ligands are omitted in the drawings). The $^{31}P\{^1H\}$ NMR spectrum of this mixture shows that **8** is unsymmetrical, displaying an AA'BB' pattern at δ -18.3 and δ -29.2, while **9a** is symmetrical, displaying a singlet at δ -33.5. The $^{13}C\{^1H\}$ NMR spectrum of the mixture displays two equal intensity carbonyl resonances (triplets) at δ 174.1 and 172.9 and another (a broad singlet) at δ 172.8. Based on selective ^{31}P-decoupling experiments and on the integrations of these signals, the two triplets are assigned to **8** and the singlet to **9a**. The IR spectrum of a mixture of these species shows three carbonyl bands; the two at 2018 and 2009 cm^{-1} are assigned to **8**, while the one at 2027 cm^{-1} is assigned to **9a** based on a comparison with the IR spectrum of its BF_4^- analogue **9b** (*vide infra*). Additional information about the natures of these products was obtained from ^{13}C NMR experiments in which ^{13}C-enriched acetylene was used in the preparation of **5** and in the subsequent



8: X=I

9a: X=Y=I

9b: X=Y=BF_4

Scheme II

formation of the final products. The $^{13}C\{^1H\}$ NMR spectrum of the product mixture, shown in Figure 4.4, displays seven resonances in the range δ 128-155, superimposed on the phenyl carbon resonances between δ 127 and 136, and their assignments are made possible by selective heteronuclear decoupling experiments. Based on these experiments the doublet of quintets at δ 152.0, the broad singlet at δ 147.3, and the doublet at δ 128.6 were shown to arise from **9a**. For the low-field signal, the quintet

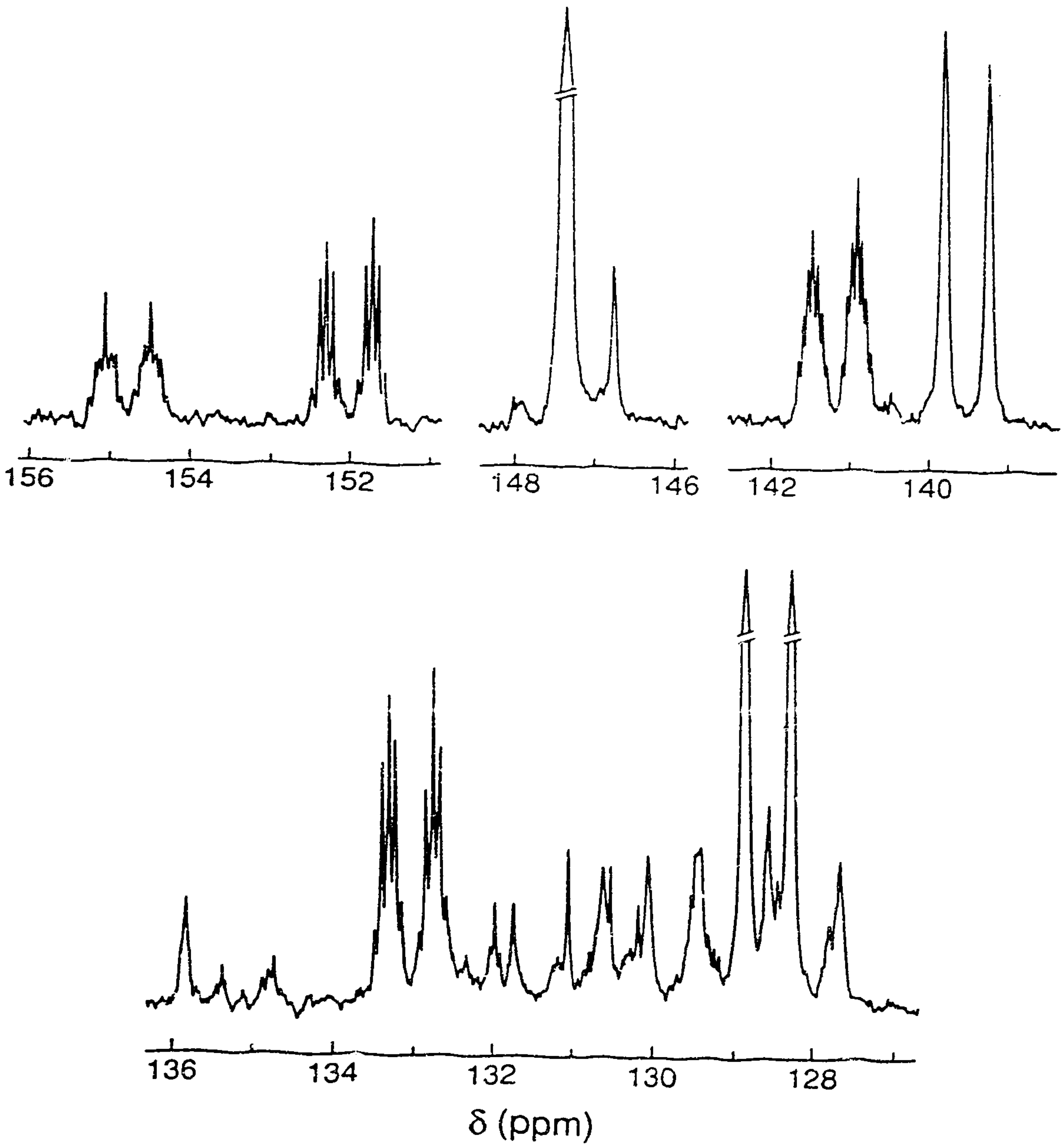


Figure 4.4. $^{13}C\{^1H\}$ NMR spectrum of complexes **8** and **9a** prepared from ^{13}C-enriched acetylene.

results from coupling to all four phosphorus nuclei, and the doublet results from coupling to the carbon at δ 128.6 ($^1J_{CC}$ = 57 Hz); these two signals clearly result from the α and β carbons of a bridging vinylidene moiety. Gated decoupling experiments confirm the assignment, establishing that the high-field carbon bears two protons ($^1J_{HC}$ = 151 Hz) while the low-field carbon is quaternary. As was the case for **5**, no proton resonance was observed for this vinylidene unit in the ^{1}H NMR spectrum. The acetylenic carbons, corresponding to the ^{13}C resonance at δ 147.3, has one proton attached, the resonance for which is located at δ 9.34 in the ^{1}H NMR spectrum (integrating as 2H). The assignment of the proton resonance is in agreement with both the gated experiment and the ^{1}H NMR spectrum, with both showing carbon-hydrogen coupling of 142 Hz, and further confirmed by heteronuclear carbon-hydrogen decoupling. The structure shown for compounds **9**, having the carbonyl ligands opposite the acetylene unit, is based on the structures of analogous compounds in which an alkyne bridge lies opposite either a bridging methylene[36] or carbonyl group.[37] It must be however that the alkyne-Ir-CO angles deviate significantly from linearity in this case since a sample of **9a**, in which the vinylidene, acetylene and carbonyl groups were all ^{13}C-enriched, showed coupling between the acetylene carbons and the carbonyls of only 4Hz; no coupling between Cα of the vinylidene moiety and the carbonyls was observed. The ^{13}C resonances for the vinylidene moiety of **8** appear as a doublet of multiplets at δ 154.7 for Cα and a doublet at δ 139.5 for Cβ ($^1J_{CC}$ = 57 Hz), while those for the alkyne appear as two doublets of multiplets at δ 141.2 and 133.0. In this case when the compound is also enriched in ^{13}CO, one carbonyl at δ 174.1 displays strong coupling (29 Hz) with Cα of the vinylidene unit while the other (δ 172.9) displays coupling of the same magnitude with one of the acetylenic carbons. These carbon-carbon coupling constants are quite substantial and support a structure, as shown, in which one carbonyl is opposite the vinylidene unit while the other is opposite the acetylene ligand. Clearly, based on the substantial coupling observed, the arrangements must be closer to trans than in **9a**.

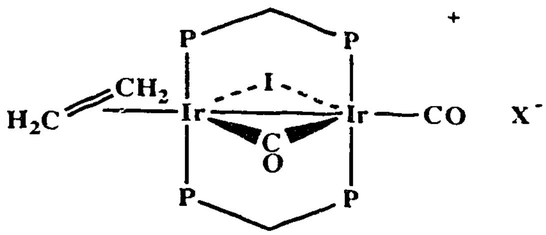
Reaction of the cationic, iodo-bridged A-frame, $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**2**) with acetylene yields the analogous monocationic and dicationic species **8** and **9** except having a BF_4^- anion, in approximately the same mole ratio as obtained in the previous reaction of **5**. In addition, this solution can be converted completely to **9b**, in which both anion are BF_4^-, by reaction with $AgBF_4$, supporting the mono- and dicationic nature of the respective species. Compound **9b** is unstable, slowly decomposing to two unidentified species, and is only spectroscopically characterized. Surprisingly the addition of iodide ion to **9b** does not regenerate the monocationic species **8**, but instead results in no reaction. It appears therefore that species **8** and **9** are not in equilibrium, but are generated by two competing pathways, probably resulting from alkyne attack at two different sites in some cationic vinylidene-bridged precursor.

The ^1H NMR spectra of **8** and its BF_4^- salt are essentially superimposable and show the presence of all four protons on the vinylidene and acetylene groups. The vinylidene protons appear at δ 8.84 and 7.96, whereas the acetylene protons are observed at δ 9.18 and 8.02. The gated ^{13}C NMR spectrum reveals carbon-hydrogen coupling constants of 143-153 Hz for these protons. In addition to phosphorus coupling, the acetylenic protons show proton-proton coupling of 6.4 Hz.

It is noteworthy that the ^{13}C chemical shifts for the α-carbons of the vinylidene units of **8** and **9a** are at unusually high field (δ 154.7, 152.0, respectively). Generally such resonances appear downfield of δ 230. These shifts are at even higher field than those noted for **5** and **7** (*ca.* δ 193). The vinylidene unit is isoelectronic with a carbonyl and a parallel high-field shift in the carbonyl resonances (by *ca.* 40 ppm) also occurred upon insertion of alkynes into the carbonyl-bridged metal-metal bond in some related dirhodium complexes.[37a] In both cases expansion of a 3-membered metallocycle ring to a 5-membered ring occurred upon alkyne insertion.

The reaction of **2** with acetylene to give the acetylene- and vinylidene-bridged species is unexpectedly fast, completed almost immediately after the introduction of acetylene, in sharp contrast to the reaction of **1** with acetylene to produce **5**, which takes *ca.* 20 h to complete. When **1** is treated with excess acetylene, the final products are the same as obtained in the reaction of **5** with excess acetylene, and it can be easily shown by NMR monitoring that the former reaction proceeds via the initial formation of **5**. Keeping in mind that the formation of **8** and **9a** from **5** and acetylene is instant, it appears that the reaction of **2** with acetylene is either via a different mechanism from the one between **1** and acetylene or the rate for the formation of **5** is affected by the iodo ligand, which might hinder the reaction through re-coordination. The latter seems more plausible, since the reaction of **1** with excess acetylene, leading to complexes **8** and **9a**, is completed within one or two hours, when conducted in a polar solvent mix such as CH_2Cl_2/CH_3CN or $CH_2Cl_2/MeOH$. However, the same reaction, when carried out in CH_2Cl_2, takes about the same time as required for the generation of **5**.

The preceding sections have been devoted to the acetylene-vinylidene tautomerism. In the remaining part of this chapter, we present a describtion of the ethylene chemistry of **1** and **2**. Before beginning the discussion of this, it is interesting to note that vinylidene species can also be generated from ethylene. Thus, treatment of $[Os_3(CO)_{12}]$ with ethylene yields a μ-vinylidene complex,[38] and a recent study on a modified Ru (001) surface shows that π-bonded ethylene is converted to ethylidyne which subsequently undergoes dehydrogenation to give surface-bonded vinylidene.[39] Both complexes **1** and **2** react readily with ethylene affording compounds, $[Ir_2I(CO)(C_2H_4)(\mu\text{-}CO)(dppm)_2][X]$ ($X^- = I^-$ (**10a**), BF_4^- (**10b**)). Compoounds **10a** and **10b** appear, on the basis of their spectral data, to be identical apart from the anions involved and appear to be the first characterized olefin adducts of A-frame species. In solution both **10a** and **10b** have carbonyl stretches at ca. 1979 and 1816 cm^{-1}, suggesting that one carbonyl ligand is terminal while the other is bridging. Both compounds show ^1H resonaces for the dppm methylene protons at ca δ 4.2 and 4.0 and for the ethylene group at ca. δ 2.7 and 1.6. Although the two phosphorus resonances are separated by only about 1.2 ppm in each of these compounds, selective phosphorus decoupling experiments were achieved through a careful choice of decoupling power. Decoupling the lower field ^{31}P resonance in **10b** results in a collapse of both ethylene proton resonances to apparent triplets (as is observed on broad-band ^{31}P decoupling) whereas decoupling the high-field ^{31}P resonance results in no change in these proton resonances. These experiments confirm that the ethylene molecule is bound to only one iridium center, as shown. This



X = I (10a); BF$_4$ (10b)

structure is also consistent with the $^{31}C\{^1H\}$ NMR spectra, in which the two resonances at δ 38.5 and 31.2 are assigned to the coordinated ethylene, on the basis of the similarity of their chemical shifts to other terminally bound ethylene ligands.[40]

Although the stucture shown for the cation of compounds **10a** and **10b** is not unambiguously determined from the data available, the doubly bridged A-frame structure is favored owing to the very close resemblance of the IR and $^{31}P\{^1H\}$NMR spectral parameters with those of the closely related tricarbonyl species,[10] $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]^+$. Unfortunately, we have not yet succeeded in obtaining suitable crystals of **10a** and **10b** to confirm the ethylene binding mode, which as noted is unprecedented in these A-frame compounds. Olefin complexation has been shown to be quite sensitive to steric effects.[13] It appears that the substituents on the olefins are generally involved in unfavorable repulsions with the ortho-hydrogens of the dppm phenyl groups. Consistent with these ideas, tetrafluoroethylene, having larger fluorine substituents, does not react with **1**. It seems that for the very electron-rich metal centers in **1** and **2** the small ethylene ligand is an effective enough π-acid to give strong binding of this group, while being small enough to minimize repulsions. Neither the neutral mixed-metal species, $[RhIrI_2(CO)(\mu\text{-}CO)(dppm)_2]$ nor its related cationic A-frame $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2]^+$ reacts directly with ethylene.[10] It appears that the presence of Rh has the effect of deactivating the Ir center. Given the fact that the basicity of Rh is lower than that of Ir, the consequence of this effect could be a decrease in the basicity of the iridium center. The compound, *trans*-$[IrCl(CO)(dppm)]_2$, also fails to react with ethylene. In this compound the metal basicity is undoubtedly lower than that in the diiodo species **1**. Since π-backbonding from metal to olefin ligand plays a significant role in stabilizing metal-olefin compounds,[13] and such backbonding can be expected to diminish when the metal basicity is decreased, the failure of the complexes above to react with ethylene may not be surprising.

Although the reaction between **1** and ethylene is reversible upon flushing the system with N_2, the ethylene molecule is not lost from **10b**. It appears that ethylene loss is promoted by iodide coordination; therefore, the addition of (PPN)I (PPN = $(Ph_3P)_2N$) to solutions of **10b** results in loss of ethylene. The effect of the iodo ligand in these reactions is reminiscent of the one noted in the reaction of **1** with acetylene, where the coordination of the iodo ligand apparently slows the reaction leading to the vinylidene complex **5**.

Conclusions

This study, in which the diiodo species $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ reacts with acetylene and phenylacetylene, to give the respective vinylidene-bridged products $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$, is the first in which several binuclear intermediates have been observed, allowing a mechanism to be proposed for the 1,2-hydrogen shift. For the first time in a binuclear species evidence for an acetylide-hydride intermediate has been obtained. The precursor to this acetylide-hydride species, in which a parallel-bound alkyne slides from a symmetrical position to that where it is closer to one Ir center than to the other, is also a pivotal intermediate in the acetylene-to-vinylidene transformation.

Although the phenylvinylidene-bridged species does not react further with alkynes, the vinylidene-bridged compound does react with acetylene to give the unusual products $[Ir_2I(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HCCH)(dpp$ [illegible] nd $[Ir_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HCCH)(dppm)_2][I]_2$ in which the metals are simultaneously bridged by a vinylidene *and* an acetylene group. Analogous mono- and dicationic species can also be obtained in the direct reaction of $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ with acetylene. In these compounds the vinylidene and the acetylene groups that may potentially condense are on opposite faces of the binuclear framework and cannot come together; consequently carbon-carbon bond forming was not observed. Coordinated vinylidenes are known to condense with free alkynes, presumably via an intermediate in which alkyne precoordination to the metal has occurred.[1] The formation of these vinylidene- and alkyne-bridged products indicates that vinylidene and alkyne units can co-exist, and more importantly perhaps, that if the two units are disposed at a trans position, condensation may not take place. It is also noteworthy that alkyne-bridged units in related, diphosphine-bridged complexes are notoriously unreactive.[31,36]

The formation of **5** and **7** is possibily promoted by the enhanced basicity of the metal centers in **1**, brought about by the good π-donor iodide ligand. This may not be surprising since the reaction leading to these vinylidene complexes appears to be controlled by the oxidative addition of the C-H bond to form the acetylide-hydride species.

The greater basicity of the iodo complexes is also dramatically seen in the formation of the unusual ethylene adducts, $[Ir_2I(CO)(C_2H_4)(\mu\text{-}CO)(dppm)_2][X]$ ($X = I^-, BF_4^-$), which are formed directly in the reactions of **1** or **2** with ethylene. No such complex was ever observed with the chloride analogues. The binding of ethlylene in this cationic iodo species is a clear manifestation of the greater basicity of the metals.

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Chapter 5

Conclusions

As noted in previous chapters, dppm- and anion-bridged complexes comprise two major classes of binuclear compounds of rhodium and iridium. Typical binuclear complexes formed by dppm ligands are those of A-frames, whereas those formed by anionic bridging groups generally have an open-book structure. One of the goals of this thesis was to develop chemistry of complexes which might combine the features of both the A-frame and the open-book complexes. In this study the bifunctional anion, 2-mercaptothiazolinate (mtz), was chosen as a starting point. This ligand had been shown to form typical open-book compounds,[1] such as the tetra-carbonyl species $[Rh(CO)_2(\mu\text{-mtz})]_2$. It was of particular interest to determine the structure of the compounds having both dppm and mtz as bridging ligands. As demonstrated in Chapter 2, a stepwise transformation of the mtz-bridged open-book complexes to the dppm-bridged A-frames has been achieved. Of more interest than this transformation is the finding that the complexes prepared, which contain two mtz and one diphosphine ligands, do exhibit the features of both the A-frame and open-book species. This is clearly seen in the reaction of $[Rh(CO)_2(\mu\text{-mtz})]_2$ with the dppm ligand. Thus, treatment of the tetra-carbonyl, open-book species with one equiv of dppm gives the complex, $[Rh_2(CO)_2(\mu\text{-mtz})_2(dppm)]$, in which the dppm group is *trans* to one mtz ligand, and the two mtz ligands are mutually *cis* as evidenced by the spectroscopic data. This compound can therefore be equally described as an A-frame or an open-book species, and because of this the distinction between these two classes of complexes becomes blurred. With two equivalents of dppm the product is [Rh_2(mtz)$(CO)_2$(μ-mtz)$(dppm)_2$], a typical A-frame complex, having two trans-oriented dppm ligands, and one capping and one dangling mtz group.

The complexes [$M_2(CO)_2$(μ-mtz)$_2$(μ-L)] (M=Rh, Ir, L=dppm; M=Rh, L=dppe), appear to be the first examples in which a diphosphine ligand has been incorporated into a dianion-bridged open-book, binuclear complex of the group VIII metals. The rhodium species readily undergo oxidative-addition reactions with iodine, giving the metal-metal bonded complexes [$Rh_2I_2(CO)_2$(μ-mtz)$_2$(μ-L)] (L=dppm, dppe). Noteworthy in this study are the complexes having dppe as a bridging ligand. As noted previously, dppe overwhelmingly favors the formation of chelates. The formation of these dppe-bridged species may result from the presence of the two mtz bridges, which provide the stability needed for the dppe-bridged binuclear framework. Although the dppe group could still act as a chelating instead of a bridging ligand with the binuclear framework remaining intact, the compound so formed would be expected to be less stable than the one found, since in the chelated species one of the Rh(II) centers would only have two carbonyls while the other one would only be bound to two phosphorus atoms, aside from the bridging-mtz groups and the iodo ligand at each metal. It is also noted that the two mtz-ligand planes in [$Rh_2I_2(CO)_2$(μ-mtz)$_2$(μ-dppe)], as shown in Chapter 2, are tipped with respect to each other. Such an arrangement appears to suit the bridging-dppe group, providing enough room for the diphosphine to span without imposing undue strain within this bridging group.

The A-frame complexes containing two mtz goups have also been prepared by reaction of *trans*-[MCl(CO)(dppm)]$_2$ (M=Rh, Ir) with two equiv of mtz anions. As expected, when one equiv of the mtz anion is utilized the mono-mtz-substituted products, [$M_2Cl(CO)_2(\mu$-mtz)(dppm)$_2$], are obtained, in which the mtz ligand is at the apical position. The rhodium species having either one or two mtz ligands show complicated dynamic behavior. This is particularly the case for the complex [Rh(mtz)(CO)$_2$(μ-mtz)(dppm)$_2$], in which the dangling mtz group is in exchange with both the free and the bridging mtz groups.

The dynamic behavior noted for the rhodium species is of special interest. As mentioned in Chapters 1 and 2, bridge opening has been suggested to play a crucial role in substrate activation by anion-bridged binuclear complexes.[2] This study provides evidence that bridge opening is feasible even in the absence of substrate molecules. It will be of interest to determine if such behavior can play a role in the reactivity of these species. In addition, in the mtz-capped A-frames noted above, the two metals are electronically different due to the bifunctionality of the mtz group. In principle, different bifunctional ligands can be chosen in order to tune the electronic properties of the metals involved in the binuclear framework, so that unique reactivity patterns might be achieved. It is therefore of interest to pursue the chemistry of the A-frames capped by the mtz as well as by other bifunctional ligands.

Our initial interest in the dppm-bridged binuclear complexes was prompted by the very unusual peroxo compound $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$, in which the dioxygen moiety is accompanied by a metal-metal bond. As mentioned in Chapter 3, the dioxygen coordination mode in this complex is unprecedented, so it was of obvious interest to investigate the reactivity of this species. In particular, it was anticipated that the long O-O separation found for the peroxo moiety and the inherent strain associated with this unit might result in unusual reactivity, either at the O_2 moiety or at the Ir-Ir bond. The study of the dioxygen compound $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ has been fruitful. As shown in Chapter 3, the peroxo species reacts with a variety of inorganic and organic substrates including H^+, NO^+, NO, NO_2, SO_2, CO and RNC. In reactions involving H^+, SO_2 and NO_2, the chemistry of the peroxo complex is as expected. Thus the dioxygen moiety can be readily protonated with HCl and H_2SO_4, yielding the anion-substituted complexes together with hydrogen peroxide, and in reactions with SO_2 and NO_2, the sulfate- and the nitrate-bridged complexes, $[Ir_2I_2(CO)_2(\mu\text{-}SO_4)(dppm)_2]$ and $[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][NO_3]$, are formed, respectively. These reactions, as noted in Chapter 3, are typical of mononuclear dioxygen compounds. In this regard, this new type of peroxo complex displays similar chemistry to its mononuclear analogues.

However, in reactions with CO, NO and isocyanides the peroxo species exhibits unusual chemistry. The reaction of the peroxo complex with CO appears to proceed via two pathways. One involves the oxidation of CO to give $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ and CO_2, while the other involves CO insertion into the Ir-Ir bond, yielding the unusual dioxygen compound, [$Ir_2I_2(CO)_2(\mu$-$CO)(\mu$-$O_2)(dppm)_2$]. In this complex, a carbonyl group is for the first time incorporated into a five-membered metallocycle involving dioxygen. The reaction with CO proceeds much faster in a polar solvent system such as $CH_2Cl_2/MeOH$ than in CH_2Cl_2, indicating that a polar intermediate may be involved at some stage of the reaction, which could be formed by opening of one of the Ir-O bonds or by iodide dissociation. However it should be noted that it is not clear how such an intermediate is involved in the reaction, considering that the reaction may proceed via two pathways. The peroxo species readily reacts with NO, affording a rare complex, [$Ir_2I_2(CO)_2(\mu$-$NO)(dppm)_2$][NO_3], in which the dppm-bridged binuclear framework contains a bridging nitrosyl ligand. Surprisingly perhaps, isocyanides are not oxidized by the dioxygen species, instead the interesting hydroxide-bridged methoxycarbonyl complexes [$Ir_2(RCN)_3(CO_2CH_3)(\mu$-$OH)(dppm)_2$][I]$_2$ (R=^{i}Pr, ^{t}Bu) are formed through involvement of the methanol solvent. This reaction is unusual in that formation of the alkoxycarbonyls is less common between carbonyls and methanol, because of the low nucleophilicity of the latter. The fate of the dioxygen moiety is not clear in this reaction, although protonation to give hydrogen peroxide by the methanol solvent is not impossible.

As mentioned in Chapter 3, mononuclear dioxygen compounds of iridium were shown to be generally less reactive than those of the nickel triad,[3] especially towards species such as CO and NO. The enhanced reactivity of [$Ir_2I_2(CO)_2(\mu$-$O_2)(dppm)_2$] towards these two species, compared with closely related mononuclear complexes, might relate to the strain in the dioxygen moiety imposed by the metal-metal bond or the posssibly-enhanced basicity of this group brought about by the the *two* good π donor iodide ligands.

During the study of the peroxo complex, it was realized that the enhanced basicity of the metal centers in the diiodo precursor, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$, in comparison with *trans*-$[IrCl(CO)(dppm)]_2$, might also promote other unusual reactions, aside from the activation of dioxygen. We were especially interested in the reactions involving olefins and unactivated alkynes, since in the numerous dppm-bridged complexes of Rh and Ir, examples containing these substrate molecules are very rare. The diiodo compound, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$, reacts with both ethylene and terminal alkynes. The former gives ethylene-coordinated A-frames which had not previously been reported for either dppm-bridged rhodium or iridium compounds, while the latter, for the first time, provides details on the isomerization of 1-alkynes to vinylidenes on a binuclear framework. Ethylene coordinates to the neutral diiodo iridium compound at a terminal position yielding $[Ir_2(CO)(C_2H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$, and the reaction is reversible. The same cationic complex is also obtained in the reaction of $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ with ethylene, however the reaction is irreversible. It appears that the reversibility is caused by the iodide ligand coordination, since addition of I^- to the BF_4^- salt results in the loss of ethylene.

Unlike the reactions with ethylene, which yield complexes with ethylene as a terminal ligand, the reaction of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ with terminal alkynes yields vinylidene-bridged compounds, $[Ir_2I_2(CO)_2(\mu\text{-}$

CC(H)R)(dppm)$_2$] (R=H,Ph), via C-H bond activation. By spectroscopically monitoring the reactions at various temperatures, we were able to identify key intermediates in the reactions and propose a mechanism for the isomerization of terminal alkynes to vinylidenes mediated by the binuclear iodo complex. The first step of the acetylene-vinylidene transformation involves the formation of a normal parallel-acetylene-bridged compound, such as [Ir$_2$(CO)$_2$(μ-I)(μ-HC$_2$H)(dppm)$_2$][I] characterized in the reaction of the diiodo complex with acetylene. This species is unstable and readily transforms to a new complex [Ir$_2$I(CO)$_2$(μ-HCCH)(dppm)$_2$][I], in which the symmetrically-bound acetylene moiety slides to become closer to one of the iridium atoms, as indicated by various spectroscopic data. It is by virtue of this unusual species that C-H activation takes place yielding an acetylide-hydrido species, which results in the formation of the vinylidene products. Although the acetylide-hydrido complex is not observed in the case of acetylene, its formation is established in the reaction of the diiodo complex with phenylacetylene, which gives [Ir$_2$(H)I(CO)$_2$(μ-CCPh)(dppm)$_2$][I]. It is significant to note that although a theoretical study[4] shows that acetylene-vinylidene isomerization is unlikely via a concerted mechanism on a binuclear complex, our study indicates that an alternative pathway is feasible, involving the generation of an acetylide-hydrido species from a parallel-bound acetylene, which slides to allow a stronger interaction with one of the metals than with the other, presumably via the additional bonding between the π or π^* orbital of the acetylene ligand and the orbital of the former.

Carbon-carbon bond-forming reactions between a vinylidene complex and hydrocarbon fragments are of great interest because of the relevance of such reactions to elementary processes involved in the production of hydrocarbons from simpler molecules.[5] Unfortunately no coupling between the coordinated vinylidene in $[Ir_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2]$ and free acetylene is observed. However, the vinylidene compound does react with acetylene, giving the acetylene- and vinylidene-bridged complexes, $[Ir_2I(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]$ and $[Ir_2(CO)_2(\mu\text{-}HC_2H)(\mu\text{-}CCH_2)(dppm)_2][I]_2$. In these species the two hydrocarbon units are on opposite sides of the binuclear framework, and thus can not come together for coupling. In vinylidene-alkyne condensation and alkyne polymerization reactions, the intermediate species have been proposed to involve alkyne precoordination to a vinylidene complex.[5] The complexes above are a clear indication that vinylidene and alkyne units can co-exist. However these species also indicate that when such units are mutually trans, condensation may not take place. It remains of great interest to examine the reactivity of these vinylidene complexes towards species such as R^+, CR_2, and protons, and to determine if the bridging vinylidene unit can undergo reactions such as carbon-carbon bond forming.

Although it is not so clear whether electronic effects have played a significant role in the reactions of the dioxygen complex, which as shown in Chapter 3, is more reactive than its mononuclear analogues, such effects are clearly displayed in the reactions of the diiodo complex $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ with acetylene and ethylene. As noted in Chapter 4, the dichloro compound *trans*-$[IrCl(CO)(dppm)]_2$ also reacts with acetylene, however the product is a normal species containing a bridging alkyne group, which is bound parallel to the Ir-Ir bond. Substitution of the chloride ligand with the better π-donor iodide ligand yields the diiodo complex, accompanied with an increase in the metal basicity. The electron richness of the diiodo species is reflected in its unusual structure, having a bridging carbonyl group, which is suggested to relieve the metal centers of some excess electron density brought about by the iodo ligand.[6] Substitution of the chloride ligand may also give rise to significant steric effects because of the bulkiness of the iodide ligand. It is difficult to envisage if steric effects have played any notable role in the activation of acetylene by the diiodo complex, however the unusual reactivity of this species towards the substrate is consistent with the increase in the metal basicity. In Chapter 4, it has been shown that the key step in the acetylene-vinylidene tautomerism involves the oxidative addition of the C-H bond to give an acetylide-hydrido species. Therefore the promotion of the tautomerism by the electron-rich metal centers is not a surprise. As with the reaction involving acetylene, the reaction of the diiodo complex with ethylene is again a manifestation of the greater basicity of the metal centers in the complex, in comparison with the dichloro analogue, *trans*-$[IrCl(CO)(dppm)]_2$, which does not react with ethylene. As noted in the previous chapter, π-backbonding from the metal to the coordinated olefin plays an important role in stabilizing metal-olefin complexes, therefore more stable complexes can be expected to form with an increase in metal basicity. The formation of the ethylene adduct in the reaction of the diiodo complex is reminiscent of a general observation, noted in Chapter 1, that more electron-releasing ligands promote stronger binding of electrophilic substrates to the metal centers.

The quite unusual reactivity of the diiodo compound as well as its mono-cationic derivative, $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$, indicates that metal basicity can play a crucial role in the activation of substrates and in the way that the substrates are activated. In this regard, it will be of interest to prepare dppm-bridged compounds with other good-donor ligands and to explore compounds without carbonyl ligands, which are known as one of the best π-acids.

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Appendix

Solvents and Drying Agents

Acetone	$CaSO_4$
Acetonitrile	CaH_2
Benzene	Na
Dichloromethane	P_2O_5
Diethyl Ether	Na/benzophenone
Ethanol	Na
Hexane	Na/K
Methanol	Mg turnings
Tetrahydrofuran	Na/benzophenone