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The Activation of H_2S, Thiols and Alkynes by Adjacent Metal Centers

by

Li-Sheng Wang ©

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

Department of Chemistry

Edmonton, Alberta

Fall, 1995

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Date: August, 1995

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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 **The Activation of H_2S, Thiols and Alkynes by Adjacent Metal Centers** submitted by Li-Sheng Wang in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(University of Wisconsin)

Date: Aug. 22nd 1995

To Mom, Xiaodong and Amy

Abstract

The complex, $[RhMn(CO)_4(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) (**1**), reacts with H_2S and thiols to yield $[RhMn(SR)(CO)_3(\mu\text{-}H)(dppm)_2]$ (R = H, (**2**); Et, (**3**); Ph, (**4**)), containing the Rh-bound sulfhydryl or thiolato groups. The terminal sulfhydryl species loses H_2 and scavenges CO to yield $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]$ (**5**). This sulfide-bridged product can be protonated or alkylated to give the cationic species, $[RhMn(CO)_4(\mu\text{-}SR)(dppm)_2]^+$ (R= H, (**6**); CH_3, (**7**); CH_2SiMe_3, (**8**)). The bridging sulfhydryl group in $[RhMn(CO)_4(\mu\text{-}SH)(dppm)_2]^+$ undergoes a Michael-type addition to alkynes to yield $[RhMn(CO)_4(\mu\text{-}SC(R)=C(H)R')(dppm)_2]^+$ (R = H, R' = C(O)Me, (**9**); R = R' = CO_2Me, (**10**)) in which the unsaturated thiolato group bridges the metals. With hexafluoro-2-butyne, $[RhMn(SC(CF_3)=C(H)CF_3)(CO)_4(dppm)_2]^+$ (**11**) is obtained, but in this case the thiolato group is Rh-bound.

Complex **1** reacts with alkynes (RC≡CR; R = CO_2Me, CF_3) to yield the alkyne-bridged products $[RhMn(CO)_4(\mu\text{-}RC_2R)(dppm)_2]$ (**12a, 12b**). These species lose one carbonyl to yield two isomers in which the bridging alkyne group is either parallel or perpendicular to the Rh-Mn vector (**13** or **14**). Unusually facile interconversion between these two alkyne binding modes occurs. Protonation of the different alkyne-bridged species yields a series of vinyl complexes, which can also be obtained from the reaction of $[RhMn(CO)_4(\mu\text{-}H)(dppm)_2]^+$ (**15**) with alkynes. A related vinyl species $[RhMn((CH_3)C=CH_2)(CO)_4(dppm)_2]^+$ (**16a**) is obtained in the reaction of **15** with allene; also obtained is the isomeric η^1-allyl complex $[RhMn(\eta^1\text{-}CH_2C(H)=CH_2)(CO)_4(dppm)_2]^+$ (**16b**), which converts to **16a** upon refluxing.

The reaction of **1** with 3-butyn-2-one at -40°C yields the alkyne-bridged product, $[RhMn(CO)_4(\mu\text{-}HC_2C(O)Me)(dppm)_2]$ (**17**), which undergoes a 1,2-hydrogen shift, yielding two isomers of the vinylidene-bridged species, $[RhMn(CO)_4(\mu\text{-}CC(H)C(O)Me)(dppm)_2]$ (**18**), as the temperature is raised. Species

18 undergoes facile CO loss to give [RhMn(CO)$_3$(μ-η^1:η^2-CC(H)C(O)Me)(dppm)$_2$] (**19**) in which the ketonic moiety of the bridging vinylidene group coordinates to Mn. Protonation of **17-19** yields a series of vinyl complexes. Addition of methyl triflate to **18** and **19** yields the respective methyl-substituted vinyl complexes. Alkylation of **19** at low temperature yields an intermediate, [RhMn(CH$_3$)(CO)$_3$(μ-η^1:η^2-CC(H)C(O)Me)(dppm)$_2$]$^+$ (**20**), having a bridging vinylidene and a Rh-bound methyl ligand, which rearranges to a vinyl complex upon warming.

Reaction of the A-frame complex, [Ir$_2$(CO)$_2$(μ-I)(dppm)$_2$)]$^+$ (**21**), with either acetylene or phenylacetylene at -78°C yields the respective species, [Ir$_2$(CO)(HCCR)-(μ-I)(μ-CO)(dppm)$_2$]$^+$ (R=H, (**22**); Ph, (**23**)), having terminal alkyne ligands. An analogous allene adduct is obtained in the reaction of **21** with allene. At ambient temperature these alkyne adducts slowly rearrange to the vinylidene-bridged species, [Ir$_2$(CO)$_2$(μ-I)(μ-CC(H)R)(dppm)$_2$]$^+$ (R=H, (**24**); Ph, (**25**)), which can also be obtained from the reaction of [Ir$_2$I$_2$(CO)$_2$(μ-CC(H)R)(dppm)$_2$] (R = H, (**26**); Ph, (**27**)) with methyl triflate, through loss of CH$_3$I. Protonation of complex **26** at -40°C yields an ethylidyne-bridged product which rearranges to a vinylidene- and hydride-bridged product at ambient temperature. Reaction of complex **25** with either acetylene or phenylacetylene yields alkyne- and phenylvinylidene-bridged products, and the X-ray structure of a derivative, [Ir$_2$I$_2$(CO)$_2$(μ-CC(H)Ph)(μ-HCCH)(dppm)$_2$] (**28**), was determined. The reaction of **24** with phenylacetylene yields an unusual bis-vinylidene product, [Ir$_2$I(CO)$_2$(CCH$_2$)(CC(H)Ph)(dppm)$_2$]$^+$ (**29**), in which each vinylidene is terminally bound to a different metal. Reaction of **29** with either I$^-$ or CO converts the terminal vinylidenes to bridging groups yielding [Ir$_2$I(L)(CO)$_2$(μ-CCH$_2$)(μ-CC(H)Ph)(dppm)$_2$]$^{n+}$ (L = I, n = 0, (**30**); L = CO, n = 1, (**31**)). The diiodo species (**30**) was structurally characterized by X-ray techniques.

Acknowledgment

I wish to express my gratitude to my supervisor, Professor Martin Cowie, for his guidance, encouragement and help during my graduate studies. I am also grateful to Professor Martin Cowie and his wife Gail for their hospitality in hosting many group get-togethers at their home.

I thank Dr. Robert McDonald for his expert assistance in crystal structure determination. His enthusiastic help especially on matters related to X-ray crystallography is deeply appreciated.

I appreciate the great help given by Dr. Frederick Antwi-Nsiah and his wife Christina, especially for his help when I just moved to Norman, Oklahoma to assume a postdoctoral position there.

The help and encouragement given by our group members (present and past) are deeply appreciated. They are Dr. David Antonelli, Dr. Jianliang Xiao, Brian Sterenberg, Darren S.A. George, Dr. Giovanni Moro, Todd Graham, Oke Okemona, Jeff Torkelson and Dr. Angela Llamazares.

I appreciate the help given by Dr. Tom Nakashima on the matters related to NMR spectroscopy. I also thank Mrs. G. Aarts, Mrs. L. Kong, Mr. G. Bigam and Mr. T. Brisbane for their assistance on NMR techniques.

I am indebted to the staff of the Elemental Analysis Lab, the Spectral Services, the Glass Shop, the General Office, the Purchasing Section, the Store Room and the Mail Room.

I also thank Dr. George Richter-Addo for letting me join his group in Chemistry and Biochemistry Department of Oklahoma University as a postdoctoral fellow before I complete my Ph. D. thesis.

I thank Dr. Jianzhong Zhang and his wife Yu Fang for their immense help and friendship.

Special thanks go to my mother, my father and my brother for their support and encouragement during these years.

Very special thanks go to my wife Xiaodong for her help and encouragement. She took care of our new-born baby and did most of house work while I was busy writing my thesis. Very special thanks also go to my daughter Amy for bringing me so much happiness.

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List of Schemes

Chapter 1

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Chapter 4

List of Abbreviations and Symbols

anal	analyses
ca.	circa (approximately)
calcd	calculated
DMAD	dimethyl acetylenedicarboxylate, $CH_3O_2C\text{-}C{\equiv}C\text{-}CO_2CH_3$
dppm	bis(diphenylphosphino)methane, $(C_6H_5)_2PCH_2P(C_6H_5)_2$
Et	ethyl, CH_3CH_2-
h	hour(s)
HFB	hexafluoro-2-butyne, $F_3C\text{-}C{\equiv}C\text{-}CF_3$
IR	infrared
Me	methyl, CH_3-
MeOH	methanol, CH_3OH
mg	milligrams
min	minute(s)
mL	milliliters
mmol	millimoles
NMR	nuclear magnetic resonance
Ph	phenyl, C_6H_5-
sec	second(s)
THF	tetrahydrofuran, C_4H_8O
μL	microliters
μmol	micromoles

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) ($1Å=10^{-10}$ meters)
α, β, γ	angles between b and c, a and c, and a and b axes, respectively, of unit cell
β_{ij}	anisotropic displacement parameters
λ	wavelength
ρ	density
σ	standard deviation

Chapter 1

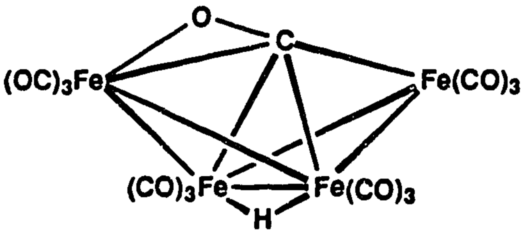
Introduction

The concept of coordination compounds, as developed by Alfred Werner in 1900,[1] has been pivotal in the development of inorganic chemistry. In coordination compounds the metal atom or ion is surrounded by a set of ligands (neutral molecules or anions) arranged in a distinct geometry, and the physical and chemical properties of these compounds are determined by the metal, the ligands, the resulting metal-ligand bonds and the geometry of the compound.[2] Although the concepts of Werner are still applicable, there have been a number of important developments not derived therefrom. These include the bonding in metal-carbonyl complexes, organometallic complexes and transition-metal clusters.[3] In this last group the key concept of metal-metal bonding, which we now take for granted, became widely accepted only about 30 years ago, although the earliest structural evidence of a metal-metal bond appeared in 1926.[3-5] A metal-atom cluster can be defined as: "a group of two or more metal atoms in which there are substantial and direct bonds between the metal atoms".[2] The properties of metal-metal bonds have been the subject of several reviews.[2-6]

In the past few years studies on metal clusters have undergone a rapid expansion within inorganic and organometallic chemistry due in part to their relevance to catalysis.[7] Catalytic process can be divided into homogeneous and heterogeneous depending on the physical states of the catalysts and substrates under reaction conditions. A homogeneous catalyst is normally a transition-metal complex dissolved in the reaction solution, whereas heterogeneous catalysts usually are metals, metal oxides or sulfides of transition elements which are in a different phase from the substrate and can therefore be readily separated from liquid or gaseous reactants and products.[8a] A fundamental difference between homogeneous and heterogeneous catalysts relates to the catalytically active species. Whereas homogeneous systems generally utilize well defined catalytic precursor complexes and ideally (although not always) involve only one catalytically active species, processes occurring on surfaces can occur at a number of chemically different sites, owing to the fact that surfaces are not uniform but instead present a number of reactivity sites to the reactants. Even well defined metal crystallites have sites that can be defined as platforms, edges or corners, and each of these displays different physical properties and gives rise to different reactivities towards substrates.[8] In addition, the complexity of solid surfaces limits the information that can be obtained. The use of uniform faces, such as a specific crystal face, provided by single crystals, helps to avoid this problem and information about the surface can be obtained by techniques such as LEED (low energy electron diffraction), AES (Auger electron spectroscopy) and HREELS (high resolution electron energy loss spectroscopy).[7a,8a,9] But information about the interactions between surface atoms and substrate molecules is still difficult to obtain.[7a]

Metal clusters have the potential to be excellent models for processes occurring at metal surfaces, with the chemisorbed substrates being modelled by the ligands within the cluster complexes, on the assumption that the coordination of organic or inorganic molecules and groups on surface metal atoms is analogous to that in discrete organometallic compounds.[7] In support of this idea, comparison of metal clusters with surfaces having chemisorbed species shows several basic analogies in: (a) the metal framework structure, the metal-metal bond distances and the bond energies; (b) ligand-to-cluster and ligand-to-surface bond stereochemistry, bond distances and bond energies; and (c) the mobility of ligands on metal clusters and absorbed species on surfaces.

Although mononuclear compounds can be used as models for reactions on metal surfaces, clusters are better models owing to the neighboring metals, which give a better modelling of the adjacent metal atoms on a surface. The ability of clusters to utilize the adjacent metals in the activation of substrate molecules, much as proposed for surfaces, is uniquely demonstrated by the tetrairon complex $[Me_3NCH_2Ph][Fe_4(CO)_{13}H]$ (A) in which a carbonyl is bound to four metals, to three through carbon, and to the fourth in a side-on fashion through the C-O bond as shown in following diagram.[10]



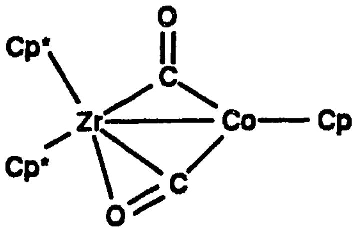
(A)

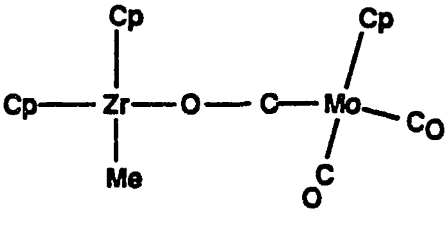
This structure demonstrates one of the attractive features of metal clusters in allowing the activation of multiple bonds in molecules like carbon monoxide and nitrogen.[7,11] The dissociative chemisorption of CO or N_2 on a metal surface occurs under reasonably mild conditions and it is proposed that this occurs by binding of these molecules to surface metal atoms in a side-on fashion.[7a,7b,11,12] Although such binding modes are difficult to confirm on a surface,[12] complex A serves as a model for such a process. Furthermore, simple bonding arguments allow a rationalization of the bond-order reduction through donation of electron density from the occupied π orbitals of the substrate and concomitant back donation from the metals into the substrate π^* antibonding orbitals. In contrast, the triple bonds of such substrates are not readily cleaved at a single metal center of mononuclear complexes.

Dinuclear compounds in which only two metals are involved can be viewed as the prototypical cluster,[5] being the smallest unit that can display metal-metal bonding, and can give rise to effects of metal-metal cooperativity. It is anticipated that the chemistry of bimetallic compounds, in which the two metal atoms are held in close proximity, may show differences from that of mononuclear compounds, owing to the possibilities of the interactions between the metals and/or between bridging ligands and the metals – features that are absent in mononuclear compounds.[13] The structures and reactivity patterns of these dinuclear compounds are expected to be unique as a result of cooperative involvement of the two adjacent metals.[14]

Metal-metal cooperativity effects can manifest themselves in a number of ways. They may result simply as a consequence of the ligands assuming bridging modes, giving rise to different reactivity patterns,[15] or they may result from an adjacent metal functioning as an electron or ligand reservoir, receiving or supplying electrons and/or ligands as required by the nearby metal.[16] Ligand coupling may be facilitated in binuclear complexes in which terminal ligands on each adjacent metal can be brought together to give a coupled product.[15] One major advantage of binuclear compounds is their ability to show metal-metal cooperativity effects in a system that is simpler to study than larger clusters by virtue of having fewer metal centers.

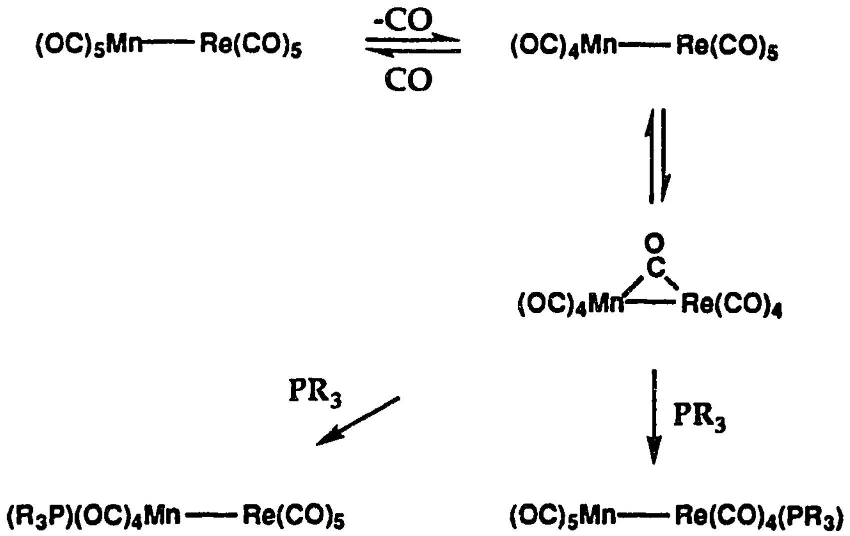
Initially, most attention on binuclear systems was focused on homobimetallic compounds in which both metals are the same. However, lately interest in heterobimetallic compounds has increased owing to the expectation that two adjacent metal atoms, each having different chemical properties, may give rise to novel reactivity patterns which are different from those of homobimetallic compounds.[17] For instance, the early-late transition metal compounds may cooperatively activate substrate molecules such as CO, as shown in following diagram. This could result from the oxophilicity of early transition metals, which usually are electron deficient and function as hard Lewis acids,[17] while late transition metals in low oxidation states are generally electron rich and can serve as either soft Lewis bases or acids.





One of the significant aspects of the chemistry of heteronuclear compounds is the introduction of chemical reactivity to an inert metal center by the adjacent reactive metal center. This is exemplified by the substitution reactions occurring at the Re and Mn metal centers in $[ReMn(CO)_{10}]$ as shown in Scheme 1.1.[18a] The more kinetically labile manganese center loses one carbonyl and introduces unsaturation at the adjacent rhenium center by the formation of the presumed carbonyl-bridged species. The monosubstituted complexes are formed upon the subsequent nucleophilic attack either on the rhenium or manganese center by a phosphine or phosphite (PR_3; R=Ph, *n*-C_4H_9 or OPh). This observation is consistent with the fact that the reaction rate of $[ReMn(CO)_{10}]$ with triphenylphosphine (PPh_3) is faster than that of dirhenium carbonyl complex $[Re_2(CO)_{10}]$ due to the presence of the labile Mn center in the former.[18a-d]

Scheme 1.1



One of the common problems encountered in studies of binuclear compounds is their fragmentation to mononuclear complexes under certain reaction conditions. This can be rationalized by the fact that metal-metal bond enthalpies are comparable to those of metal-ligand bonds and the formation of metal-ligand bonds may result in the cleavage of a metal-metal bond.[6] In the absence of bridging ligands to hold the two metal atoms together, fragmentation of dinuclear compounds is probable; such a fate rules out the possibility of investigating the influence of the adjacent metals on the reactivity. Shown below are two examples of addition reactions that result in the fragmentation of a dinuclear complex.[19]

$$[(PEt_3)_2(CO)Rh{-}Co(CO)_4] + MeCN \rightarrow [Rh(CO)(MeCN)(PEt_3)_2]^+ + [Co(CO)_4]^-$$

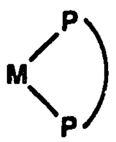
$$[(PEt_3)_2(CO)Rh{-}Co(CO)_4] + HCl \rightarrow \textit{trans}\text{-}[RhCl(CO)(PEt_3)_2] + [CoH(CO)_4]$$

To prevent fragmentation of dinuclear species, a large number of bridging ligands have been employed in efforts to hold metals together in the absence of metal-metal bonding. One common class of bridging groups are aryl or alkyl diphosphine ligands ($R_2P(CH_2)_nPR_2$), in which two phosphorus atoms are joined by one or more methylene units. These diphosphines bind to the metals through the phosphorus lone pairs functioning much like two monodentate phosphines.

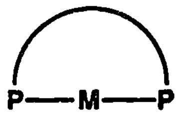
Generally aryl phosphines are more stable and more easily handled than alkyl phosphines.[20] For instance, triphenylphosphine, a ubiquitous ligand in mononuclear chemistry and an important ligand in the development of homogeneous catalysis by transition metal complexes,[20] is an air-stable solid whereas trimethylphosphine is a liquid which is inflammable in air. Likewise, dppm (bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$) is an air-stable solid while dmpm (bis(dimethylphosphino)methane, $Me_2PCH_2PMe_2$) is a pyrophoric liquid, a property which partially limits its application in terms of convenience. Therefore, the choice of aryl diphosphine instead of alkyl diphosphine is reasonable.

Diphosphine ligands, having the chemical formula $R_2P(CH_2)_nPR_2$, can assume a number of coordination modes from monodentate, to cis-chelating, to trans-chelating or bridging, depending on the length of the backbone (the number of methylene units) connecting the two phosphorus atoms as diagrammed below.[21-22, 29]

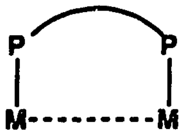
monodentate



cis-chelating



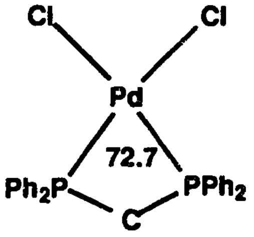
trans-chelating

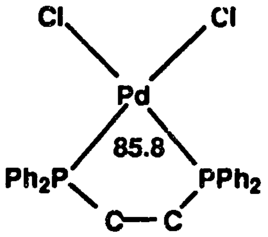


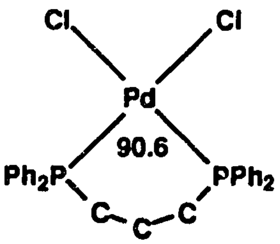
bridging

The coordinatively saturated complexes containing monodentate diphosphine(s) such as $M(CO)_5L$ (M=Cr, Mo, W; L=$Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Me_2P(CH_2)_2PMe_2$ (dmpe))[23a] can be achieved from ligand substitution reactions.[22] However a monodentate diphosphine ligand tends to chelate the metal center as a chelating ligand[23] due to the chelate effect,[24] or to bind another metal center as a bridging ligand (vide infra).

For dppm which has only one methylene unit, the trans chelating mode is clearly ruled out since the backbone is far too short to span trans-related phosphorus atoms; however the other modes are all observed. The bidentate chelating mode has substantial ring tension as shown by X-ray studies.[25] The observed P-M-P angles in the chelating compounds are substantially smaller than that expected from the ideal geometry. For example in $[Mo(CO)_4(dppm)]$ the P-M-P angle is 67.3°,[25d] which deviates significantly from the ideal bond angle in an octahedral geometry. In addition, the P-C-P angle (95.6(4)°) is significantly less than 109.5°, showing the strain within the $\overline{\text{M-P-C-P}}$ ring. Therefore the dppm ligand has a strong tendency to adopt the bridging mode instead of chelating, in which the angles are usually close to the idealized values. As the number of methylene units increases (n=2 to 4) the cis-chelating form becomes more favorable owing to the decrease in steric strain,[22] as demonstrated by the intraligand P-M-P angles in the series of compounds $[PdCl_2(Ph_2P(CH_2)_nPPh_2)]$ (n=1, 2 or 3),[25b] shown below.







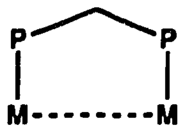
Parallelling the crystallographic studies, thermodynamic experiments show that the strain energy of [Cp*Ru(dppm)Cl] is 10 kcal/mol, whereas the strain energy with long-chain diphosphines such as in [Cp*Ru(dppe)Cl] (dppe=bis(diphenylphosphino)ethane, $Ph_2P(CH_2)_2PPh_2$) and [Cp*Ru(dppp)Cl] (dppp=bis(diphenylphosphino)propane, $Ph_2P(CH_2)_3PPh_2$) is close to zero.[26a] Further increasing the backbone length to four methylene units causes an increase in strain due to the large size of the diphosphine chelating ligand; therefore [Cp*Ru(dppb)-Cl] (dppb=bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$) has a small, but non-zero strain energy of 4.7 kcal/mol. Analogous results are observed in the series of compounds $[CpRu(Ph_2P(CH_2)_nPPh_2)Cl]$ [26b] and $[(Ph_2P(CH_2)_nPPh_2)Mo(CO)_4]$.[26c] Within the series of diphosphine compounds, $\{RhCl(CO)(Ph_2P(CH_2)_nPPh_2)\}_m$ (n=2, m=1; n=1, 3 and 4, m=2),[27] the dppe ligand was shown to have the strongest tendency to chelate a metal.

When the backbone lengths are further increased, these diphosphines can function either as bridging or trans-chelating ligands, since the large ring size is unfavorable for the cis-chelating mode.[22,28-29] The structurally characterized compounds [*cis,cis,trans*- $RuCl_2(CO)_2(Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2)$], having a trans-chelating diphosphine, and [*cis,cis,trans*- $RuCl_2(CO)_2(Ph_2P(CH_2CH_2O)_4$-$CH_2CH_2PPh_2)]_2$ in which the diphosphine is bridging, are interesting examples of compounds in which the diphosphine ligands have long backbone lengths.[30] In the latter case the metal-metal separation is 9.1961(9)Å–a separation that is so large that the metals are practically isolated from one another.[16] Among diphosphine ligands, dppm shows the desirable property of holding two metal centers in close proximity while still having a large degree of flexibility in the range of metal-metal distances that can be spanned (vide infra). This ligand has therefore attracted the most attention and has been the subject of several review articles.[15-16, 21-22, 31-33]

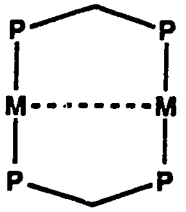
Unfavorable ring tension within a chelated dppm group has been used to advantage in the synthesis of bimetallic complexes in which the strained chelate ring readily opens allowing it to bridge to another metal atom. For example, the reaction of [RhCl(η^2-dppm)$_2$] with the [M(CO)$_5$]$^-$(M=Mn or Re) anions results in opening of the dppm chelate and coordination to Mn or Re to yield [RhM(CO)$_4$(dppm)$_2$] (M=Mn, Re) in which both dppm groups bridge the metals.[34] In addition, compounds having monodentate dppm ligands or mixed chelating and monodentate dppm ligands are also good candidates for the preparation of bimetallic compounds. Shaw and coworkers have carried out extensive studies in which they prepared heterobimetallic compounds by utilizing mononuclear compounds having chelating or monodentate dppm.[35] While dppm-bridged heterobimetallic compounds can be prepared by the method mentioned above, some dppm-bridged homobimetallic compounds are synthesized by the reaction of preformed dinuclear compounds with dppm.[33, 36(a,e,f,i,k,l,n)] An example is the reaction of [Mn$_2$(CO)$_{10}$] with dppm yielding the dppm-bridged compounds [Mn$_2$(CO)$_8$(dppm)] and [Mn$_2$(CO)$_6$(dppm)$_2$].[36a, 36o]

Dinuclear complexes can be bridged by one, two or three dppm ligands.[21, 31] The number of dinuclear complexes bridged by one dppm ligand (such as [Mn$_2$(CO)$_8$(dppm)][36a], [Re$_2$(CO)$_8$(dppm)][36e] and [Fe$_2$(CO)$_6$(μ-CO)(dppm)][36f]) is substantially fewer than that of those bridged by two dppm ligands, and dinuclear compounds with three bridging dppm ligands are extremely rare with the only reported compounds being [Pt$_2$(dppm)$_3$] and [Pd$_2$(dppm)$_3$].[37-38] The scarcity of this latter class may result from the unfavorable steric interactions between the bulky phenyl groups of the dppm ligands. The core geometries of dinuclear complexes bridged by one, two or three dppm ligand(s) are shown below, where the broken lines indicate that there may or may not be metal-metal bonds.

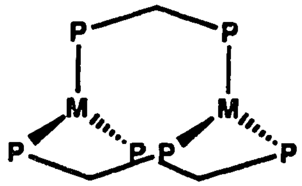
In addition to its ability to bridge two metal centers in close proximity, dppm is flexible enough to allow it to span a wide range in metal-metal separations (from 2.4 to 3.6Å).[16] This flexibility allows the cleavage or formation of metal-metal bonds which often occur in reactions involving dinuclear compounds. For example the insertion of hexafluoro-2-butyne into the metal-metal bond of [$Pd_2Cl_2(dppm)_2$] yields a parallel-bridged alkyne compound, [$Pd_2Cl_2(\mu\text{-}CF_3CCCF_3)(dppm)_2$], accompanied by an increase in the metal-metal separation from 2.651(1)Å to 3.492(1)Å [39,40]. In contrast to the dppm ligand, the closely related, bridging ligand 2(diphenylphosphino)pyridine has quite limited flexibility, and the metal-metal separation in the bis(2(diphenylphosphino)pyridine)-bridged dinuclear compounds lies in the very narrow range between 2.5 to 2.7Å. This lack of flexibility may confine the reactivities of these dinuclear compounds to reactions which maintain metal-metal bonds upon coordination of substrates.[16]



mono

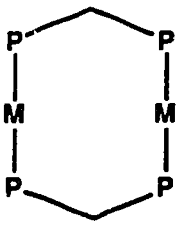


bis

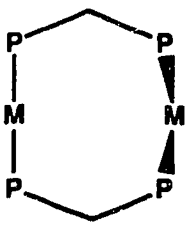


tris

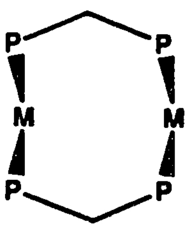
When two diphosphine ligands bridge two metals they are usually trans to each other at both metals, as shown in the first reported dppm-bridged dinuclear compound, [$RhCl(CO)(dppm)]_2$.[41,42] In this orientation the trans alignment can minimize any unfavorable steric interactions between bulky phenyl substituents. However, a number of compounds in which the two phosphorus atoms are trans on one metal and cis on the other are observed,[43] and a few compounds are also known in which diphosphines occupy cis positions at both metals.[44]



trans, trans



trans, cis

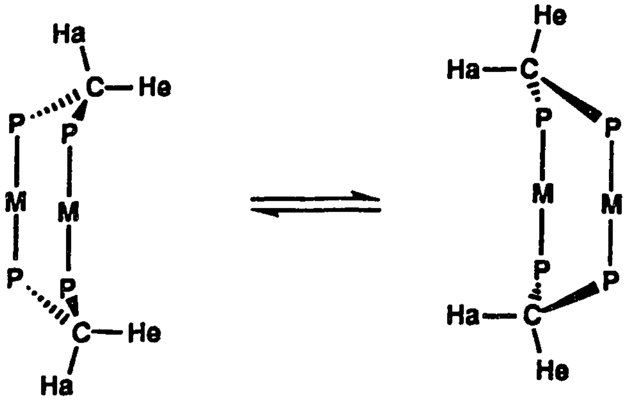


cis, cis

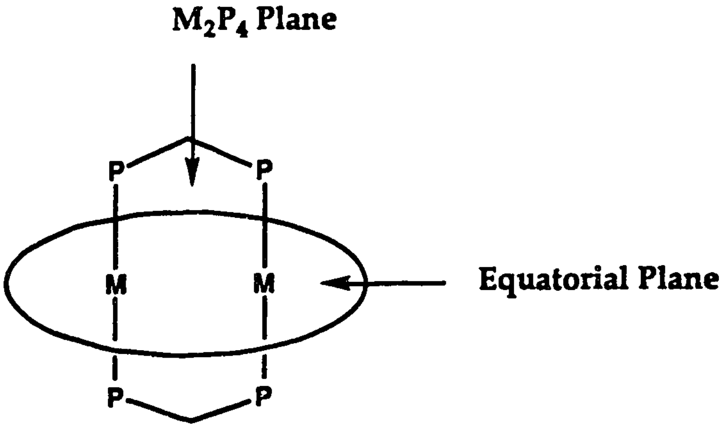
Interestingly all three geometries are seen in a series of closely related diplatinum methyl compounds, *cis,cis*-$Pt_2Me_4(dppm)_2$] [44c], *cis,trans*-[$Pt_2Me_3(dppm)_2$][PF_6] [43d,43e] and *trans,trans*-[$Pt_2I_2Me_2(dppm)_2$].[45]

NMR spectroscopy is of great value in the characterization of diphosphine-bridged dinuclear complexes.[16] In compounds having a trans, trans geometry, the equatorial plane has mirror symmetry, leading to a 'top-bottom' equivalence of the chemical environment of the phosphorus atoms, so analysis of the NMR spectra is quite straightforward. If, in addition, both metals have equivalent chemical environments, then only one phosphorus signal is expected in the ^{31}P NMR spectrum. Furthermore, if the complex has 'front-back' symmetry, in other words if the environment on each side of the M_2P_4 plane is equivalent, then the axial and equatorial hydrogens on the CH_2 groups can readily exchange as shown below, so only one methylene proton signal is observed in the ^1H NMR spectrum.

When the chemical environment on the two sides of the M_2P_4 frame is such that there is front-back asymmetry, such as is observed in A-frame compounds, two methylene proton signals are observed for the dppm ligands in the ^{1}H NMR spectrum, although one signal would still arise in the ^{31}P NMR spectrum.



In the case of heterobimetallic compounds two signals are usually observed in their ^{31}P NMR spectra, since the chemical environments of the two metal centers are not the same. As in homobinuclear complexes the number of methylene proton signals in their ^{1}H NMR spectra can be used to judge the symmetry on either side of $MM'P_4$ plane. In all the situations mentioned above, precautions should be taken since an accidental equivalence of the methylene protons can give rise to only one signal in the ^{1}H NMR spectrum instead of the expected two.



Occasionally the equatorial plane of the dppm-bridged compounds loses mirror symmetry due to the nature of the equatorial ligands. For example in $[Pt_2H_2(\mu\text{-}SMe)(dppm)_2][PF_6]$, the methyl group can be oriented either above or below the equatorial plane owing to the trigonal pyramidal geometry at sulfur.[46] Although inversion at sulfur can equilibrate the phosphorus nuclei at elevated temperature, the low-temperature limiting spectrum would be expected to reflect the top-bottom asymmetry.

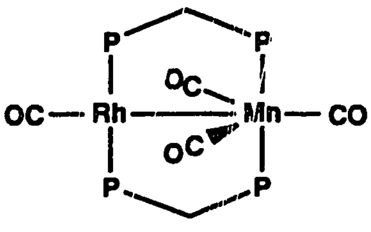
Since the $MM'P_4$ (or M_2P_4) plane and the equatorial plane in many dinuclear compounds are orthogonal, ligands such as hydrides and carbonyls in the equatorial plane show cis-coupling to the phosphorus nuclei in the $MM'P_4$ (or M_2P_4) plane. For example, a bridging hydride should display coupling to all four phosphorus nuclei whereas a terminal one would usually only couple to the adjacent pair of phosphorus atoms. From the coupling patterns and from selective decoupling experiment ($^1H\{^{31}P\}$) one can determine not only the binding mode of a hydride (i.e. terminal or bridging) but also the metal to which a terminal hydride is bound. The same principles can be applied to the determination of the positions of carbonyl or hydrocarbyl ligands by $^{13}C\{^1H\}$NMR and by selective heteronuclear decoupling experiments ($^{13}C\{^1H\}\{^{31}P\}$) (usually in these experiments ^{13}C-enriched carbonyl or hydrocarbyl samples are used).

The coupling constants obtained from the NMR spectra also yield valuable information about the coordination geometry of dinuclear compounds. This can be exemplified by the coupling constants between rhodium and the carbonyl carbon in Rh_2 or RhM complexes (M=Mn, Re, Os and Ir). Generally, a terminal carbonyl bound to Rh shows a rhodium-carbon coupling constant ($^1J_{RhC}$) of 50-80 Hz, whereas a typical bridging carbonyl has an intermediate coupling constant of ca. 35 Hz.[47] In the case of a semibridging carbonyl, which is primarily bound to the adjacent metal while interacting weakly with Rh, coupling to Rh is observed, which is less than that expected for a symmetrically bridged carbonyl, typically giving $^1J_{RhC}$ values of less than 20 Hz.[48]

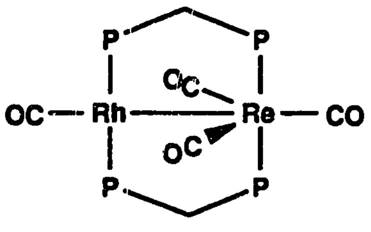
The coupling constants between ^{13}C-enriched carbonyls in the equatorial plane can be used to establish their relative positions. The trans coupling constant ($^2J_{C(M)C}$) of two carbonyl ligands bound to the same metal is greater than the cis coupling constant. For example, the trans and cis coupling constants in the complex $[RhRe(CO)_4(\mu\text{-}RC{\equiv}CR)(dppm)_2]$ (R=COOMe) are 21 Hz and 4 Hz respectively.[48] The same principle can be applied to determine the relative positions of hydrides and ^{13}C-enriched hydrocarbyl ligands.

IR spectroscopy plays an important role in the determination of coordination modes of carbonyl ligands in dinuclear complexes. A terminal carbonyl absorbs at a higher frequency (2125-1850cm^{-1}).[49] For example, $[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2][BPh_4]$ shows carbonyl stretches at 2006 and 1992 cm^{-1} in CH_2Cl_2 solution.[50] A bridging carbonyl on the other hand typically absorbs at lower frequency (1860-1700 cm^{-1}).[49] For example, $[Rh_2Cl_2(\mu\text{-}CO)(dppm)_2]$ shows a carbonyl stretch at 1764 cm^{-1} in CH_2Cl_2 solution.[51] The range of bridging carbonyl absorptions given above is generally valid for the carbonyls which donate two electrons. However in the compound $[Mn_2(CO)_4(\mu\text{-}CO)(dppm)_2]$, one carbonyl absorbs at an unusually low frequency (1648 cm^{-1}) while the other four absorb in the normal terminal carbonyl region;[52] the low frequency stretch is rationalized as resulting from a σ,π bridging carbonyl which donates four electrons to the two metal centers, a suggestion that is confirmed by the X-ray determination of the compound.[53]

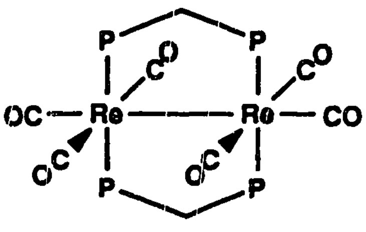
In the first part of this thesis the reactivity of the heterobinuclear complex $[RhMn(CO)_4(dppm)_2]$ (**B**) is probed, with ideas of establishing how the first row metal might influence the chemistry at Rh.[48] In previous studies the reactivity of the closely related species [RhRe(CO)$_4$(dppm)$_2$] (C),^{48,54} with nucleophiles such as sulfur-containing substrates and alkynes, was investigated. In contrast to the coordinatively saturated compound [Re$_2$(CO)$_6$(dppm)$_2$], which exhibits much lower reactivity to substrates, requiring ejection of one carbonyl ligand before the reaction can occur, either through thermolysis or photolysis,^{55} complex C shows high reactivity toward nucleophiles. The high reactivity of complex C stems from



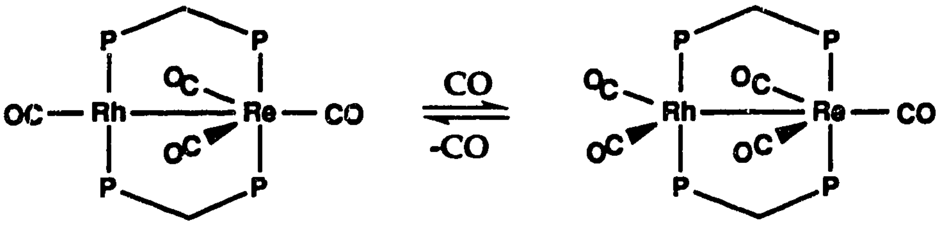
(B)



(C)



the coordinatively unsaturated 16-electron rhodium center, which is susceptible to nucleophilic attack and is capable of inducing chemistry at the adjacent rhenium center.^{48} This can be illustrated by CO addition to complex C to give the pentacarbonyl species [RhRe(CO)$_5$(dppm)$_2$] ^{48} as shown in the following equation.



(C)

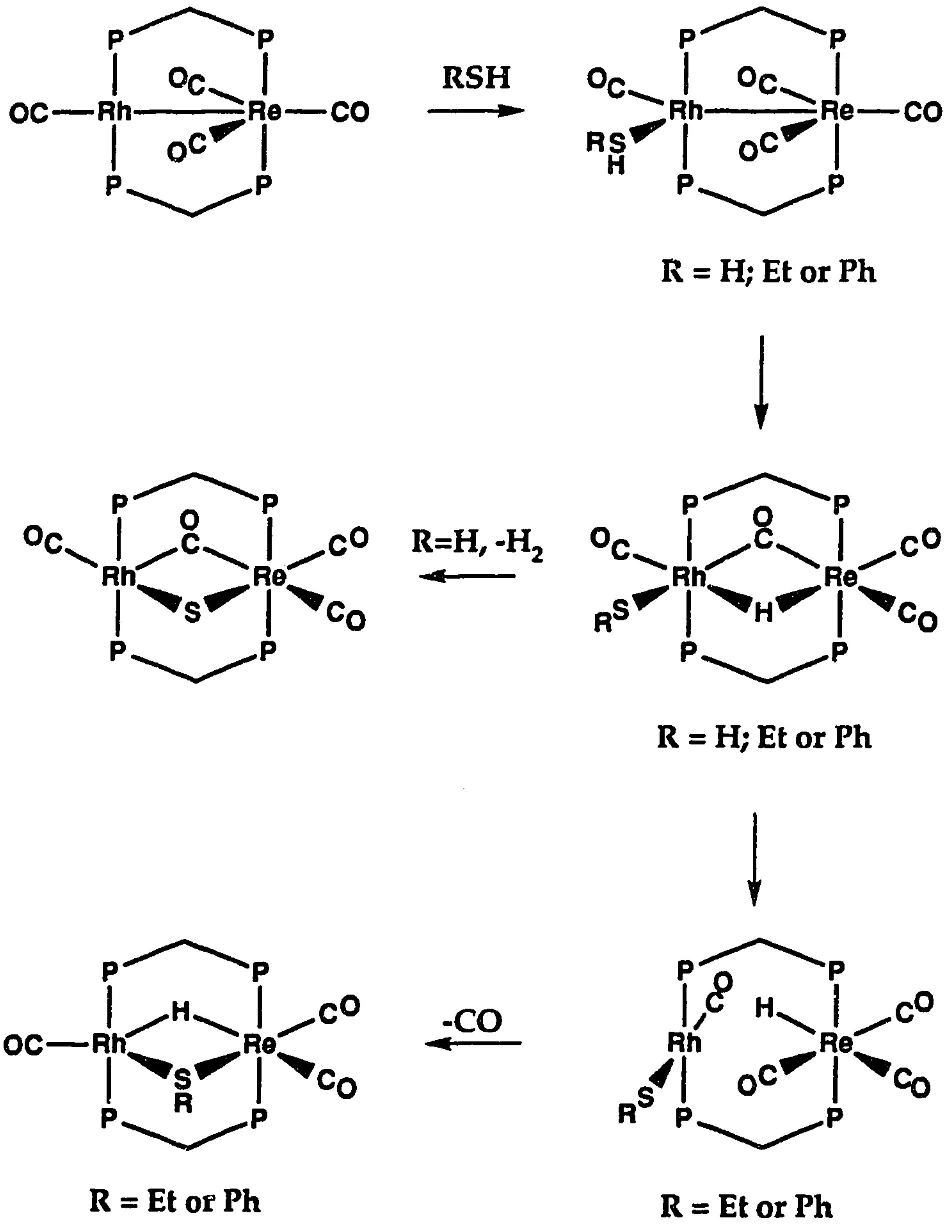
The pentacarbonyl species undergoes facile CO scrambling as indicated by ^{13}CO enrichment monitored by ^{13}C{^{1}H}NMR spectroscopy. It can be visualized that other nucleophiles would initially coordinate to rhodium, although subsequent migration to the bridging position or to the adjacent rhenium center is then possible. Due to the structural similarities between complex **B** and **C**,[34] it was expected that the coordinatively unsaturated Rh centers in complex **B** would also induce chemistry at its adjacent Mn center.

Since manganese and rhenium are congeneric, some similarity in reactivity between complex **B** and **C** was anticipated. On the other hand, manganese and rhenium are first and third row transition metals, respectively, therefore differences in reactivity [56] are to be expected. Complexes **B** and **C** have been structurally characterized by X-ray techniques.[34] In both cases Rh has a distorted square-planar coordination, while the Re and Mn centers have trigonal-bypyramidal arrangements. These geometries suggest that the $[M(CO)_3L_2]^-$ (M=Re, Mn) moieties function as anionic groups which donate one pair of electrons to Rh(+1) centers.[34] Surprisingly, in these two compounds the Rh-Re bond length of 2.7919(6)Å is shorter than that of Rh-Mn (2.8428(8)Å) in spite of the opposite trend in covalent radii of Mn and Re,[34] indicating a stronger Rh-Re bond. It was rationalized that the basicity of the $[Re(CO)_3L_2]^-$ fragment is stronger than that of $[Mn(CO)_3L_2]^-$, based on the relative basicities of the $[M(CO)_5]^-$ (M=Re, Mn) anions,[34] and this variance may result in different reactivities of the RhRe and the RhMn complexes.

The first goal of this thesis was to study the reactions of complex **B** with H_2S and thiols. The reactions of some bimetallic complexes with sulfur-containing substrates have been investigated by our group.[54,57] As a continuation of our previous chemistry of the RhRe complex with sulfur-containing substrates, we investigated the analogous chemistry with the RhMn analogue. The activation of the highly polarized S-H bonds in H_2S or thiols by metal complexes can occur by oxidative-addition at the coordinatively unsaturated metal centers. Mononuclear complexes containing four-coordinate d^8 metal centers such as $[RhCl(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$ can usually activate only one S-H bond in H_2S, possibly because the +3 oxidation state in the first oxidation products makes further oxidation unfavorable.[58] However, in the presence of an adjacent metal center the activation of the second S-H bond in H_2S or two S-H bonds in two thiols by a binuclear complex is possible, since both metals can be oxidized. The two metals not only provide more coordination sites for the incoming substrates and subsequent oxidative-addition fragments than does a mononuclear complex, but they also minimize the oxidation-state change required at any one metal. Unlike binuclear complexes containing two coordinatively unsaturated metals, heterobinuclear complexes such as **C** have only one reactive site (Rh) due to the strong tendency for Re to maintain coordinative saturation.[54] Nevertheless, the activation of <u>both</u> S-H bond in H_2S readily occurs to give a sulfido-bridged complex as shown in Scheme 1.2.[54] The ligand rearrangements involving the two metals apparently play an important role in the second S-H bond activation although Re appears not to directly participate in the oxidation-addition reaction. By ligand rearrangements and metal-metal bond cleavage the coordinative unsaturation at Rh can be regenerated making the activation of the second S-H bond by this metal possible.

Previous studies in our research group also showed the initial formation of HSR adducts (R=H, Et and Ph) at low temperature which transform to unstable intermediates containing terminal SR groups.[54] For H_2S, the presumed oxidative-addition of a second S-H bond is followed by the elimination of H_2, yielding $[RhRe(CO)_4(\mu\text{-}S)(dppm)_2]$ while in the case of thiols an important intermediate, which shows the regeneration of the reactive Rh(+1) center, is detected before the formation of the thiolato-bridged product $[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SR)(dppm)_2]$. It was

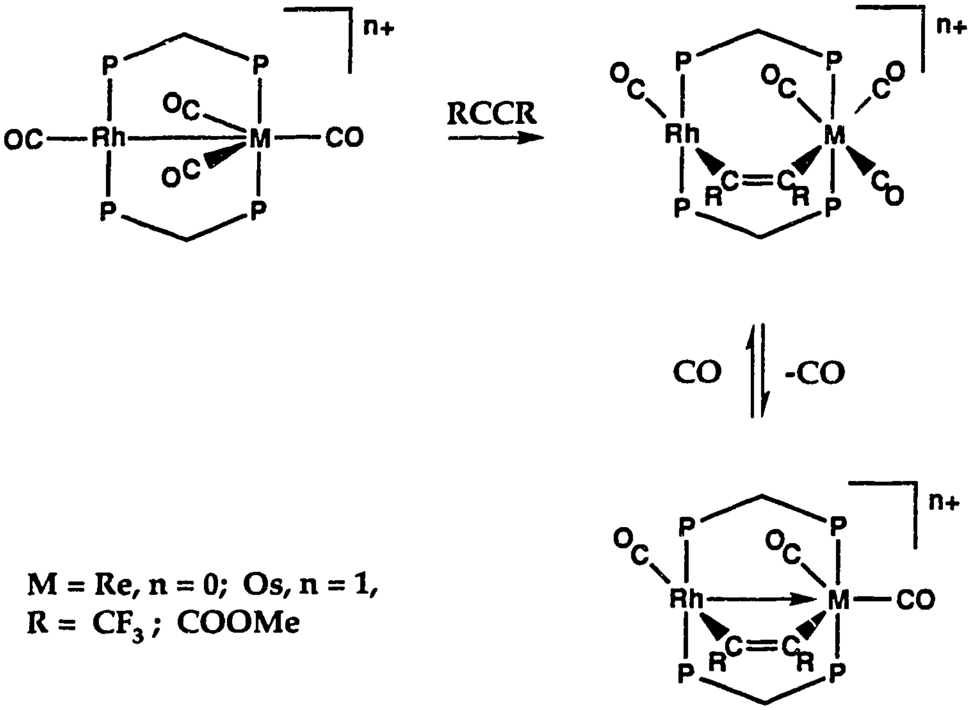
Scheme 1.2



noted that these intermediates having terminal sulfhydryl or terminal thiolate ligands are unstable and are detected only at low temperature. It was anticipated that substitution of Re by the lighter congener, Mn, might have a significant effect on the chemistry, yielding some intermediates that were not observed in the RhRe chemistry.

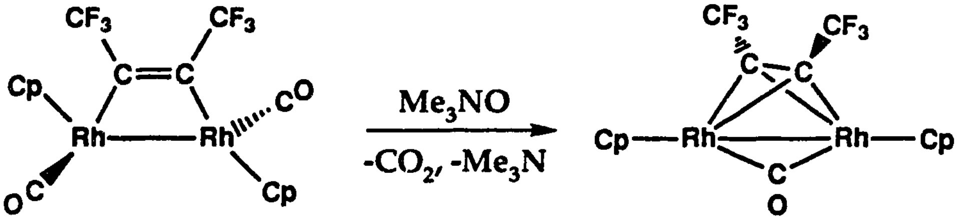
The second goal of this thesis was to investigate the reactivity of complex **B** with alkynes and to monitor the alkyne transformations that might occur at RhMn centers. The reactivities of dinuclear complexes with alkynes have been extensively investigated by our research group[48, 59-66] and others.[67-69] In the reactions of complex C[48] and the isoelectronic compound, $[RhOs(CO)_4(dppm)_2][BF_4]$,[61] with internal alkynes such as HFB ($F_3CC{\equiv}CCF_3$) and DMAD ($MeOC(O)C{\equiv}CC(O)OMe$) the products $[RhM(CO)_3(\mu\text{-}RC{\equiv}CR)(\mu\text{-}CO)(dppm)_2]^{n+}$ ($R=CF_3$ or COOMe; M=Re, n=0; M=Os, n=1) were obtained as shown in Scheme 1.3. In these, the alkyne is bound in a bridging position parallel to the metal-metal axis, and can be considered as a cis-dimetalated olefin. These compounds can be converted to $[RhM(CO)_3(\mu\text{-}RC{\equiv}CR)(dppm)_2]^{n+}$ upon CO loss. The coordinative unsaturation created at the Re or Os center as a result of carbonyl loss can in principle be remedied by the rotation of the alkyne [68, 69] to the perpendicular orientation with respect to the metal-metal vector, transforming the two-electron-donor alkyne to a four-electron-donor ligand. An example of alkyne rotation on dirhodium centers involving CO loss is shown in Scheme 1.4.[68] However, in the RhRe and RhOs compounds the coordinative unsaturation at Re or Os is remedied instead by the formation of a dative bond from the Rh center to the adjacent metal, with the alkynes maintaining their parallel coordination, as shown by the crystal structure of $[RhOs(CO)_3(\mu\text{-}RC{\equiv}CR)(dppm)_2][BF_4]$ (R=COOMe).[61] It was anticipated that, by changing from Re to its lighter congener Mn, differences in the nature of Rh-M interactions may give rise to subtle differences in the natures of the alkyne adducts.

Scheme 1. 3



M = Re, n = 0; Os, n = 1,
R = CF_3 ; COOMe

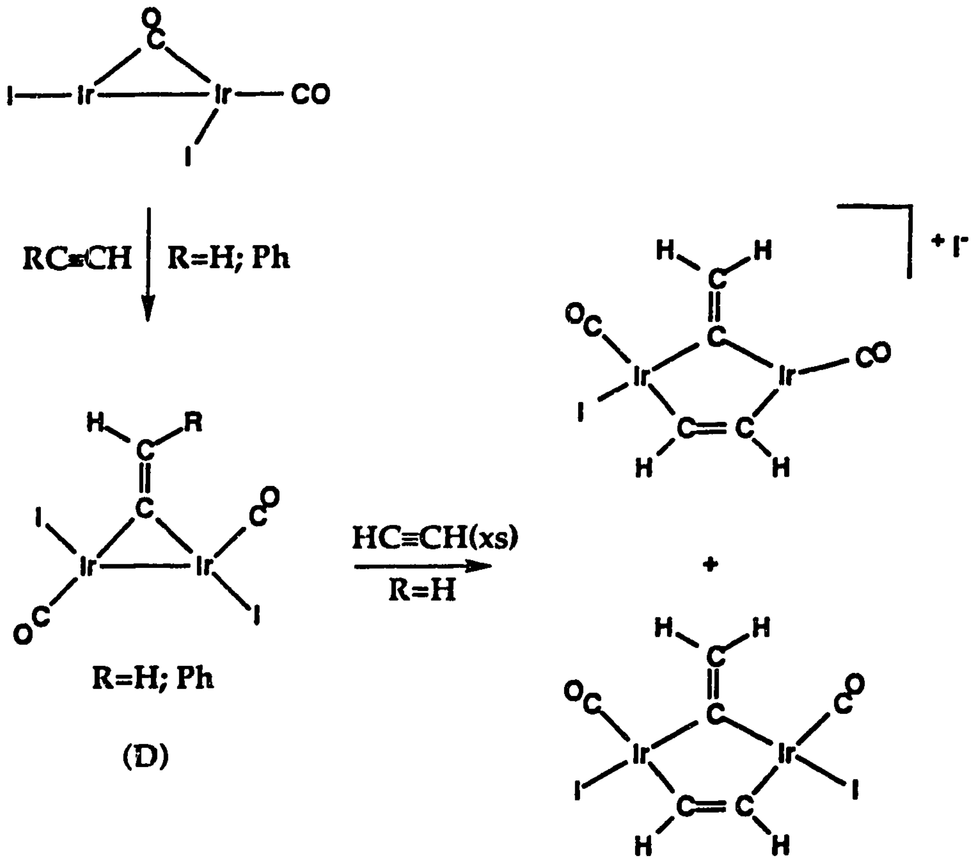
Scheme 1. 4



The insertion of alkynes into a metal-hydrogen bond to form vinyl complexes is a fundamental process in organometallic chemistry [70] and has been observed in our research group[62, 71-73] and others.[74,75] The earlier studies in our group have shown that protonation of alkyne-bridged complexes $[Rh_2(CO)_2(\mu\text{-}RC{\equiv}CR)(dmpm)_2]$ (R=CF_3, COOMe) give either the unstable hydrido- and alkyne-bridged complex $[Rh_2(CO)_2(\mu\text{-}RCCR)(\mu\text{-}H)(dmpm)_2][BF_4]$ (R=COOMe) or the unstable vinyl-bridged compound $[Rh_2(CO)_2(\mu\text{-}RC{=}CHR)(dmpm)_2][BF_4]$ (R=CF_3).[62] On obtaining the RhMn alkyne compounds (having dppm instead of dmpm), it was of interest to study their reactivity towards protonation. It was hoped that in the study of these protonation reactions the transformation from hydrido-alkyne complexes to vinyl compounds, as has been demonstrated by Stone's group on diplatinum complexes,[75] would be observed.

Studies involving the formation of vinylidene ligands upon the reaction of dinuclear complexes with acetylene or other 1-alkynes are a recent interest in our research group.[76,77] Vinylidene complexes can be prepared from 1-alkynes via a 1,2-hydrogen shift mediated by the metals.[78] Previous studies in our group had shown that the reactions of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ with acetylene or phenylacetylene readily generated the vinylidene-bridged complexes $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ (R=H, Ph) as shown in Scheme 1.5 and these compounds were structurally characterized by crystallographic techniques.[76] In light of these studies it was of interest to prepare heterobimetallic complexes containing vinylidene ligands, and to investigate their reactivity with electrophiles such as H^+ and CH_3^+. It was of particular interest to determine the site(s) of electrophilic attack, whether at the metals or at the α- or β-carbon of the vinylidene groups.

Scheme 1.5



Note: bridging dppm ligands, above and below the plane of the drawing, are omitted for the sake of clarity.

The last goal of this thesis was to study the vinylidene complexes of diiridium, completing a study that had previously been undertaken.[76] The earlier work had shown that the vinylidene-bridged complex $[Ir_2(I)_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2]$ (**D**) reacts with excess acetylene to produce complexes proposed to be the vinylidene- and alkyne-bridged, $[Ir_2(I)_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HCCH)(dppm)_2]$ and $[Ir_2I(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HCCH)(dppm)_2][I]$, as shown in Scheme 1.5.[76] Since compound **D** is coordinatively saturated, it was suggested that reaction with a second alkyne molecule was preceded by iodide loss, generating a coordinatively unsaturated cationic complex $[Ir_2I(CO)_2(\mu\text{-}CCH_2)(dppm)_2][I]$ (**E**). Two approaches into these cationic vinylidene species were considered: first via reaction of the cationic A-frame compound, $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$, with terminal alkynes; second by iodide removal from the neutral diiodo, vinylidene-bridged species **D** and its phenylvinylidene analogue $[Ir_2(I)_2(CO)_2(\mu\text{-}CC(H)Ph)(dppm)_2]$. Reaction of the resulting cationic vinylidene-bridged products with small unsaturated molecules (including terminal alkynes) was then undertaken in order to investigate the reactivity of vinylidene-bridged complexes. In addition to the alkyne- and vinylidene-bridged products proposed, it also seemed that formation of bis-vinylidene species should be possible.

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Chapter 2

S-H Bond Activation in H_2S and Thiols at RhMn Centers

Introduction

Low-valent binuclear complexes are, in principle, well suited to "double-oxidative-addition" reactions, in which two bonds, either within a single substrate or in two separate substrates, are activated by the two adjacent metals. Not only do the two metals present more available coordination sites for the oxidative-addition fragments than does a mononuclear species, but they also minimize the oxidation-state change that is required at any one metal, and present a greater electron reservoir for reduction of the substrate or substrates.

As part of an ongoing study of binuclear oxidative-addition reactions we have been investigating the activation of X-H bonds in substrates of the type H_2X or HXR (X = SiR_2, SiHR, S).[1-4] Examples of both types of double-oxidative additions have been observed for these substrates in which both activated bonds are within one substrate,[1-6] or are in two separate substrates.[3,7] In addition, the potential for utilizing both metal centers is uniquely demonstrated in a dirhodium system in which double-oxidative addition of a primary silane, followed by H_2 elimination, allows the metals to add a second silyl fragment.[5]

Our interest in the chemistry of H_2S lies in its potential utilization in hydrogen recovery,[8] in the chemistry of the sulfhydryl group generated therefrom, which has applications in the synthesis of sulfur-containing organic groups,[9] and in studies of model systems for hydrodesulfurization catalysts.[10] Binuclear systems have already demonstrated their potential applicability in H_2 recovery as shown by James and coworkers[11] in studies in which dipalladium complexes stoichiometrically generated H_2 from H_2S. Related studies in our group on dirhodium,[3] diiridium,[3] and mixed systems involving Rh with either Re,[2] Ru[4] or Os[4] gave similar results. In the Rh/Re system it had been possible to characterize several key intermediates in the H-S bond-activation processes;[2] however, some presumed intermediates were not observed. It was anticipated that substitution of Re by the lighter congener, Mn, may have a significant effect on the chemistry, yielding species, for which the Re analogues were not observed. In this paper we present our results on the oxidative addition of H_2S and thiols to $[RhMn(CO)_4(dppm)_2]$.

Experimental Section

General Procedures. Purified argon and carbon monoxide were obtained from Linde and hydrogen sulfide from Matheson. The 99% carbon-13-enriched carbon monoxide was purchased from Isotec Inc. All gases were used as received. Diethylether and hexane were dried over Na-benzophenone ketyl, whereas CH_2Cl_2 was dried over P_2O_5; all solvents were distilled under argon before use. The perdeuterated methylene chloride was dried over molecular sieves and deoxygenated by repeated freeze-pump-thaw cycles. The compounds, ethanethiol, benzenethiol, tetrafluoroboric acid–diethyl etherate, triflic acid, methyl triflate, trimethylsilylmethyl triflate, dimethyl acetylenedicarboxylate and 3-butyn-2-one, were used as received from Aldrich, elemental sulfur was purchased from Sargent-Welch and hexafluoro-2-butyne from PCR Inc. Reactions were routinely conducted under Schlenk conditions. Hydrated rhodium trichloride was purchased from Johnson Matthey and $Mn_2(CO)_{10}$ from Strem Chemicals Inc. Compound **1**, $[RhMn(CO)_4(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$), was prepared as previously reported.[12]

All routine NMR experiments were conducted on a Bruker AM-400 Spectrometer, whereas the $^{13}C\{^{31}P\}$ NMR experiments were conducted on a Bruker AM-200 spectrometer. For all NMR experiments CD_2Cl_2 was used as solvent. The PANIC program, supplied by Bruker, was used to simulate the $^{31}P\{^1H\}$ NMR spectra of selected compounds. IR spectra were recorded either on a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer as solids (Nujol mull or CH_2Cl_2 cast) or CH_2Cl_2 solutions. Elemental analyses were performed by the microanalytical service within the department. The spectral data for all compounds are given in Table 2.1. All compounds were moderately air sensitive in solution so were

Table 2.1. Spectroscopic Data for the Compounds.[a]

Compound	IR, cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
$RhMn(SH)(CO)_2(\mu\text{-}CO)(\mu\text{-}H)(dppm)_2$ (2)	1940 (s),[b] 1871 (s), 1840 (sh), 1751 (m) 1938 (s),[c] 1868 (s), 1757 (m)	69.3 (m),[d] 30.9 (dm, $^1J_{RhP}$ = 124 Hz)	3.39 (m, 2H),[e] 3.03 (m, 2H), -0.31 (dt, $^2J_{RhH}$ = 2 Hz, $^3J_{P(Rh)H}$ = 16 Hz, 1H), -14.03 (dtt, $^1J_{RhH}$ = 26 Hz, $^2J_{P(Rh)H}$ = $^2J_{P(Mn)H}$ = 13 Hz, 1H)	260.9 (dt, $^1J_{RhC}$ = 17 Hz, $^2J_{P(Mn)C}$ = 17 Hz, 1C),[d] 227.2 (t, $^2J_{P(Mn)C}$ = 21 Hz, 1C), 226.7 (t, $^2J_{P(Mn)H}$ = 23 Hz, 1C)
$RhMn(SEt)(CO)_2(\mu\text{-}CO)(\mu\text{-}H)(dppm)_2$ (3)	1935 (s),[c] 1865 (s), 1760 (m)	69.8 (m),[e] 27.6 (dm, $^1J_{RhP}$ = 134 Hz)	3.44 (m, 2H),[e] 2.94 (m, 2H), -14.13 (dtt, $^1J_{RhH}$ = 22 Hz, $^2J_{P(Rh)H}$ = 11 Hz, $^2J_{P(Mn)H}$ = 12 Hz, 1H)	260.4 (bd, $^1J_{RhC}$ = 14 Hz, 1C), 227.7 (b, 2C)[e]

Table 2.1. (continued)

Compound	IR, cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
$RhMn(SPh)(CO)_2(\mu\text{-}CO)(\mu\text{-}H)(dppm)_2$ **(4)**	1932 (s),[b] 1861 (s), 1764 (s) 1934 (vs),[c] 1861 (s), 1759 (m)	69.3 (m),[f] 25.8 (dm, $^1J_{RhP}$ = 144 Hz)	3.32 (m, 2H),[f] 3.02 (m, 2H), -14.88 (dtt, $^1J_{RhH}$ = 23 Hz, $^2J_{P(Rh)H}$ = 12 Hz, $^2J_{P(Mn)H}$ = 12 Hz, 1H)	259.3 (dt, $^1J_{RhC}$ = 17 Hz, $^1J_{P(Mn)C}$ = 23 Hz, 1C),[f] 227.4 (t, $^2J_{P(Mn)C}$ = 20 Hz, 1C), 226.7 (t, $^2J_{P(Mn)C}$ = 25 Hz, 1C)
$RhMn(CO)_5(dppm)_2$ **(5)**		73.5 (m),[d] 29.5 (dm, $^1J_{RhP}$ = 99 Hz)	4.16 (b, 4H)[d]	241.7 (b, 2C),[d] 228.4 (b, 1C), 200.3 (vb, 2C)
$RhMn(SPh)(CO)_4(\mu\text{-}H)(dppm)_2$ **(6)**		61.0 (m),[f] 30.3 (dm, $^1J_{RhP}$ = 107 Hz)	4.71 (m, 2H),[f] 3.81 (m, 2H), -12.20 (td, $^2J_{P(Mn)H}$ = 20 Hz, $^1J_{RhH}$ = 5 Hz, 1H)	229.0 (b,1C),[d] 222.3 (b, 1C), 219.8 (t, $^2J_{P(Mn)C}$ = 21 Hz, 1C), 200.9 (dt, $^1J_{RhC}$ = 78 Hz, $^2J_{P(Rh)C}$ = 15 Hz, 1C)

Table 2.1. (continued)

Compound	IR, cm^{-1}	NMR		
		$\delta(^{31}P\{^{1}H\})$	$\delta(^{1}H)$	$\delta(^{13}C)$
$RhMn(CO)_4(\mu\text{-}S)(dppm)_2$ (**7**)	1984 (m),^{b}	57.4 (m),^{f}	4.60 (m, 2H),^{f}	239.1 (dt, $^{1}J_{RhC}$ =
	1962 (s),	25.6 (dm,	2.48 (m, 2H)	8 Hz, $^{2}J_{P(Mn)C}$ =
	1866 (s),	$^{1}J_{RhP}$ = 136 Hz)		14 Hz, 1C),^{g}
	1796 (m)			225.3 (t, $^{2}J_{P(Mn)C}$ =
				20 Hz, 1C),
	1980 (sh),^{c}			222.2 (t, $^{2}J_{P(Mn)C}$ =
	1955 (vs),			18 Hz, 1C),
	1876 (s),			192.8 (dt, $^{1}J_{RhC}$ =
	1799 (m)			69 Hz, $^{2}J_{P(Rh)C}$ =
				19 Hz, 1C)
$[RhMn(CO)_4(\mu\text{-}SH)(dppm)_2][BF_4]$	2004 (w),^{b}	55.2 (m, 1P),^{d}	3.82 (m, 2H),^{d}	224.4 (b, 1C),^{d}
(**8a**)	1987 (vs),	51.2 (m, 1P),	3.69 (m, 1H),	219.3 (b, 1C),
	1934 (s),	$^{2}J_{P(Mn)P}$ = 38 Hz	3.23 (m, 1H),	216.2 (b, 1C),
	1858 (m)	28.0 (dm, 1P	-2.67 (tt, 1H,	190.4 (dt, 1C
	2021 (sh),^{c}	$^{1}J_{RhP}$ = 115 Hz),	$^{3}J_{P(Mn)H}$ = 11 Hz,	$^{1}J_{RhC}$ = 74 Hz,
	1990 (vs),	18.8 (dm, 1P	$^{3}J_{P(Rh)H}$ = 13 Hz)	$^{2}J_{P(Rh)C}$ = 13 Hz)
	1932 (s),	$^{1}J_{RhP}$ = 112 Hz)	3.92 (b, 2H),^{e}	
	1845 (w)	$^{2}J_{P(Rh)P}$ = 302 Hz	3.52 (b, 2H),	
			-2.50 (tt, 1H)	

Table 2.1. (continued)

Compound	IR, cm^{-1}	NMR		
		$\delta(^{31}P\{^{1}H\})$	$\delta(^{1}H)$	$\delta(^{13}C)$
[RhMn(CO)$_4$(μ-SH)(dppm)$_2$][SO$_3$CF$_3$]	2008 (w),[b]	55.2 (m, 1P),[d]	3.81 (m, 2H),[d]	
(8b)	1986 (vs),	51.2 (m, 1P),	3.68 (m, 1H),	
	1936 (s),	28.1 (dm, 1P,	3.23 (m, 1H),	
	1864 (m)	$^{1}J_{RhP}$ = 115 Hz),	-2.66 (tt, 1H),	
	2020 (sh),[c]	18.7 (dm, 1P,	$^{3}J_{P(Mn)H}$ = 11 Hz,	
	1992 (vs),	$^{1}J_{RhP}$ = 112 Hz)	$^{3}J_{P(Mn)H}$ = 13 Hz	
	1933 (s),			
	1845 (w)			
[RhMn(CO)$_4$(μ-SMe)(dppm)$_2$]-	2003 (w),[b]	56.8 (m),[e]	3.68 (m, 2H),[e]	226.9 (b),[c]
[SO$_3$CF$_3$] **(9)**	1974 (vs),	26.8 (dm,	3.25 (m, 2H),	224.0 (b), 216.7 (b),
	1917 (s),	$^{1}J_{RhP}$ = 116 Hz)	1.68 (b, 3H)	189.8 (dt, $^{1}J_{RhC}$ =
	1826 (m)	61.6 (m, 1P),[d]		71Hz, $^{2}J_{P(Rh)C}$=16Hz
		53.4 (m, .P),	3.87 (m, 1H),[d]	227.6 (t, 1C,
	2020 (sh),[c]	$^{2}J_{P(Mn)P}$ = 43 Hz	3.55 (m, 1H),	$^{2}J_{P(Mn)C}$ = 18 Hz),[d]
	1991 (vs),	33.1 (dm, 1P,	3.12 (m, 1H),	223.2 (t, 1C,
	1914 (s),	$^{1}J_{RhP}$ = 119 Hz),	2.78 (m, 1H),	$^{2}J_{P(Mn)C}$ = 18 Hz),
	1837 (w)	23.8 (dm,	1.68 (s, 3H)	216.5 (b, 1C),
		1P, $^{1}J_{RhP}$=113 Hz)		189.2 (dt, 1C
		$^{2}J_{P(Rh)P}$ = 296Hz		$^{1}J_{RhC}$ = 71 Hz
				$^{2}J_{P(Rh)C}$ = 16 Hz)

Table 2.1. (continued)

Compound	IR, cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
$[RhMn(CO)_4(\mu\text{-}SCH_2SiMe_3)(dppm)_2]$-	2021 (m),[b]	63.0 (m, 1P),[d]	4.11 (m, 1H),[d]	229.3 (b, 1C),[d]
$[SO_3CF_3]$ **(10)**	1997 (vs),	52.2 (m, 1P),	3.47 (m, 1H),	223.7 (b, 1C),
	1917 (s),	$^2J_{P(Mn)P}$ = 42 Hz	3.24 (m, 1H),	217.1 (b, 1C),
	1830 (m)	36.8 (dm, 1P,	2.77 (m, 1H),	189.0 (dt, 1C,
		$^1J_{RhP}$ = 119 Hz),	0.98 (m, 1H),	$^1J_{RhC}$ = 71 Hz,
	2025 (sh),[c]	20.2 (dm, 1P,	0.67 (m, 1H),	$^2J_{P(Rh)C}$ = 16 Hz)
	1995 (vs),	$^1J_{RhP}$ = 113 Hz)	-0.43 (b, 9H)	
	1920 (s),	$^2J_{P(Rh)P}$ = 298Hz		
	1843 (w)			
$[RhMn(CO)_4(\mu\text{-}SC(R){=}CHR)(dppm)_2$-	2010 (sh),[b]	49.0 (m),[e]	5.78 (s, 1H),[e]	222.9 (b, 1C),[e]
$[SO_3CF_3]$ **(11)**	2000 (vs),	21.4 (dm,	3.94 (m, 2H),	220.1 (b, 1C),
(R = COOMe)	1917 (s),	$^1J_{RhP}$ = 115 Hz)	3.68 (m, 2H),	214.5 (b, 1C),
	1837 (w)		3.49 (s, 3H),	190.3 (dt,
		48.9 (m, 1P),[d]	3.28 (s, 3H)	$^1J_{RhC}$ = 74 Hz,
	2030 (sh),[c]	47.2 (m, 1P),	4.04 (b, 1H),[d]	$^2J_{P(Rh)C}$ = 15 Hz,
	2004 (vs),	23.5 (m, 1P),	3.92 (b, 1H),	1C)
	1930 (s),	38.5 (m, 1P)	3.73 (b, 1H),	
	1852 (w)		3.52 (b, 1H),	
			3.14 (b, 3H),	
			3.10 (b, 3H)	

Table 2.1. (continued)

Compound	IR, cm^{-1}	NMR δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C)
[RhMn(CO)$_4$(μ-SC(H)=CHCO(Me)- (dppm)$_2$][SO$_3$CF$_3$] (**12**)	1991 (vs),^{b} 1914 (s), 1810 (w) 2020 (sh),^{c} 2004 (vs), 1924 (s), 1804 (w)	54.5 (m),^{e} 25.0 (dm, $^{1}J_{RhP}$ = 116 Hz) 57.4 (m, 1P),^{d} 53.3 (m, 1P), 28.8 (m, 1P), 24.0 (m, 1P)	6.94 (d, $^{3}J_{HH}$ = 15.2 Hz, 1H),^{e} 5.99 (d, $^{3}J_{HH}$ = 15.2 Hz, 1H), 3.71 (m, 2H), 3.37 (m, 2H), 1.93 (s, 3H)	224.3 (b, 1C),^{e} 223.6 (b, 1C), 215.7 (b, 1C), 189.7 (dt, $^{1}J_{RhC}$ = 74 Hz, $^{2}J_{P(Rh)C}$ = 16 Hz, 1C)
[RHMn(CO)$_4$(SC(R)=CHR)(dppm)$_2$]- [SO$_3$CF$_3$] (**13**) (R = CF$_3$)	2032 (s),^{b} 1990 (vs), 1924 (m), 1824 (s) 2037 (s),^{c} 2000 (s), 1929 (m), 1821 (s)	56.8 (m),^{e} 19.3 (dm, $^{1}J_{RhP}$ = 107 Hz) 55.4 (m),^{d} 18.4 (dm)	5.14 (1H, q, $^{4}J_{HF}$ = 9 Hz),^{e} 3.17 (4H, m) 4.96 (1H, b),^{d} 3.07 (4H, b)	238.1 (b, 2C),^{e} 216.6 (b, 2C) 237.8 (m, 1C),^{d} 236.5 (m, 1C), 218.1 (m, 1C), 212.8 (m, 1C)

Table 2.1. (continued)

Compound	**IR, cm^{-1}**	**NMR**		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
$[RhMn(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ (**14**)	2020 (w),^{b}	61.7 (m),^{e}	3.63 (m, 4H),^{e}	224.6 (b, 1C),^{h}
	1991 (s),	25.6 (dm,	-15.32 (dtt, $^1J_{RhH}$ = 18 Hz,	219.7 (b, 1C),
	1922 (s),	$^1J_{RhP}$ = 110 Hz)	$^2J_{P(Rh)H}$ = 15 Hz,	219.0 (b, 1C),
	1880 (sh)		$^2J_{P(Mn)H}$ = 15 Hz)	179.1 (bd, 1C,
		61.7 (m),^{d}		$^1J_{RhC}$ = 74 Hz)
	2030 (w),^{c}	25.3 (dm,	3.67 (b, 2 H),^{i}	
	2000 (s),	$^1J_{RhP}$ = 111 Hz)	3.48 (b, 2H),	
	1941 (s),		-15.36 (b)	
	1900 (sh)			
$[RhMn(SEt)(CO)_4(dppm)_2][BF_4]$ (**15**)		49.6 (m),^{e}	4.03 (b, 2H),^{e}	222.6 (b, 1C),^{e}
		22.4 (dm,	3.47 (b, 2H)	221.3 (b, 1C),
		$^1J_{RhP}$ = 110 Hz)		214.2 (b, 1C),
			3.94 (b, 2H),^{d}	188.2 (dt, 1C,
		49.4 (m),^{d}	3.37 (b, 2H)	$^1J_{RhC}$ = 83 Hz,
		22.1 (dm,	j	$^2J_{P(Rh)C}$ = 13 Hz)
		$^1J_{RhP}$ = 111 Hz)		

Table 2.1. (continued)

Compound	IR, cm^{-1}	NMR $\delta(^{31}P\{^1H\})$	NMR $\delta(^1H)$	NMR $\delta(^{13}C)$
[RhMn(CO)$_4$(μ-SEt)(dppm)$_2$][BF$_4$] (**16**)		56.7 (m),^{e} 26.5 (dm, $^1J_{RhP}$ = 116 Hz)	3.62 (b, 2H),^{e} 3.25 (b, 2H), 2.02 (q, 2H, $^3J_{HH}$ = 7 Hz), 0.92 (t, 3H)	226.4 (t, 1C, $^2J_{P(Mn)C}$ = 16 Hz),^{e} 223.8 (t, 1C, $^2J_{P(Mn)C}$ = 19 Hz), 216.7 (t, 1C, $^2J_{P(Mn)C}$ = 12 Hz), 190.1 (dt, 1C, $^1J_{RhC}$ = 72 Hz, $^2J_{P(Rh)C}$ = 16 Hz)
		60.2 (m, 1P),^{d} 54.1 (m, 1P), 30.0 (dm, 1P, $^1J_{RhP}$ = 115 Hz) 25.9 (dm, 1P, $^1J_{RhP}$ = 114 Hz)		

a. abbreviations used:IR: s = strong, sh = shoulder, m = medium, vs = very strong, w = weak; NMR: m = multiplet, dm = doublet of multiplets, t = triplet, dt = doublet of triplets, dtt = doublet of triplet of triplets, bd = broad doublet, b = broad, q = quartet.

b. nujol mull. c. CH_2Cl_2 solution. d. -80°C. e. 22°C. f. -40°C. g. -60°C. h. -90°C. i. -100°C.

j. The ethyl protons in the intermediate species **15** are masked by those of EtSH which is present in vast excess.

$^{31}P\{^1H\}$ chemical shifts are referenced vs. external 85% H_3PO_4 while ^1H and $^{13}C\{^1H\}$ are referenced vs. external TMS. Chemical shifts for the phenyl hydrogens are not given in ^1H NMR data.

routinely handled using Schlenk techniques. Compounds isolated as solids were not air sensitive over short periods of time and could be handled in air; however they were routinely stored under nitrogen. Unless otherwise noted, gases added by gas-tight syringe are at *ca.* 1 atm pressure.

Preparation of Compounds. **(a) [RhMn(SH)(CO)$_3$(μ-H)(dppm)$_2$] (2).** Compound 1 (50 mg, 48.1 μmol) was dissolved in 10 mL of CH_2Cl_2 then 10 mL of H_2S (*ca.* 400 μmol) was added via gas-tight syringe. Over a 2 h period the stirred solution gradually changed from light yellow to orange. After this time the solvent was removed under vacuum and the residue was recrystallized from CH_2Cl_2/Et_2O to generate a red powder (yield 64%). Anal. Calcd. for $C_{53}H_{46}O_3P_4MnRhS$: C, 60.46; H, 4.32. Found: C, 60.20; H, 4.37.

(b) [RhMn(SEt)(CO)$_3$(μ-H)(dppm)$_2$] (3). Compound 1 (5 mg, 4.8 μmol) was dissolved in 0.5 mL of CD_2Cl_2 and transferred to a 5 mm NMR tube to which 50 μL of EtSH (675 μmol) was added. The color changed to orange from yellow within 5 min. After 1 h the NMR spectra were recorded and compound 3 was observed in *ca.* 5-10% yield by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H NMR and IR spectra. Compound 3 was only observed spectrally and was not isolated; only decomposition products were obtained in attempts to isolate 3.

(c) [RhMn(SPh)(CO)$_3$(μ-H)(dppm)$_2$] (4). Compound 1 (50 mg, 48.1 μmol) was dissolved in 10 ml of CH_2Cl_2 to which 100 μL of PhSH (973 μmol) was added. After *ca.* 4 h the solution had turned red and the reaction was judged to be complete, as shown by IR spectra. Removal of the solvent under vacuum and recrystallization from CH_2Cl_2/hexane yielded an orange-brown solid (yield 85%). Anal. Calcd. for $C_{59}H_{50}O_3P_4MnRhS$: C, 62.73; H, 4.39. Found: C, 62.73; H, 4.68.

(d) [RhMn(CO)$_5$(dppm)$_2$] (5). Compound **1** (5 mg, 4.8 µmol) was dissolved in 0.5 mL of CD_2Cl_2, transferred to a 5 mm NMR tube, freeze-thaw degassed and then exposed to ^{13}CO at -78°C, resulting in a red solution. Compound **10** was identified in solution at low temperature by ^1H, ^{13}C and ^{31}P NMR experiments.

(e) [RhMn(SPh)(CO)$_4$(µ-H)(dppm)$_2$] (6). Compound **1** (5 mg, 4.8 µmol) was dissolved in 0.5 mL of CD_2Cl_2, was transferred to a 5 mm NMR tube, then 50 µL of PhSH (487 µmol) was added. The color changed to orange within 10 min. After leaving the sample at R.T. for 2 h the NMR experiments ($^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H) were conducted at temperatures between -40 and -80°C, showing the presence of compound **6**. This species disappeared upon raising the temperature.

(f) [RhMn(CO)$_4$(µ-S)(dppm)$_2$] (7). Method (i). Compound **1** (50 mg, 48.1 µmol) was dissolved in 10 mL of CH_2Cl_2 then 1.54 mg of sulfur (48.1 µmol), suspended in 1.0 mL of CH_2Cl_2, was added, causing the solution to turn deep orange instantly. The solvent was removed under vacuum and the residual was recrystallized from CH_2Cl_2/Et_2O yielding a yellow powder (yield 75%). **Method (ii).** Compound **1** (50 mg, 48.1 µmol) was dissolved in 10 mL of CH_2Cl_2 then 10 mL of H_2S (g) (about 400 µmol, excess) was added via gas-tight syringe. After 48 h the reaction was complete as shown by IR spectra, leaving a deep orange solution. Removal of the solvent under vacuum and recrystallization from CH_2Cl_2/Et_2O yielded a yellow solid (yield 60%). Anal. Calcd. for $C_{54}H_{44}O_4P_4MnRhS{\bullet}CH_2Cl_2$: C, 57.16; H, 4.01; S, 2.77. Found: C, 57.07; H, 4.14; S, 3.30.

(g) [RhMn(CO)$_4$(µ-SH)(dppm)$_2$][BF$_4$] (8a). Compound **7** (50 mg, 46.7 µmol) was dissolved in 10 mL of CH_2Cl_2 then 6.7 µL of $HBF_4{\bullet}Et_2O$ (47 µmol) was added, causing an immediate color change to yellow from orange. Removal of the solvent and recrystallization of the residue from CH_2Cl_2/Et_2O gave a yellow powder (yield 83%). Anal. Calcd. for $C_{54}H_{45}O_4P_4MnRhSBF_4 \cdot 0.84\ CH_2Cl_2$: C, 53.55; H, 3.83; Cl, 4.85. Found: C, 53.29; H, 3.86; Cl, 4.85. The presence of CH_2Cl_2 in the solid was confirmed by ^1H NMR spectra with $CDCl_3$ as solvent.

(h) [RhMn(CO)$_4$(μ-SH)(dppm)$_2$][SO$_3$CF$_3$] (8b). Compound 7 (50 mg, 46.7 μmol) was dissolved in 10 mL of CH_2Cl_2 then 4.1 μL of CF_3SO_3H (47 μmol) was added *via* syringe. The color changed immediately from orange to yellow. Removal of the solvent under vacuum and recrystallization of the residue from CH_2Cl_2/Et_2O gave a yellow powder (yield 85%). Spectroscopically compound **8b** was essentially identical to **8a** apart from differences due to the anions.

(i) [RhMn(CO)$_4$(μ-SCH$_3$)(dppm)$_2$][SO$_3$CF$_3$] (9). Compound 7 (50 mg, 46.7 μmol) was dissolved in 10 mL of CH_2Cl_2 then 5.4 μL of $CF_3SO_3CH_3$ (47 μmol) was added, causing an immediate change in color to light orange. After 0.5 h removal of the solvent under vacuum and recrystallization from CH_2Cl_2/Et_2O gave a yellow-orange powder (yield 84%). Anal. Calcd. for $C_{56}H_{47}O_7P_4MnRhF_3S_2$: C, 54.47; H, 3.84. Found: C, 54.39; H, 4.05.

(j) [RhMn(CO)$_4$(μ-SCH$_2$SiMe$_3$)(dppm)$_2$][SO$_3$CF$_3$] (10). Compound 7 (50 mg, 46.7 μmol) was dissolved in 10 μL of CH_2Cl_2 then 9.4 μL of $CF_3SO_3CH_2SiMe_3$ (47 μmol) was added. The color changed to yellow from orange immediately but was stirred for an additional 0.5 h. Removal of the solvent under vacuum and recrystallization from CH_2Cl_2/Et_2O gave a yellow powder (yield 80%). Anal. Calcd. for $C_{59}H_{55}O_7P_4MnRhF_3SiS_2$: C, 54.22; H, 4.21. Found: C, 54.43; H, 4.55.

(k) [RhMn(CO)$_4$(μ-SC(CO$_2$Me)=C(H)CO$_2$Me)(dppm)$_2$][SO$_3$CF$_3$] (11). Compound **8b** (50 mg, 41.0 μmol) was dissolved in 10 mL of CH_2Cl_2 then 100 μL of $MeO_2CC{\equiv}CCO_2Me$ (810 μmol) was added. The solution was stirred for 24 h resulting in a change in color from yellow to deep orange. Removal of the solvent under vacuum and recrystallization of the residue from CH_2Cl_2/Et_2O gave a yellow solid (yield 84%). Anal. Calcd. for $RhMnC_{61}H_{51}S_2P_4O_{11}F_3$: C, 53.76; H, 3.77. Found: C, 53.33; H, 4.00.

(l) $[RhMn(CO)_4(\mu\text{-}SC(H)=C(H)COMe)(dppm)_2][SO_3CF_3]$ (12). Compound **8b** (50 mg, 41.0 μmol) was dissolved in 10 mL of CH_2Cl_2 then 10 μL of 3-butyn-2-one (128 μmol) was added. The solution was stirred for 24 h during which time it turned orange. The solvent was removed *in vacuo* and the residue was recrystallized from CH_2Cl_2/[illegible]ng a yellow powder in 78% yield. Anal. Calcd. for $RhMnS_2P_4O_8F_3$ [illegible] C, 54.97; H, 3.80. Found: C, 54.06; H, 4.02.

(m) $[RhMn(CO)_4(\mu\text{-}SC(CF_3)=C(H)CF_3)(dppm)_2][SO_3CF_3]$ (13). Compound **8b** (50 mg, 41.0 μmol) was dissolved in 10 mL of CH_2Cl_2. The nitrogen atmosphere above the solution was replaced by hexafluoro-2-butyne, and the solution was stirred for 5 days, during which time it changed to deep orange. Removal of the solvent under vacuum and recrystallization of the residue from CH_2Cl_2/hexane gave a red solid (yield 70%). Anal. Calcd. for $RhMnC_{59}H_{45}P_4S_2O_7F_9$: C, 51.23; H, 3.26. Found: C, 50.97; H, 3.23.

(n) $[RhMn(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ (14). Compound **1** (50 mg, 48.1 μmol) was dissolved in 10 mL of CH_2Cl_2 then 8.2 μL $HBF_4{\cdot}Et_2O$ (48 μmol) was added. Instantly the color changed to deep red. Monitoring the solution by IR spectroscopy indicated that the reaction was complete. Removal of the solvent under vacuum and recrystallization from CH_2Cl_2/Et_2O gave a red solid (yield 90%). Anal. Calcd. for $C_{54}H_{45}O_4P_4MnRhBF_4$: C, 57.58; H, 4.03. Found: C, 57.12; H, 4.43.

(o) [RhMn(SEt)(CO)$_4$(dppm)$_2$][BF$_4$] (15). Compound **1** (5 mg, 4.8 μmol) was dissolved in 0.5 mL of CD_2Cl_2 and transferred to a 5 mm NMR tube to which 50 μL of EtSH (675 μmol) was added. After 1 day 10 μL of $HBF_4 \cdot Et_2O$ (68 μmol) was added to the solution. After 4 days the $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra showed the formation of compound **15**. Compounds **15** and **16** (prepared below) were identified on the basis of their spectroscopic properties and were not isolated.

(p) [RhMn(CO)$_4$(μ-SEt)(dppm)$_2$][BF$_4$] (16). Compound **14** (5 mg, 4.4 μmol) was dissolved in 0.5 mL of CD_2Cl_2 and was transferred to a 5 mm NMR tube, which was capped by a serum stopper. Then 50 μL of EtSH (675 μmol) was added. After 1 week, the $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra showed the formation of compound **16**.

Reaction of Compound 2 with CO. 50 mg of compound **2** was dissolved in 5 mL of CH_2Cl_2 and the solution was purged with a slow stream of CO for 24 h. Precipitation was induced by the addition of ether. Recrystallization of the solid residue from CH_2Cl_2/Et_2O gave a mixture of compounds **1** (*ca.* 70%) and **7** (*ca.* 30%).

Reaction of Compound 3 with CO. To a CD_2Cl_2 solution of compound 1 (10 mg, 9.6 μmol in 0.5 mL) in a serum-capped NMR tube, was added 50 μL of EtSH (675 μmol). After 1 h the ^{31}P NMR spectrum showed the formation of compound **3** (*ca.* 10%). The solution was put under CO at -78°C for 10 min then warmed to room temperature. The addition of CO resulted in a color change from orange to yellow and the subsequent ^{31}P NMR spectrum showed the presence of only compound **1**.

Reaction of Compound 4 with CO. A CH_2Cl_2 solution of compound **4** (50 mg in 5 mL) was placed under an atmosphere of CO and stirred for 0.5 h. Complete conversion to compound **1** was observed as shown by the IR spectrum.

Deprotonation of Compound 8. To a CD_2Cl_2 solution of compound **8a** (10 mg, 9 μmol in 0.5 mL) in a 5 mm NMR tube was added 2 μL of piperidine (20 μmol). After 4 h the ^{31}P NMR spectrum showed the presence of only compound **7**.

X-ray Data Collection. Deep red-orange crystals of $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]\cdot CH_2Cl_2$ (**7**) were grown by diffusion of hexanes into a concentrated CH_2Cl_2 solution of the compound. Several of these were mounted and flame-sealed in glass capillaries under an atmosphere of N_2 and solvent vapor to minimize decomposition and/or solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo $K\alpha$ radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $20.0° \leq 2\theta \leq 24.0°$. The monoclinic diffraction symmetry and the systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) defined the space group as $P2_1/n$ (a non-standard setting of $P2_1/c$ [No. 14]).

Intensity data were collected at 22 °C by using the $\theta/2\theta$ scan technique, covering reflections having indices of the form $+h$ $+k$ $\pm l$ to a maximum $2\theta = 50.0°$. Of the data collected 9352 reflections were unique after merging. Backgrounds were scanned for 25% of the scan width on either side of the scan region. Three reflections were chosen as intensity standards, being remeasured after every 120 min of X-ray exposure time. The intensities of these standards remained approximately constant over the duration of data collection so no decomposition correction was deemed necessary. The data were processed in the usual way, with a value of 0.04 for p employed to downweight intense reflections;[13] 5865 reflections were considered observed ($F_o^2 \geq 3\sigma(F_o^2)$) and were used in subsequent calculations.[14] Absorption corrections were applied to the data according to the method of Walker and Stuart.[15] See Table 2.2 for crystal data and more information on X-ray data collection.

Structure Solution and Refinement. The structure of [RhMn(CO)$_4$(μ-S)(dppm)$_2$]•CH$_2$Cl$_2$ was solved in the space group $P2_1/n$ using 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 the weighting factor $w = 4F_o^2/\sigma^2(F_o)^2$. Atomic scattering factors[16,17] and anomalous dispersion terms[18] were taken from the usual tabulations. The hydrogen atoms were generated at idealized calculated positions by assuming a C–H bond length of 0.95 Å and the appropriate sp^2 or sp^3 geometry. All hydrogen atoms were then included in the calculations with fixed, isotropic Gaussian parameters 20% greater than those of the attached atoms, and were constrained to 'ride' on the attached atoms. There was no evidence for secondary extinction therefore no correction was applied.

The final model for [RhMn(CO)$_4$(μ-S)(dppm)$_2$]•CH$_2$Cl$_2$, with 598 parameters varied, converged to values of R = 0.055 and R_w = 0.071. In the final difference Fourier map the 10 highest residuals (1.5–0.6 e/Å^3) were found in the vicinity of the CH$_2$Cl$_2$ solvent molecule and the Rh atom (a typical carbon atom in an earlier synthesis had an intensity of 5.0 e/Å^3). The atomic coordinates and thermal parameters for selected atoms of [RhMn(CO)$_4$(μ-S)(dppm)$_2$]•CH$_2$Cl$_2$ are given in Table 2.3, while the parameters for the phenyl groups and the solvent atoms are available upon request from Professor Martin Cowie. Selected bond lengths and angles are given in Table 2.4 and 2.5, respectively. We thank Dr. R. McDonald for his assistance in collecting X-ray data, solving and refining the structure of [RhMn(CO)$_4$(μ-S)(dppm)$_2$]•CH$_2$Cl$_2$.

Table 2.2. Crystallographic Data for $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]\cdot CH_2Cl_2$ (7)

formula	$C_{55}H_{46}Cl_2MnO_4P_4RhS$
formula weight	1155.69
space group	$P2_1/n$ (a non-standard setting of $P2_1/c$ (No. 14))
unit cell parameters	
a, Å	12.419 (4)
b, Å	25.735 (2)
c, Å	16.464 (2)
β, deg	97.70 (2)
V, Å^3	5215 (3)
Z	4
ρ(calcd), g cm^{-3}	1.472 g cm^{-3}
linear absorption coeff (μ), cm^{-1}	8.502 cm^{-1}
diffractometer	Enraf-Nonius CAD4
temperature (°C)	22
radiation (λ), Å	graphite-monochromated Mo K_α (0.71069)
crystal–detector distance, mm	173
scan type	$\theta/2\theta$
scan rate, deg/min	6.7–1.4
scan width, deg	$0.60 + 0.347 \tan\theta$
maximum 2θ, deg	50
total unique reflections	9352
total observations	5865
range of transmission factors	0.9113–1.0834
final no. parameters varied (NV)	598
R^a	0.055
$R_w{}^b$	0.071
error in obs. of unit weight (GOF)^c	2.148

$^aR = \sum||F_o| - |F_c|| / \sum|F_o|$.

$^bR_w = [\sum w(|F_o| - |F_c|)^2 / w F_o{}^2]^{1/2}$.

^{c}GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$.

Table 2.3. Atomic Coordinates and Thermal Parameters for Selected Atoms of $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]\cdot CH_2Cl_2$ (7)[a]

Atom	x	y	z	B_{eq}, Å^2
Rh	0.19364(4)	0.12378(2)	-0.10942(3)	1.90(1)
Mn	0.37000(8)	0.14463(4)	-0.21062(6)	1.86(2)
S	0.1725(1)	0.15200(7)	-0.2458(1)	2.43(4)
P(1)	0.1498(1)	0.04560(7)	-0.1715(1)	2.01(4)
P(2)	0.3454(1)	0.06444(7)	-0.2711(1)	2.15(4)
P(3)	0.1771(1)	0.21013(7)	-0.0727(1)	2.12(4)
P(4)	0.3783(1)	0.22715(7)	-0.1564(1)	2.13(4)
O(1)	0.1723(4)	0.0837(2)	0.0587(3)	4.0(1)
O(2)	0.4181(4)	0.0898(2)	-0.0468(3)	3.4(1)
O(3)	0.6075(4)	0.1413(2)	-0.1976(4)	4.1(2)
O(4)	0.3743(6)	0.1926(2)	-0.3737(3)	5.1(2)
C(1)	0.1815(6)	0.0996(3)	-0.0044(4)	2.5(2)
C(2)	0.3710(5)	0.1115(3)	-0.1034(4)	2.3(2)
C(3)	0.5124(6)	0.1413(3)	-0.2015(4)	2.4(2)
C(4)	0.3709(6)	0.1741(3)	-0.3115(4)	3.0(2)
C(5)	0.2171(5)	0.0306(3)	-0.2604(4)	2.3(2)
C(6)	0.2473(5)	0.2531(3)	-0.1365(4)	2.2(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. All atoms above were refined anisotropically. Thermal parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian diplacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos\beta)\beta_{13}]$. Phenyl carbons and solvent atoms are given as supplementary material.

Table 2.4. Selected Distances (Å) in $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]\cdot CH_2Cl_2$ (7)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	S	2.341 (1)	Mn	C(4)	1.828 (6)
Rh	P(1)	2.289 (1)	P(1)	C(5)	1.821 (5)
Rh	P(3)	2.319 (1)	P(2)	C(5)	1.845 (5)
Rh	C(1)	1.863 (5)	P(3)	C(6)	1.825 (5)
Rh	C(2)	2.214 (5)	P(4)	C(6)	1.828 (5)
Mn	S	2.450 (2)	O(1)	C(1)	1.137 (6)
Mn	P(2)	2.294 (2)	O(2)	C(2)	1.173 (6)
Mn	P(4)	2.300 (2)	O(3)	C(3)	1.173 (6)
Mn	C(2)	1.959 (5)	O(4)	C(4)	1.135 (6)
Mn	C(3)	1.757 (5)			

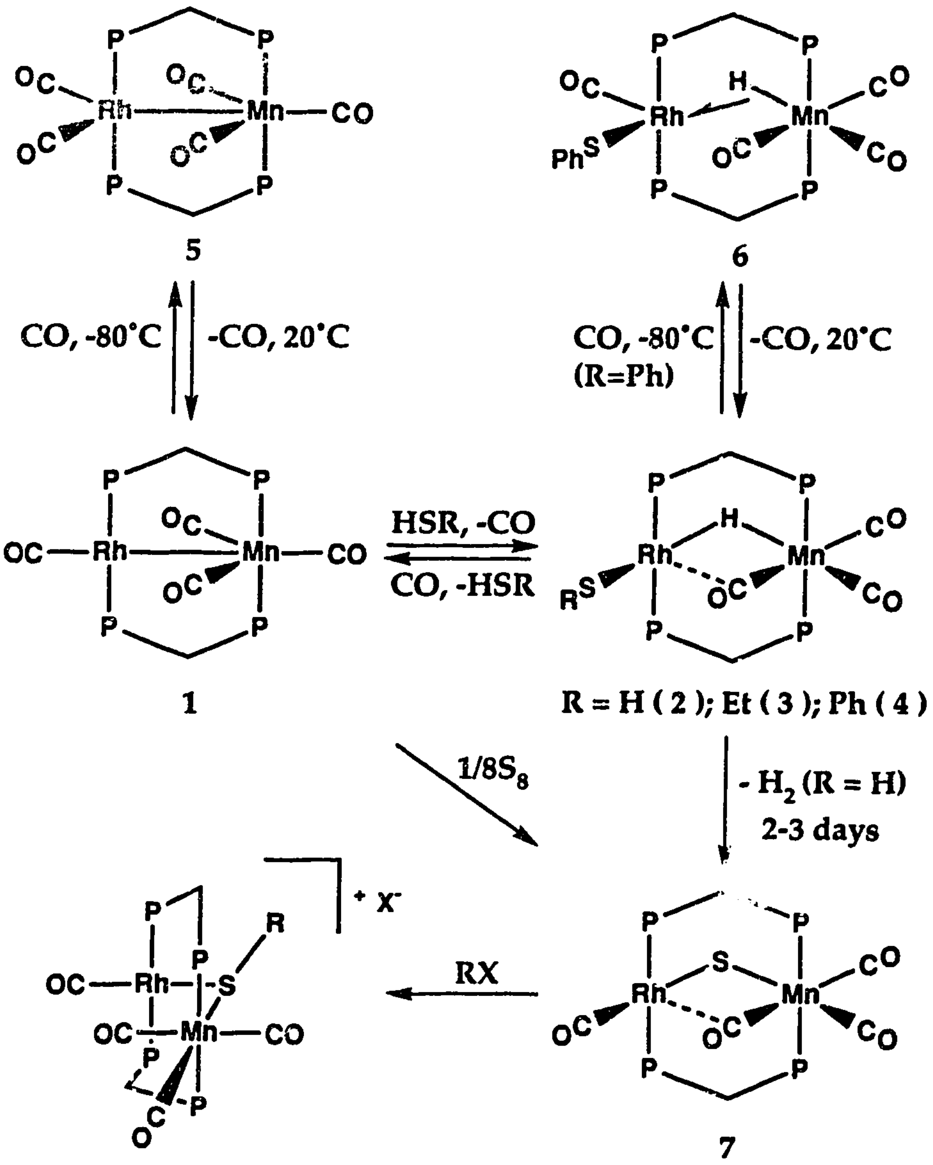
Table 2.5. Selected Angles (deg) in [RhMn(CO)$_4$(μ-S)(dppm)$_2$]•CH$_2$Cl$_2$ (7)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
S	Rh	P(1)	81.66 (5)	P(4)	Mn	C(2)	93.3 (2)
S	Rh	P(3)	87.16 (5)	P(4)	Mn	C(3)	91.1 (2)
S	Rh	C(1)	169.0 (2)	P(4)	Mn	C(4)	87.9 (2)
S	Rh	C(2)	94.0 (1)	C(2)	Mn	C(3)	91.0 (2)
P(1)	Rh	P(3)	159.16 (5)	C(2)	Mn	C(4)	178.6 (2)
P(1)	Rh	C(1)	94.4 (2)	C(3)	Mn	C(4)	88.2 (2)
P(1)	Rh	C(2)	94.0 (1)	Rh	S	Mn	76.66 (4)
P(3)	Rh	C(1)	93.2 (2)	Rh	P(1)	C(5)	116.0 (2)
P(3)	Rh	C(2)	104.3 (1)	Mn	P(2)	C(5)	116.7 (2)
C(1)	Rh	C(2)	96.6 (2)	Rh	P(3)	C(6)	111.4 (2)
S	Mn	P(2)	84.04 (5)	Mn	P(4)	C(6)	114.3 (2)
S	Mn	P(4)	90.66 (5)	Rh	C(1)	O(1)	177.9 (5)
S	Mn	C(2)	97.6 (1)	Rh	C(2)	Mn	90.6 (2)
S	Mn	C(3)	171.1 (2)	Rh	C(2)	O(2)	119.3 (4)
S	Mn	C(4)	83.1 (2)	Mn	C(2)	O(2)	149.9 (4)
P(2)	Mn	P(4)	174.44 (6)	Mn	C(3)	O(3)	176.8 (5)
P(2)	Mn	C(2)	89.1 (2)	Mn	C(4)	O(4)	178.2 (5)
P(2)	Mn	C(3)	93.9 (2)	P(1)	C(5)	P(2)	118.1 (3)
P(2)	Mn	C(4)	89.8 (2)	P(3)	C(6)	P(4)	112.7 (3)

Results and Discussion

At ambient temperature [$RhMn(CO)_4(dppm)_2$] (**1**) (dppm = $Ph_2PCH_2PPh_2$) reacts with H_2S, EtSH and PhSH generating compounds **2** - **4**, respectively, as shown in Scheme 2.1. For these species the $^{31}P\{^1H\}$ NMR spectra display resonances typical of an AA'BB'X spin system, in which the Mn-bound phosphorus nuclei resonate near δ 70 and the Rh-bound phosphorus nuclei appear at *ca.* δ 30. The ^1H NMR spectra show two signals for the dppm methylene protons, consistent with the structure shown in which the environment on one side of the $RhMnP_4$ plane differs from that on the other side. The hydride resonances for the three compounds are found at typically high field (δ -14.03 to -14.88) and display coupling to Rh of between 22 and 26 Hz and almost equal coupling ($^2J_{P\text{-}H}$ = 12 Hz) to both sets of phosphorus nuclei (on Rh or Mn), establishing that the hydride ligands bridge the metals. In compound **2** the sulfhydryl proton resonates at δ -0.31 and displays coupling to Rh and to the phosphorus nuclei on Rh, as demonstrated by selective ^{31}P decoupling experiments. The absence of coupling of this sulfhydryl proton to the Mn-bound phosphorus nuclei is consistent with the terminal, Rh-bound sulfhydryl formulation shown, but does not unequivocally establish this. In the $^{13}C\{^1H\}$ NMR spectra three equal-intensity carbonyl resonances are observed for each of the three products. In each case two resonances (at *ca.* δ 227) display coupling of *ca.* 20 Hz to only the Mn-bound phosphorus nuclei, establishing that these carbonyls are terminally bound to Mn. The remaining resonance (at *ca.* δ 260) displays coupling to the Mn-bound phosphorus atoms ($^2J_{P\text{-}C}$ ~ 20Hz) in addition to Rh coupling of *ca.* 17 Hz; no coupling of this carbonyl to the Rh-bound phosphines is observed. These data indicate that this low-field resonance corresponds to a semi-bridging carbonyl which is sigma bound to Mn while interacting weakly with Rh. By comparison, terminal carbonyls on Rh typically

Scheme 2.1



R=H; X=BF_4(8a), SO_3CF_3(8b)
=Me; X=SO_3CF_3(9)
=CH_2SiMe_3; X=SO_3CF_3(10)

+ decomposition products

display Rh-C coupling of about 50-80 Hz, whereas symmetrically bridged carbonyls display Rh-C coupling of about 35 Hz.[19] With the bridging sites on both sides of the $RhMnP_4$ plane occupied by the hydride and the semi-bridging carbonyl group, and with the absence of any other terminally bound ligand on Rh, the sulfhydryl or thiolato ligands in **2** - **4** are, by necessity, terminally bound to Rh as shown in the Scheme.

Although examples of terminally bound SR groups are well known,[3,8a,20] there is a strong tendency for these ligands to bridge two metals.[2,4,7,8a,21] The isolation of the stable complexes **2** and **4** (compound **3** was not isolated), containing terminal sulfhydryl or thiolato groups was of some surprise to us, since all related chemistry with Rh/Re,[2] Rh/Ru[4] and Rh/Os[4] complexes had yielded products in which the thiolato groups bridged the metals; terminal SR groups had only been observed in this chemistry as labile low-temperature intermediates, rearranging to give SR-bridged complexes at ambient temperature. However, stable complexes with terminally bound thiolato groups *had* been obtained in a related diiridium system.[3] It is also notable that compounds **2**-**4** are tricarbonyl species whereas the labile thiolato intermediates, observed in the Rh/Re system[2] were all tetracarbonyl species. Carbonyl loss *was* observed for the ethane- and benzenethiolato Rh/Re complexes, but this was accompanied by movement of the thiolato group to a bridging position. Compound **1** and its Rh/Re analogue also show significant differences in their rates of reaction with H_2S and thiols. In all cases, reactions with $[RhRe(CO)_4(dppm)_2]$, carried out at -80°C, showed complete consumption of the complex within minutes.[2] By contrast, compound **1** is unreactive with these substrates at temperatures below 0°C, and reacts slowly with large excesses (>8x) even at ambient temperature. We were also unable to observe the presumed initial H_2S and HSR adducts of compound **1**, analogous to the

Rh/Re compounds, $[RhRe(HSR)(CO)_4(dppm)_2]$ (R = H, Et, Ph), which were observed at temperatures below -50°C in the previous study.[2]

Although compounds **2** and **4** can be isolated as the sole products in their respective reactions, compound **3** is only ever observed spectroscopically in low yield (*ca.* 5-10%) in reaction mixtures. The only other species observed are unidentified decomposition products in which the RhMn framework is apparently no longer intact.

The reactivity of **1** with H_2S parallels that observed with another isoelectronic heterobinuclear complex, $[RhIr(CO)_3(dppm)_2]$,[3] but is in contrast to that observed in the analogous Rh/Re system,[2] in $[RhOs(CO)_4(dppm)_2]^+$,[4] and in the homobinuclear complexes, $[Pd_2Cl_2(dppm)_2]$,[8f] $[Rh_2(CO)_3(dppm)_2]$,[3] and $[Ir_2(CO)_3(dppm)_2]$.[3] Only the present Rh/Mn complex and that involving Rh/Ir stopped at activation of one S-H bond; all others resulted in facile cleavage of both S-H bonds, yielding sulfido-bridged products. For the diiridium complex[3] the dihydride species initially formed is inert, and undergoes H_2 loss only after days at room temperature, whereas for the others the presumed dihydride intermediates were never observed, with H_2 loss occurring instantly. The reluctance of the Rh/Mn complex to activate the second S-H bond is understandable in terms of a double oxidative addition involving both S-H bonds, since only the unsaturated Rh center is susceptible to oxidative addition (although as noted later, slow loss of H_2 does occur from **2** to yield a sulfide-bridged product). In this respect the difference between Re and Mn is interesting given that activation of <u>both</u> S-H bonds in H_2S occurred readily with the Rh/Re complex.[2]

In all cases the S-H activation step in the reaction of **1** with H_2S, HSEt and HSPh is reversible, so reaction of compounds **2**, **3**, and **4** with CO regenerates **1** and the respective thiols.

One consequence of carbonyl loss upon reaction of **1** with HSR is the observation of the labile carbonyl adduct, $[RhMn(CO)_5(dppm)_2]$ (**5**), as shown in Scheme 2.1. This species was observed only upon cooling the reaction mixture to -80°C and results from reaction of **1** with liberated CO; predictably it can also be prepared directly by the addition of CO to **1** at -80°C. The $^{13}C\{^1H\}$ NMR of **5** at -80°C shows three carbonyl resonances at δ 241.7, 228.4 and 200.3 in a 2:1:2 intensity ratio, respectively. No coupling to either Rh or P is obvious although the high-field signal is extremely broad, presumably masking the expected 60 to 80 Hz coupling to Rh. The broadness of this signal is probably due to the facile, reversible loss of CO which undoubtedly is occurring at Rh. Raising the temperature results in the disappearance of **5** due to CO loss, leaving only **1**.

When a mixture of **1** and HSPh is cooled to -40°C an additional species $[RhMn(SPh)(CO)_4(\mu\text{-}H)(dppm)_2]$ (**6**) is observed. The ^1H NMR spectrum displays a high-field signal at δ -12.20 and selective and broad-band ^{31}P decoupling experiments establish that this hydride is coupled strongly to the Mn-bound phosphorus nuclei ($^2J_{P\text{-}H}$ = 20 Hz) and weakly coupled to Rh ($^1J_{Rh\text{-}H}$ = 5 Hz). The magnitudes of these couplings and the absence of coupling to the Rh-bound phosphorus nuclei suggest a structure in which the hydride ligand is primarily bound to Mn, yet interacting weakly with Rh; this can be viewed as a weak agostic interaction between Rh and the Mn-H bond. In the $^{13}C\{^1H\}$ NMR four equally intense resonances appear for the carbonyls, with the high-field signal at δ 200.9 showing strong coupling to Rh ($^1J_{Rh\text{-}C}$ = 78 Hz) and to the two adjacent phosphorus nuclei ($^2J_{P\text{-}C}$ = 15 Hz). This species is a labile CO adduct of **4** and disappears with time or upon warming. The structure shown for **6** in Scheme 2.1 is based on the assumption that CO attack will occur at the vacant site opposite the semibridging CO in **4**. This CO adduct would not necessarily be an intermediate in the displacement of HSPh from 4 by CO but may instead be an isomer, since the H and SPh fragments are not adjacent, as expected for their subsequent reductive elimination. (It should be noted however, that movement of a bridged hydride between the metals is known to be facile,[12,22,23] and this would bring the hydrido and thiolato ligands into a position to undergo reductive elimination.)

Attempts to obtain single crystals of the sulfhydryl species 2 have resulted instead in the isolation of the sulfide-bridged, tetracarbonyl complex $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]$ (7) in *ca.* 66% yield. This transformation occurs slowly over the period of 2-3 days, during which time no intermediate can be detected. In particular, no dihydride intermediate, of the type observed in the analogous Ir_2 system,[3] was ever observed. The additional carbonyl ligand that is required in the transformation of the tricarbonyl species 2 to the tetracarbonyl 7, is presumably scavenged from the unidentified decomposition products which appear as a number of low-intensity resonances in the $^{31}P\{^1H\}$ NMR spectrum. Compound 7 can also be prepared quantitatively from 1 via reaction with elemental sulfur. This species shows one low-frequency carbonyl stretch at 1796 cm^{-1} in the IR spectrum and a corresponding resonance at δ 239.1 in the $^{13}C\{^1H\}$ NMR spectrum. This carbonyl is identified as a semibridging group which is primarily bound to Mn while interacting weakly with Rh, based on the rather small magnitude of the Rh-C coupling of 8 Hz. By comparison, the carbonyl that is terminally bound to Rh (δ 192.8) shows Rh-C coupling of 69 Hz, and those terminally bound to Mn show no Rh coupling. This semibridging carbonyl displays no coupling to the Rh-bound P nuclei, but does show coupling to the Mn-bound phosphines of 14 Hz, that is slightly less than the 18-20 Hz couplings displayed by the terminal carbonyls coupled to the appropriate adjacent P nuclei.

The X-ray structure of 7 confirms this formulation and clearly shows the semibridging interaction with one carbonyl. An ORTEP diagram of this compound is shown in Figure 2.1. The geometry at Mn is as expected for an octahedral Mn(+1) compound, having an almost undistorted geometry. At Rh the geometry is distorted from that of a square plane, having Rh lying 0.282Å out of the P(1), P(3), S, C(1) plane in the direction of C(2).[24] As such, the geometry at Rh can be described as a tetragonal pyramid having C(2) at the apical site.

The sulfido ligand bridges the metals in a slightly asymmetric manner. Surprisingly, the Mn-S distance is longer than that of Rh-S (2.450(2) *vs.* 2.341(1)Å), the reverse of what is expected based on the covalent radii of the metals.[25] The Rh-S distance is comparable to that observed in [$Rh_2(CO)_2(\mu\text{-}S)(dppm)_2$] (2.367(3)Å)[26] and does not appear to be unusual. It may be that the Mn-S distance is longer because of increased steric crowding at the more crowded octahedral Mn center. However another explanation is that the shorter Rh-S distance results from π donation from sulfur to the unsaturated Rh, as has previously been proposed.[27] The angle at sulfur (76.66(4)°) is more acute than that observed (83.5(1)°) in [$Rh_2(CO)_2(\mu\text{-}S)(dppm)_2$] because of the shorter metal-metal separation (2.972(7) *vs.* 3.154(2)Å) in the present compound. This separation is longer than expected for a Rh-Mn single bond (compare, for example, that observed (2.8428(8)Å) in the precursor (1))[12] but is not long enough to clearly indicate the absence of such bonding. One explanation is that there is no formal Rh-Mn bond; instead the short separation results from interaction of Rh with the semibridging carbonyl (C(2)O(2)). Not only is the Mn-C(2) distance (1.959(5)Å) substantially shorter than Rh-C(2) (2.214(5)Å), but more significantly this carbonyl is more linear with respect to Mn than to Rh (Mn-C(2)-O(2) = 149.9(4)°, Rh-C(2)-O(2) = 119.4(4)°). A comparison of the structural parameters of the carbonyls shows some

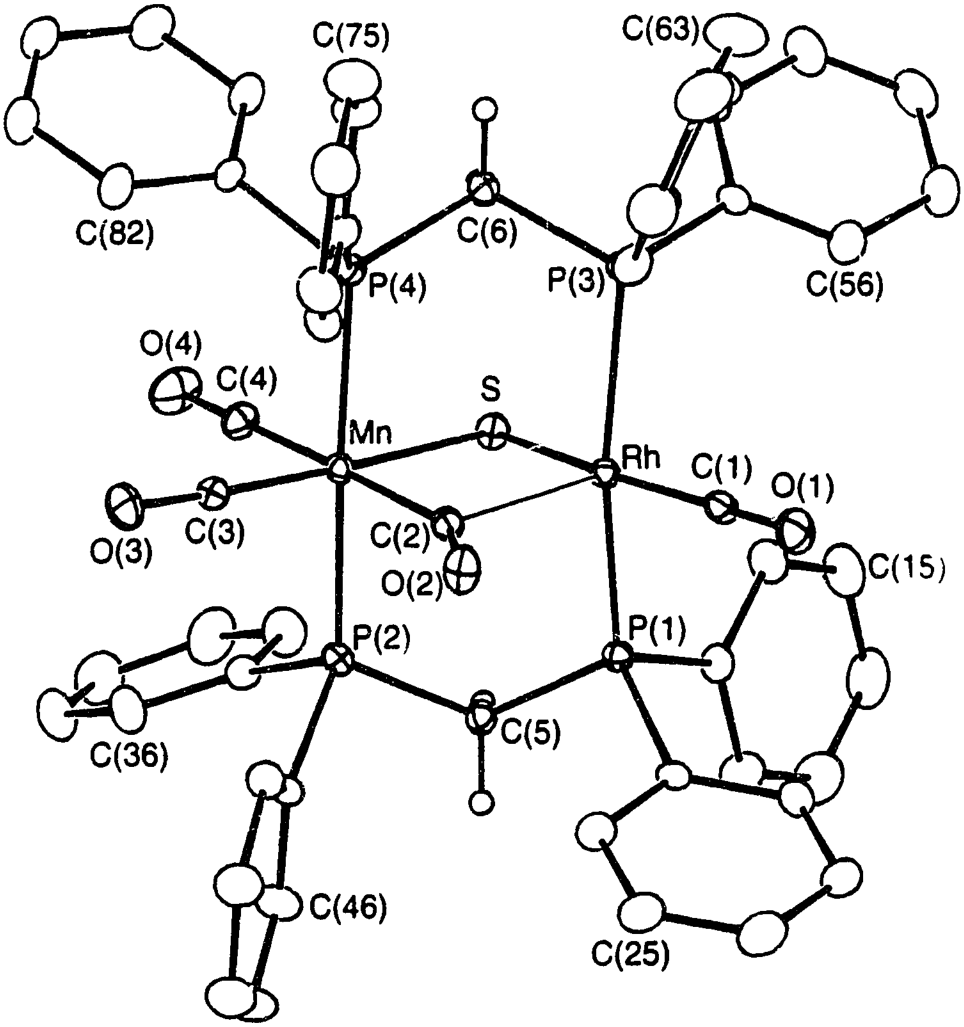
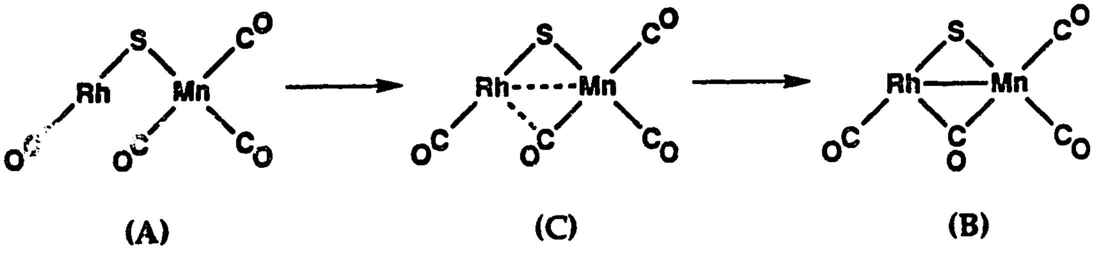


Figure 2.1. A perspective view of RhMn$(CO)_4(\mu\text{-}S)(dppm)_2$ (**7**) showing the numbering scheme. Thermal ellipsoids are drawn at the 20% level, except for methylene hydrogens which are shown arbitrarily small and phenyl hydrogens which are omitted.

interesting features. Not surprisingly, the semibridging carbonyl has the longest metal-carbon distances. By contrast Mn-C(3) is the shortest separation (1.757(5)Å), presumably because it is opposite the π-donor sulfide ligand; this is consistent with the correspondingly long C(3)-O(3) distance (1.173(6)Å), which is the same as that of the semibridging group, which interacts with both metals.

Although, as noted above, there is no need to formulate a formal Rh-Mn bond in **7**, we propose that the interaction of Rh with the semibridging carbonyl results in some metal-metal bonding interaction. A structure containing a semibridging carbonyl can be viewed as an intermediate in the transformation of a terminal carbonyl (A) to a bridging one (B) (diphosphine ligands, which are perpendicular to this plane are not shown).



In order to maintain the compound's diamagnetism and an 18-e count at Mn this transformation of a single carbonyl from terminal to bridged must be accompanied by a change in metal-metal bond order, as shown above. On this basis the intermediate (C), representing compound **7**, would be expected to show the onset of a metal-metal interaction.

Compound **7** is one of a series of sulfido-bridged, A-frame complexes involving the late transition metals.[2,11,26,28] In previous studies[11b,29] some of these and related sulfido-bridged species had been readily oxidized to give complexes containing bridging sulfoxide or sulfur dioxide complexes. However, attempts to oxidize the sulfide bridge in **7** failed, as this compound was found to be unreactive with molecular oxygen, *m*-chloroperbenzoic acid, hydrogen peroxide, *t*-butyl peroxide or sodium periodate. Similarly, attempts to at least partially reverse the reaction in which $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]$ (**7**) was obtained from $[RhMn(CO)_4(dppm)_2]$ and H_2S, by reaction of **7** with H_2 also failed. No evidence of metal hydride, or sulfhydryl resonances was observed in the ^1H NMR spectrum; only starting material was observed. This duplicated earlier findings with $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$,[30] which also proved to be unreactive with H_2, but was in contrast to $[Ir_2(CO)_2(\mu\text{-}S)(dppm)_2]$[31] and $[RhIr(CO)_2(\mu\text{-}S)(dppm)_2]$,[30] both of which yielded hydrido complexes upon reaction with H_2. Apparently the third-row metal is necessary in these systems to give a strong enough metal-hydride bond.

As expected, the bridging sulfide moiety in **7** was susceptible to attack by electrophiles. So although sulfhydryl- and thiolato-bridged species were not observed in the S-H bond-activation reactions described in this RhMn system, such species could be prepared via protonation or alkylation of the sulfide bridge in compound **7**.[8d,9f,9j,26] Therefore reaction of **7** with $HBF_4{\bullet}Et_2O$, HSO_3CF_3, $MeSO_3CF_3$, or $Me_3SiCH_2SO_3CF_3$, shown in Scheme 2.1, yields products **8**-**10**, respectively, having the appropriate counter ion (BF_4^- or $SO_3CF_3^-$). At ambient temperature the $^{31}P\{^1H\}$ NMR spectra of **8** and **10** are broad and unresolved, whereas that of **9** appears as that of a well resolved AA'BB'X spin system. On cooling the samples to -80°C, however, all species give $^{31}P\{^1H\}$ spectra characteristic of ABCDX spin systems in which all four phosphorus nuclei within the complex are chemically inequivalent, as shown for compound **9** in Figure 2.2. The coalescence temperature (from $^{31}P\{^1H\}$NMR) for **9** is -30° ±5°C whereas for **8** and **10** coalescence had not occurred by 22°C, so these temperatures were not obtained. The top-bottom asymmetry that renders the two phosphorus atoms on a given metal inequivalent is probably due to the orientation of

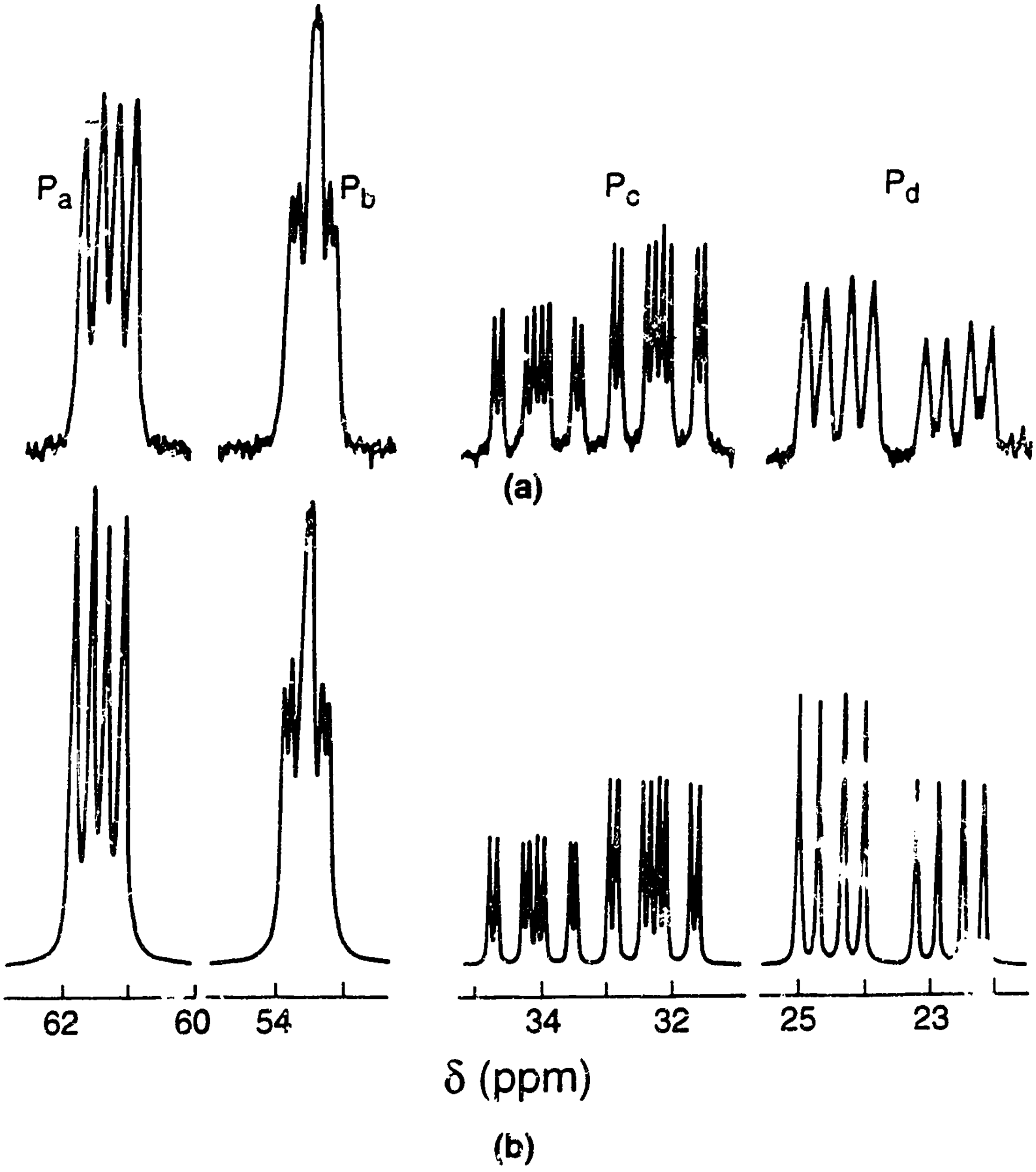
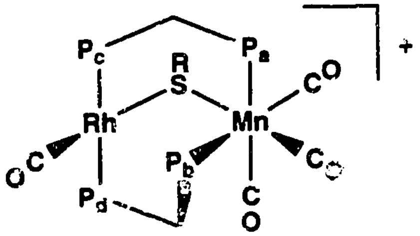


Figure 2.2. (a) Observed and (b) calculated $^{31}P\{^1H\}$ NMR spectra for $[RhMn(CO)_4(\mu\text{-}SMe)(dppm)_2][SO_3CF_3]$ (**9**) at -80°C. Parameters from the stimulation are: $^2J_{P_aP_b} = 43$ Hz, $^2J_{P_cP_d} = 296$ Hz, $^2J_{P_aP_c} = 81$ Hz, $^2J_{P_bP_d} = 52$ Hz, $^1J_{RhP_c} = 119$ Hz, $^1J_{RhP_d} = 113$ Hz.

the thiolate substituent (R = H, CH_3, CH_2SiMe_3) as diagrammed in Scheme 2.1. The fluxionality at ambient temperature, which equilibrates the phosphorus nuclei on either of the two metals, would then result from inversion at sulfur. Another ground-state structure that would render all phosphorus nuclei inequivalent is that in which the phosphines are trans at one metal but cis at another (structure **D**), a structural type that is not uncommon in such compounds.[32-35] Fluxionality of such a species would then result from pivoting about the Mn-S bond bringing P_a out of and P_b into the $RhMnP_cP_d$ plane, accompanied by inversion at sulfur. This latter possibility can be ruled out with



(D)

reasonable confidence based on the NMR studies. The simulation of the NMR spectrum of **9** yields a coupling constant of 296 Hz between the two Rh-bound phosphorus nuclei, consistent with a trans arrangement of phosphines at this metal and can be compared to the values of 321-337 Hz reported for *trans*-$[RhX(CO)(PH^tBu_2)_2]$.[36] The coupling between the Mn-bound phosphorus nuclei is much smaller (43 Hz) but is still believed to result from a trans, or almost-trans, diphosphine arrangement at this metal. By comparison, the $^2J_{PP}$ values for trans phosphine arrangements in *trans*-$[PhC(O)Mn(CO)_3P_2]$ and *trans*-$[PhMn(CO)_3P_2]$ (P = $P(OCH_2)_3CEt$) are 70 and 110 Hz, respectively, whereas the cis phosphines in *cis*-$[PhC(O)Mn(CO)_3P_2]$ display P-P coupling of only 5 Hz.[37] Although the P-Mn-P coupling in **9** is significantly smaller than the trans coupling noted above for these mononuclear Mn complexes, larger coupling is expected when more electronegative phosphite substituents are involved.[38] In addition, a cis-diphosphine arrangement at Mn (D) in compounds **8**-**10** can be ruled out since it would require the Mn-bound ends of the phosphines to be opposite carbonyl ligands, and no P-C coupling consistent with such an arrangement is observed. The $^{13}C\{^1H\}$ NMR spectra of the three compounds show one Rh-bound carbonyl at *ca.* δ 190 ($^1J_{Rh-C}$ = 72 Hz, $^2J_{P-C}$ = 14 Hz), and three Mn-bound carbonyls between δ 216 and 230 with $^2J_{P-C}$ values about 18 Hz, consistent with an arrangement in which the carbonyls are cis to the phosphines. The IR spectra of compounds **8-10** are also more consistent with a trans-diphosphine arrangement, since their low frequency carbonyl stretch (at *ca.* 1850 cm^{-1}) is probably due to the carbonyl on Mn which is directed towards Rh, giving a weak semi-bridging interaction; this interaction would occur readily for the trans-diphosphine arrangement but would be less likely in structure D. Also consistent with the proposed inversion at sulfur, the $^{13}C\{^1H\}$ NMR spectra do not change substantially upon cooling. A structural rearrangement involving a cis-diphosphine geometry at Mn would require carbonyl scrambling, which would presumably be evident in the ^{13}C NMR spectra.

The fluxionality of compounds **8** and **9** is also evident in the ^1H NMR spectra, which display four resonances for the four chemically distinct dppm-methylene protons at -80°C, but only two resonances at ambient temperature. For compound **10** the four dppm methylene resonances do not coalesce into two at ambient temperature, but appear as four broad unresolved resonances. In addition, the two diastereotopic protons of the bridging CH_2SiMe_3 group appear as an AB quartet at -80°C and as two broad unresolved resonances at ambient temperature. Although inversion at sulfur, which would exchange dppm-methylene protons pairwise and would also exchange the two thiolato-methylene protons on **10**, was not obvious in the variable temperature ^1H NMR spectra, it was clearly established at -60 °C by spin-saturation-transfer experiments. These showed exchange of the dppm-methylene protons at δ 4.11 and 2.77, and at δ 3.47 and 3.24, and exchange of the thiolato-methylene protons at δ 0.98 and 0.67.

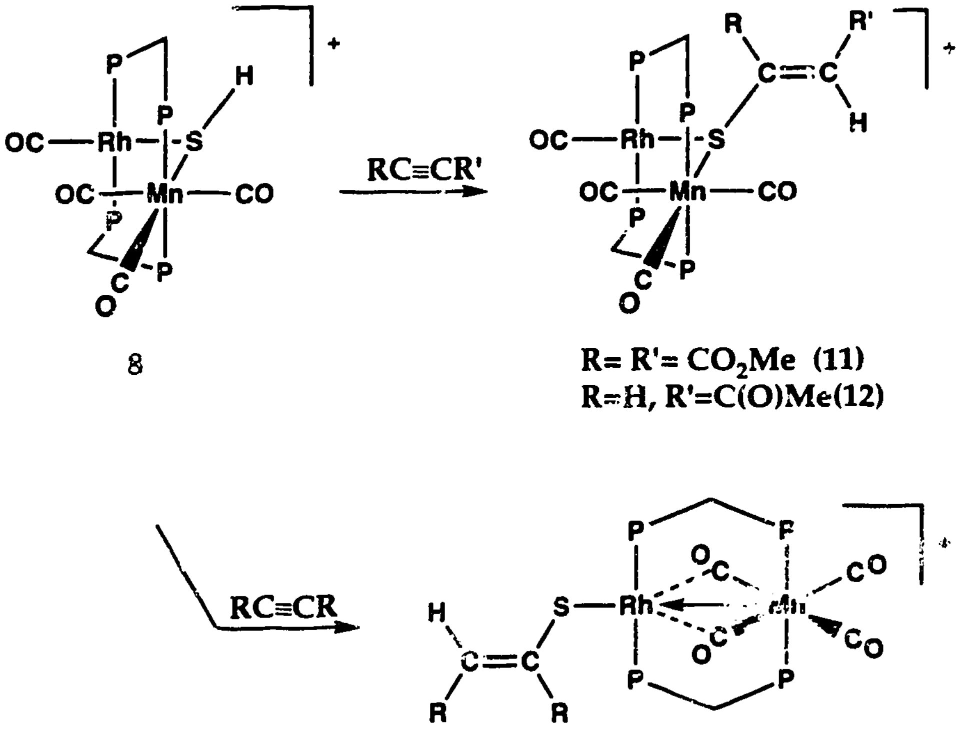
The sulfhydryl proton of 8 appears in the ^1H NMR spectrum at δ -2.67, over the temperature range noted, and displays coupling to all phosphorus nuclei, confirming the bridging arrangement of the SH group.

It was of interest to establish the relative acidities of the terminal and bridging sulfhydryl ligands in these compounds. Although we have not investigated this in depth, we have carried out the deprotonations using piperidine in CH_2Cl_2. As expected, the cationic, sulfhydryl-bridged complex 8 is readily deprotonated by piperidine, reacting instantly to regenerate 7. By contrast the neutral species, $[RhMn(SH)(CO)_3(\mu\text{-}H)(dppm)_2]$ (2) reacts only slowly in the presence of a 100-fold excess of the base yielding comparable amounts of the starting material (2) and compound 7 after 16 h (again the scavanging of CO to give 7 has yielded minor amounts of decomposition products). We had considered that loss of H_2 from 2 may proceed by deprotonation of the sulfhydryl group and subsequent reaction with the metal hydride to give H_2, as has been proposed,[11b] (instead of oxidative addition of the second S-H bond and subsequent reductive elimination of H_2 as noted earlier), however we detect no significant rate difference in the transformation of 2 to 7 in the presence or absence of base.

A characteristic reaction of mercaptans is their Michael addition to α,β-unsaturated substrates,[39] a reactivity that has also been demonstrated for metal complexes containing sulfhydryl groups.[10,40] We find that the terminal sulfhydryl complex $[RhMn(SH)(CO)_3(\mu\text{-}H)(dppm)_2]$ (2) does not react with unsaturated substrates such as dimethyl acetylenedicarboxylate (DMAD), even in the presence of added base, but instead, as noted above, shows only the formation the sulfide-bridged species **7**. However the cationic sulfhydryl-bridged species $[RhMn(CO)_4(\mu\text{-SH})(dppm)_2]^+$ (**8**) does yield the alkyne-insertion products, $[RhMn(CO)_4(\mu\text{-SC(R)=C(H)R'})(dppm)_2]$-$[SO_3CF_3]$, **11** and **12** upon reaction with DMAD and 3-butyn-2-one, respectively, as shown in Scheme 2.2. These Michael-type addition products are proposed, on the basis of their spectroscopic similarities to compounds **8-10**, to be the thiolato-bridged complexes shown. In particular, the $^{13}C\{^1H\}$ NMR spectra show one high-field carbonyl resonance with 74 Hz-coupling to Rh, indicating a terminal Rh-bound CO, and three low-field resonances for the Mn-bound carbonyls. Although none of the Mn-bound carbonyls shows resolvable coupling to Rh, the low frequency stretch in the IR (*ca.* 1800-1850 cm^{-1}) suggests that one of these carbonyls has a weak semibridging interaction with Rh. The configuration of the olefinic moiety in compound **12**, in which the original akyne substituents (H and C(O)Me) are now mutually cis, is established from the ^1H NMR, in which the resonances at δ 6.94 and 5.99 display a trans coupling of 15.2 Hz. Although the olefin stereochemistry of **11** could not be unambiguously determined, it is also assigned as having cis CO_2Me groups, based on analogies with **12**.

Hexafluoro-2-butyne also reacts with **8** to give the 1,2-addition product resulting from alkyne insertion into the S-H bond, namely $[RhMn(SC(CF_3)=C(H)CF_3)(CO)_4$-$(dppm)_2][SO_3CF_3]$ (**13**). Although not technically a Michael-addition reaction, it no doubt proceeds in a similar manner. Interestingly, compound **13** has a terminal rather than a bridging thiolato group, and consequently has different spectral parameters than compounds **8-12**. Whereas the $^{31}P\{^1H\}$ NMR spectra of the thiolato-bridged species (**8-12**) display a temperature dependence (*vide supra*), none was observed for **13**. Moreover, the $^{13}C\{^1H\}$ NMR spectrum at ambient temperature shows only two equal-

Scheme 2.2



8

R= R'= CO_2Me (11)
R=H, R'=C(O)Me(12)

R=CF_3 (13)

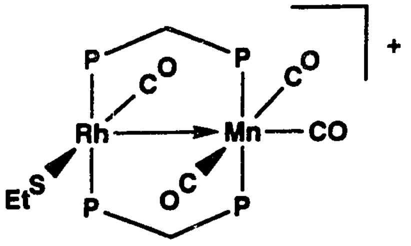
intensity low-field carbonyl resonances (δ 237.8, 236.5) with no resolvable Rh coupling, ruling out a terminally bound CO on Rh. The low-frequency CO stretch in the IR spectrum is again suggestive of a semibridging CO binding mode, leading to the formulation shown above. A dative Mn → Rh bond from the 18e "$Mn(CO)_4P_2^+$" fragment to the 14e Rh(I) center is proposed, in order to give Rh a 16e configuration. At -80°C the two carbonyl resonances resolve into four, presumably because restricted rotation about the Rh-S or S-C bonds can lead to differentiation of the "back" and "front" of the complex, on either side of the $RhMnP_4$ plane. The geometry at the olefin is established based on ^1H and ^{19}F NMR spectra. In the ^{19}F NMR the two olefin-bound CF_3 groups appear at δ -55.81 and -58.93, displaying mutual coupling ($^5J_{F-F}$) of 10 Hz. The low-field resonance also displays geminal coupling to the olefinic proton of 9 Hz, which is verified in the ^1H NMR by the quartet at δ 5.14. These results dictate a cis arrangement of CF_3 groups, based on previous studies[41] which . $^5J_{F-F}$ for a trans arrangement was only 2-2.5 Hz compared to 12-14 Hz

We propose that the destabilization of a bridging thiolato arrangement for **13** results from the effect of the more electronegative CF_3 groups (compared to CO_2Me).[42] These groups would destabilize the bridging arrangement which has a formal positive charge on sulfur by virtue of the dative sulfur-to-metal bond. Although we have no direct evidence, we suggest that the olefinic moiety in compounds **11-13** is not coordinated to either metal, since its arrangement does not appear suitable for interaction with the metals in either the bridging (**11,12**) or terminal (**13**) modes. Such an assignment is consistent with previous studies on analogous species.[10,40]

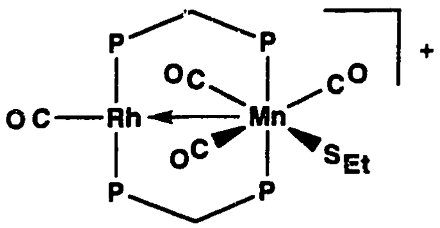
Sulfhydryl- or thiolato-bridged species have been obtained by other routes. Therefore the sulfhydryl-bridged complex **8a** can be obtained by protonation of $[RhMn(SH)(CO)_3(\mu\text{-}H)(dppm)_2]$ (**2**) with $HBF_4 \cdot Et_2O$ via reductive elimination of H_2.

Also obtained in this reaction are the hydride-bridged species, [RhMn(CO)$_4$(μ-H)(dppm)$_2$][BF$_4$] (**14**), from the elimination of H$_2$S, together with decomposition products that were presumably the source of the additional carbonyl in each of these products. Compound **14** could also be prepared directly by protonation of **1**. The hydride resonance of **14** displays coupling to rhodium and to all phosphorus nuclei, indicating that it is bridging and the ^{13}C{^{1}H} NMR at -90°C shows four unique resonances for the terminal carbonyls. Unlike **7**, no evidence for a semibridging carbonyl interaction is found. Presumably the positive charge on the complex and the absence of the π-donor sulfide group renders the rhodium too electron deficient to favor substantial π back donation to one of the Mn-bound carbonyls. The structure of **14** is proposed to be exactly analogous to that determined for the "RhRe" analogue.[22] The reaction of this hydride-bridged species (**14**) with ethanethiol yields two species. The first product, [RhMn(SEt)(CO)$_4$(dppm)$_2$][BF$_4$] (**15**), is proposed to have a terminal thiolate group, based primarily on the spectroscopic data, and in particular on its ^{31}P{^{1}H} NMR spectrum which is temperature invarient, unlike all characterized thiolato-bridged species (*vide supra*). Furthermore, compound **15** transforms with time into an isomeric species **16** which is almost identical in its spectroscopic parameters to the methylthiolato-bridged species **9** so is assigned an analogous structure. Presumably **16** could also have been generated by attack of the C$_2$H$_5$$^+$ electrophile on **7**, as were the analogous species; however this reaction was not attempted. It is particularly noteworthy that the AA'BB'X pattern in the ^{31}P{^{1}H} NMR spectrum of **16** at ambient temperature transforms to an ABCDX pattern at -80°C, exactly as for **9**. Compound **15** is subtly different than **13**, which has an analogous stoichiometry, having a terminal thiolato group and four carbonyls. Whereas **13** has all carbonyls bound to Mn, one carbonyl in **15** is terminally bound to

Rh, as shown by the large ^{103}Rh-^{13}C coupling (83 Hz) involving this group. Unfortunately we have not been able to completely characterize **15**, since it is only observed as an intermediate in the presence of vast excesses of EtSH. Whether the thiolato group is terminally bound to Rh (**E**) or to Mn (**F**) could not be established, however we tend to support structure **F** on the grounds that conversion of **15** to **16** is slow. We would expect that if the thiolato group occupied a site adjacent to the Rh-Mn bond, as in **E**, conversion to **16** would be facile (this also rules out the structure having the thiolato group terminally bound to Mn but cis to the Mn-Rh bond). Assuming the metals in both formulations are in the +1 oxidation state, these formulations differ in the direction of the metal-metal dative bond that is required to give Mn an 18 electron configuration in **E**, or Rh a 16e configuration in **F**. Compounds **15** and **16** were also obtained by protonation of [RhMn(SEt)(CO)$_3$(μ-H)(dppm)$_2$] (**3**) with HBF$_4$•Et$_2$O, although this route yields many other unidentified products since, as noted earlier, **3** is only obtained in *ca.* 10% yield together with other products. Presumably the additional CO in the transformation of **3** to **15** and **16** originates either from CO liberated in the preparation of **3** from **1**, or from decomposition products.



(E)



(F)

Summary and Conclusions

As was previously observed with [RhRe(CO)$_4$(dppm)$_2$],[2] the RhMn analogue, [RhMn(CO)$_4$(dppm)$_2$] (1) reacts with H_2S yielding a sulfido-bridged complexes via H_2 loss. Both S-H bonds in H_2S can be activated by complex 1, probably owing to the fact that the reactive Rh(I) center is regenerated by ligand rearrangement after the oxidative-addition of the first S-H bond. The formation of the terminal sulfhydryl complex [RhMn(SH)(CO)$_3$(μ-H)(dppm)$_2$] (2) clearly shows that the reactive Rh(I) site is regenerated by the hydride moving to the bridging position and one carbonyl ligand dissociating from the complex.

Interestingly, a series of RhMn complexes containing terminal SR ligands, [RhMn(SR)(CO)$_3$(μ-H)(dppm)$_2$] (R=H, 2; Et, 3 and Ph, 4), have been obtained and two of them have been isolated (R=H, 2 and Ph, 3). The formation of the stable binuclear complexes having terminal SR groups is not expected due to the strong tendency of these ligands to bridge two metals, although some dppm-bridged diiridium complexes containing terminal thiolato groups have been reported.[3] By comparison, the RhRe complexes with terminal SR (R=H, Et and Ph) are only observed at low temperature; either the sulfido-bridged complex (R=H) or the thiolato-bridged complexes (R=Et, Ph) are obtained upon warming to ambient temperature. However, it should be pointed out that these unstable RhRe intermediates containing terminal SR groups are tetracarbonyl species whereas the stable RhMn analogues contain only three carbonyl ligands.

As expected, protonation or alkylation of the sulfido-bridged complex 7 gives sulfhydryl- or thiolato-bridged complexes [RhMn(CO)$_4$(μ-SR)(dppm)$_2$]$^+$ (R=H (8), Me (9) and CH$_2$SiMe$_3$ (10), respectively). As was the case in earlier studies involving the complex, [Pt$_2$H$_2$(μ-SMe)(dppm)$_2$][PF$_6$],[43] the fluxionality of these sulfhydryl-bridged or thiolato-bridged complexes has been rationalized as resulting from the inversion of the pyramidal sulfur atoms. The sulfhydryl-bridged complex $[RhMn(CO)_4(\mu\text{-}SH)(dppm)_2]^+$ readily undergoes alkyne insertion into the S-H bond yielding thiolato-bridged complexes $[RhMn(CO)_4(\mu\text{-}SR)(dppm)_2]^+$ (R is C(COOMe)=C(H)COOMe and C(H)=C(H)C(O)Me). However, no reaction is observed in complex $[RhMn(SH)(CO)_3(\mu\text{-}H)(dppm)_2]$ (**2**) containing a terminal SH group.

Unexpectedly, the insertion of HFB into the bridging sulfhydryl group results in the formation of complex $[RhMn(SR)(CO)_2(\mu\text{-}CO)_2(dppm)_2]^+$ (R is $C(CF_3)=C(H)\text{-}CF_3$) having a <u>terminal</u> thiolato ligand. This terminal rather than the bridged bonding of this thiolato group is possibly due to the strong electron withdrawing property of the CF_3 groups that disfavors the formal +1 charge on the bridging thiolato group, resulting from bonds to both metals and to the substituent (R). This indicates that the preference of a ligand for a terminal or a bridging position can be subtly affected by the substituents on the ligand.

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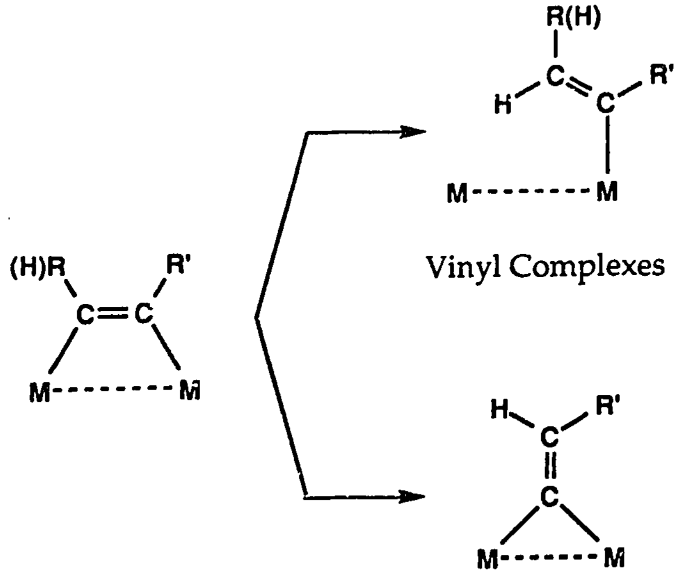
Chapter 3

Alkyne Transformations at RhMn Centers

Introduction

The coordination and activation of alkynes at two metal centers and subsequent transformations involving these substrates have attracted considerable attention.[1] Our recent interest in such chemistry has been aimed at elucidating the alkyne coordination modes in binuclear systems[2-6] with interest in determining the influence of the different binding modes on the subsequent chemistry. Two types of alkyne transformations, occurring at bimetallic cores, that our group have recently been studying involve the conversions to vinyl[7-10] and vinylidene ligands[11-13], as diagrammed below. Vinyl complexes can be prepared by the insertion of alkynes into metal-hydrogen bonds–a fundamental process in organometallic chemistry,[14] or alternately by protonation of preformed alkyne complexes, or of the tautomeric vinylidene analogues[15] (*vide infra*). Recent interest in vinyl complexes stems from reports in which surface-bound vinyl groups, rather than alkyls, have been implicated as key species in Fischer-Tropsch chemistry.[16] These ideas have been based on the ease of migratory insertions involving vinyl and bridging methylene groups, which occur more readily than for the alkyl analogues.[16b,17] The ease of these migratory insertions also suggests applications for vinyl complexes in organic synthesis.[18,19]



Vinyl Complexes

Vinylidene Complexes

Vinylidene complexes can be prepared from 1-alkynes via a 1,2-hydrogen shift occurring at the metals.[15,20] It has been suggested that, like vinyl groups, the vinylidene units also play a key role in Fischer-Tropsch chemistry,[21] as well as in alkyne polymerization,[22] and in C–C bond formation in the condensation of alkynes with a number of substrates.[18,23-31]

The similarity of the vinylidene unit to the isoelectronic carbonyl ligand has been noted,[20] and evidence suggests that a vinylidene group can be an even better π acceptor than CO.[23] Like the ubiquitous CO ligand the vinylidene group can function as a terminal group bound to one metal, or can bridge two or more metals.[15] Furthermore, like CO, the μ_2-vinylidene bridge can adopt a variety of geometries from symmetric[15] to side-on-bound,[32,33] in which it is σ-bound to one metal and π-bound to another.

In spite of the carbonyl-vinylidene analogy and the suggested role of vinylidene units in C-C bond-forming reactions, the migratory insertion of a hydrocarbyl ligand and vinylidene unit had until recently[34,35] not been clearly demonstrated, although evidence for these insertions had been obtained.[36-38] In fact, it has been noted[34] that complexes containing both a hydrocarbyl and a vinylidene unit are conspicuously lacking. This is surprising when it is recalled that migratory insertions involving CO and other unsaturated substrates are well documented and occupy a position of fundamental importance in the formation of C–C bonds.[39] Although little is known about the migratory-insertion reactions involving terminal vinylidenes even less is known about the less studied bridging vinylidene unit.

Among the reactions typical of vinylidenes are nucleophilic attack at the α-carbon or electrophilic attack at the β-carbon.[40] While protonation usually occurs at the β-carbon, generating a carbyne moiety,[15] metal basicity can dominate in square-planar iridium (I) complexes to give hydrido-vinylidene complexes via protonation at the metal.[37,41] On the assumption that binuclear complexes containing a bridging vinylidene adjacent to a Rh(I) center could also have Rh as the most basic site, we have investigated the protonation and alkylation (using CH_3^+) reactions of such species in hopes of obtaining hydrido-vinylidene and alkyl-vinylidene complexes that could be induced to undergo migratory insertions yielding vinyl complexes. The results of this study are presented in this chapter.

Experimental Section

General Procedures. Purified argon and carbon monoxide were obtained from Linde and hydrogen sulfide was obtained from Matheson. The 99% carbon-13-enriched carbon monoxide was purchased from Isotec Inc. All gases were used as received. Diethylether, hexane and tetrahydrofuran were dried over Na-benzophenone ketyl, and methylene chloride was dried over P_2O_5. All solvents were distilled under argon before use. The perdeuterated methylene chloride was dried over molecular sieves and deoxygenated by repeated freeze-pump-thaw cycles. The compounds, dimethyl acetylenedicarboxylate (DMAD), tetrafluoroboric acid-diethyletherate, tetrafluoroboric acid-dimethyletherate, triflic acid, trifluoroacetic acid, 3-butyn-2-one, and methyl triflate were used as received from Aldrich. Hexafluoro-2-butyne (HFB) was received from PCR Inc., hydrated rhodium trichloride from Johnson Matthey, and $Mn_2(CO)_{10}$ from Strem Chemicals Inc. Compounds, $[RhMn(CO)_4(dppm)_2]$ (**1**)[42] and $[RhMn(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ (**2**)[43] were prepared by the reported procedures. Reactions were routinely carried out under Schlenk conditions.

All routine NMR experiments were conducted on a Bruker AM-400 spectrometer, whereas the $^{13}C\{^{31}P\}$ NMR experiments were run on a Bruker AM-200 spectrometer. For all NMR experiments CD_2Cl_2 (except ^2D experiments for which CH_2Cl_2 was used) was used as solvent. IR spectra were recorded on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer as solids (Nujol mull or CH_2Cl_2 cast) or CH_2Cl_2 solutions. Elemental analyses were performed by the microanalytical service within the department. The spectral data for all compounds are given in Tables 3.1 and 3.2. All compounds were moderately air sensitive in solution so were routinely handled under dinitrogen or argon.

Preparation of Compounds. (a) $[RhMn(CO)_3(\mu\text{-}DMAD)(\mu\text{-}CO)(dppm)_2]$ (3a). To a CH_2Cl_2 solution of $[RhMn(CO)_4(dppm)_2]$ (**1**) (50 mg, 48 µmol in 10 mL under CO) was added 15 µL of DMAD (122 µmol) resulting in an immediate color change from yellow to red. After stirring for 1 h the solvent was reduced to *ca.* 1 mL by a rapid flow of CO; at that time a red crystalline solid precipitated from solution. The solid was separated from the mother liquor by filtration and was washed with 1

Table 3.1. Spectroscopic Data for the Compounds.

Compound	IR,cm^{-1} [a]	NMR [a]		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
$RhMn(CO)_3(\mu\text{-DMAD})(\mu\text{-CO})(dppm)_2$ **(3a)**	2003(st),[b] 1949(st), 1860(st), 1727(m), 1674(m), 1654(m)	54.7(b),[d] 17.7(dm, $^1J_{RhP}$=155Hz)	4.33(m, 2H, PCH_2P),[d] 3.09(s, 3H, CH_3), 2.93(m, 2H, PCH_2P), 1.65(s, 3H, CH_3)	248.7(dt, $^1J_{RhC}$=10Hz, $^2J_{P(Mn)C}$=25Hz, 1CO)[f], 223.5(t,$^2J_{P(Mn)C}$=14Hz, 1CO), 221.8(t, $^2J_{P(Mn)C}$=16Hz, 1CO), 193.8(dt, $^1J_{RhC}$=57Hz, $^2J_{P(Rh)C}$=11Hz, 1CO)
	1979(m),[c] 1941(vs), 1857(m), 1732(w), 1675(w), 1654(w)			
$RhMn(CO)_3(\mu\text{-HFB})(\mu\text{-CO})(dppm)_2$ **(3b)**		54.9(b),[e] 13.0(dm, $^1J_{RhP}$=94Hz)	3.98(m, 2H, PCH_2P),[e] 3.14(m, 2H, PCH_2P)	239.5(dt, $^1J_{RhC}$=11Hz, $^2J_{P(Mn)C}$=25Hz, 1CO)[e], 222.3(t,$^2J_{P(Mn)C}$=18Hz, 1CO), 220.8(t, $^2J_{P(Mn)C}$=18Hz, 1CO), 193.5(dt, $^1J_{RhC}$=58Hz, $^2J_{P(Rh)C}$=13Hz, 1CO)

Table 3.1. continued

Compound	IR,cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
$RhMn(CO)_3(\mu\text{-}DMAD)(dppm)_2$ (**4a**)	1985(st),[b] 1887(st), 1819(vs), 1682(m), 1659(sh) 1985(st),[c] 1883(st), 1815(vs), 1672(m), 1652(sh)	51.9(m),[d] 19.8(dm, $^1J_{RhP}$=124Hz)	3.75(m, 2H, PCH_2P),[d] 2.93(m, 2H, PCH_2P), 2.65(s, 3H, CH_3), 2.39(s, 3H, CH_3)	239.1(t, $^2J_{P(Mn)C}$=32Hz, 1CO),[d] 232.2(t, $^2J_{P(Mn)C}$=16Hz, 1CO), 189.7(dt, $^1J_{RhC}$=58Hz, $^2J_{P(Rh)C}$=15Hz, 1CO), 175.0(s, 1C, $\underline{C}O_2CH_3$), 168.0(s, 1C, $\underline{C}O_2CH_3$), 140.9(m, 1C, C=C), 50.3(s, 1C, CH_3), 50.1(s, 1C, CH_3), 22.7(m, 2C,PCH_2P)
$RhMn(CO)_3(\mu\text{-}HFB)(dppm)_2$ (**4b**)	1997(st),[b] 1987(st), 1896(st), 1827(vs) 2003(st),[c] 1991(sh), 1893(st), 1823(vs)	46.1(m),[e] 17.3(dm, $^1J_{RhP}$=120Hz)	3.57(b, 2H, PCH_2P),[e] 3.04(m, 2H, PCH_2P)	238.5(t, $^2J_{P(Mn)C}$=33Hz, 1CO),[e] 236.5(t, $^2J_{P(Mn)C}$=14Hz, 1CO), 190.7(dt, $^1J_{RhC}$=57Hz, $^2J_{P(Rh)C}$=14Hz, 1CO),
$[RhMn(CO)_3(\mu\text{-}\eta^2\text{:}\eta^2\text{-}DMAD)(dppm)_2$ (**5a**)		98.9(m),[d] 31.3(dm, $^1J_{RhP}$=140Hz)	3.46(m,4H, PCH_2P),[d] 3.17(s, 6H, CH_3)	242.0(t, $^2J_{P(Mn)C}$=48Hz, 1CO),[d] 225.1(t, $^2J_{P(Mn)C}$=38Hz, 1CO), 194.0(dtt, $^1J_{RhC}$=73Hz, $^2J_{P(Rh)C}$=17Hz,$^2J_{P(Mn)C}$=5Hz, 1CO), 176.0(s, 1C, $\underline{C}O_2CH_3$), 51.9(s, 2C, CH_3)

Table 3.1. continued

Compound	IR,cm^{-1}	NMR		
		δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C)
RhMn(CO)$_3$(μ-η^2:η^2-HFB)(dppm)$_2$ **(5b)**		100.0(m),^{e} 39.7(dm, $^1J_{RhP}$=130Hz)	3.57(b, 2H, PCH$_2$P),^{e} 2.61(b, 2H, PCH$_2$P)	243.2(t, $^2J_{P(Mn)C}$=46Hz, 1CO),^{d} 225.5(t, $^2J_{P(Mn)C}$=44Hz, 1CO), 192.3(dt, $^1J_{RhC}$=73Hz, $^2J_{P(Rh)C}$=15Hz, 1CO)
[RhMn(H)(CO)$_4$(μ-DMAD)(dppm)$_2$]-[BF$_4$] **(6a)**		42.0(m),^{h} 18.1(dm, $^1J_{RhP}$=104Hz)	4.11(m,2H, PCH$_2$P),^{h} 3.22(s, 3H, CH$_3$), 3.17(m, 2H, PCH$_2$P), 1.90(s, 3H, CH$_3$), -14.30(dt,$^1J_{RhH}$= 38Hz, $^2J_{P(Rh)H}$= 7Hz, 1H, hydride)	222.9(b, 1CO),^{h} 217.8(b, 1CO), 211.4(b, 1CO), 183.8(db, $^1J_{RhC}$=46Hz, 1CO)
[RhMn(H)(CO)$_4$(μ-HFB)(dppm)$_2$]-[BF$_4$] **(6b·BF$_4$)**		42.5(b),^{e} 15.0(bd, $^1J_{RhP}$=98Hz)	3.87(m,2H, PCH$_2$P),^{e} 3.29(m, 2H, PCH$_2$P), -12.28(bd,$^1J_{RhH}$= 34Hz, 1H, hydride)	222.6(b, 1CO),^{e} 221.9(b, 1CO), 211.4(b, 1CO), 183.0(dt, $^1J_{RhC}$=45Hz, $^2J_{P(Rh)C}$=10Hz, 1CO)
[RhMn(H)(CO)$_4$(μ-HFB)(dppm)$_2$]-[CO$_2$CF$_3$] **(6b·CO$_2$CF$_3$)**		42.5(b),^{e} 14.9(dm, $^1J_{RhP}$=97Hz)	3.87(m,2H, PCH$_2$P),^{e} 3.28(m, 2H, PCH$_2$P), -12.29(bd,$^1J_{RhH}$= 34Hz, 1H, hydride)	

Table 3.1. continued

Compound	IR,cm^{-1}	NMR δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C)
[RhMn(CR=CHR)(CO)$_2$(μ-CO)$_2$(dppm)$_2$]-[BF$_4$] (R=COOMe) (**7a·BF$_4$**)	2028(st),^{b} 1968(st), 1840(sh), 1813(m), 1706(st), 1585(w) 2031(st),^{c} 1982(st), 1854(m), 1809(m), 1705(st), 1585(w)	55.0(m),^{e} 23.4(dm, $^1J_{RhP}$=127Hz)	4.38(d, $^3J_{RhCCH}$=2 Hz, 1H,C$\underline{H}$R=CR),^{e} 3.13(s, 3H, CH$_3$), 3.07(s, 3H, CH$_3$), 3.07(m, 4H, PCH$_2$P)	243.4(dt, $^1J_{RhC}$=29Hz, $^2J_{P(Mn)C}$=8Hz, 1CO),^{e} 235.6(dt, $^1J_{RhC}$=$^2J_{P(Mn)C}$= 14Hz, 1CO), 219.5(t, $^2J_{P(Mn)C}$=20Hz, 1CO), 213.7(t. $^2J_{P(Mn)C}$=17Hz, 1CO)
[RhMn(CR=CHR)(CO)$_2$(μ-CO)$_2$(dppm)$_2$]-[SO$_3$CF$_3$] (R=COOMe) (**7a·SO$_3$CF$_3$**)	2028(st),^{b} 1972(st), 1848(sh), 1814(m), 1711(st), 1586(w) 2032(st),^{c} 1978(st), 1850(m), 1803(m), 1701(st), 1582(w)	55.2(m),^{d} 23.3(dm, $^1J_{RhP}$=127Hz)	4.47(d, $^3J_{RhCCH}$=2Hz, 1H, C$\underline{H}$R=CR),^{d} 3.16(s, 3H, CH$_3$), 3.10(s, 3H, CH$_3$), 3.10(m, 4H, PCH$_2$P)	

Table 3.1. continued

Compound	IR,cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
$[RhMn(CR{=}CHR)(CO)_2(\mu\text{-}CO)_2(dppm)_2]$- $[BF_4]$ $(R{=}CF_3)$ (**7b·BF$_4$**)		54.6(m),^{d} 21.9(dm, $^1J_{RhP}$=123Hz)	5.06(q, $^3J_{HCCF}$=9 Hz, 1H,$C\underline{H}R{=}CR$),^{e} 3.17(m, 2H,PCH_2P) 3.11(m, 2H,PCH_2P)	243.8(dt,$^1J_{RhC}$=29Hz, $^2J_{P(Mn)C}$=9Hz, 1CO),^{e} 237.8(dt, $^1J_{RhC}$=16Hz, $^2J_{P(Mn)C}$=12Hz, 1CO), 216.9(t, $^2J_{P(Mn)C}$=18Hz, 1CO), 214.8(t. $^2J_{P(Mn)C}$=17Hz, 1CO)
$[RhMn(CO)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CR{=}CHR)(dppm)_2]$- $[BF_4]$ $(R{=}COOMe)$ (**8a·BF$_4$**)	2031(st),^{c} 1989(m), 1850(sh), 1810(m)	48.1(m),^{h} 18.5(dm, $^1J_{RhP}$=117Hz)		238.1(t, $^2J_{P(Mn)C}$=12Hz,1CO),^{h} 233.7(t, $^2J_{P(Mn)C}$=30Hz,1CO), 190.0(dt, $^1J_{RhC}$=56Hz, $^2J_{P(Rh)C}$=13Hz,1CO)
$[RhMn(CO)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CR{=}CHR)(dppm)_2]$- $[CO_2CF_3]$ $(R{=}COOMe)$ (**8a·CO$_2$CF$_3$**)		48.0(m),^{h} 18.4(dm, $^1J_{RhP}$=118Hz)	3.12(b, 2H, PCH_2P),^{h} 2.85(b, 2H, PCH_2P), 2.34(b, 3H, CH_3), 2.13(b, 3H, CH_3)	
$[RhMn(C(Me){=}CH_2)(CO)_2(\mu\text{-}CO)_2$- $(dppm)_2][SO_3CF_3]$ (**9a**)	2004(st),^{b} 1966(vs), 1810(sh), 1796(vs) 2018(vs),^{c} 1975(st), 1810(sh), 1797(st)	58.2(m),^{d} 21.0(dm, $^1J_{RhP}$=147Hz)	4.98(m, 1H, $C{=}CH_2$),^{d} 4.40(s, 1H, $C{=}CH_2$), 3.14(m, 4H, PCH_2P), 0.91(s, 3H, CH_3)	247.0(dt, $^1J_{RhC}$=20Hz, $^2J_{P(Mn)C}$=11Hz,1CO),^{d} 246.7(dt, $^1J_{RhC}$=20Hz, $^2J_{P(Mn)C}$=11Hz,1CO), 218.9(t, $^2J_{P(Mn)C}$=20Hz,1CO), 218.0(t, $^2J_{P(Mn)C}$=19Hz,1CO),

Table 3.1. continued

Compound	IR,cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
[RhMn($CH_2CH{=}CH_2$)$(CO)_2$(μ-CO)$_2$-(dppm)$_2$][SO_3CF_3] (**9b**)		58.6(m),^{e} 26.4(dm, $^1J_{RhP}$=146Hz)	~5.30 ($C\underline{H}{=}CH_2$),^{e} 3.70(d, 1H, $^3J_{cis}$=10Hz, $CH{=}C\underline{H}_2$), 3.12(2H, m, PCH_2P), 3.06(2H, m, PCH_2P), 2.73(dt, 2H, $^3J_{HCCH}$=6Hz, $^3J_{P(Rh)CH}$=8Hz, $C\underline{H}_2CH{=}CH_2$), 2.63(d, 1H, $^3J_{trans}$=17Hz, $CH{=}C\underline{H}_2$)	247.7(dt, $^1J_{RhC}$=23Hz, $^2J_{P(Mn)C}$=12Hz, 2CO),^{d} 218.5(t, $^2J_{P(Mn)C}$=18Hz,2CO)
[RhMnMe$(CO)_2$(μ-CO)$_2$(dppm)$_2$]-[SO_3CF_3] (**10a**)	2008(st),^{b} 1973(st), 1838(m), 1800(st) 2016(vs),^{c} 1973(st), 1815(sh), 1797(st)	60.0(m),^{d} 30.4(dm, $^1J_{RhP}$=139Hz)	3.11(m, 4H, PCH_2P),^{d} 0.92(dt, 3H, CH_3, $^2J_{RhH}$=2Hz, $^3J_{P(Rh)CH}$=11Hz)	247.2(dt, 2CO, $^1J_{RhC}$=22Hz, $^2J_{P(Mn)C}$=13Hz),^{d} 219.0(t, 1CO, $^2J_{P(Mn)C}$=19Hz)

Table 3.1. continued

		NMR		
Compound	IR,cm^{-1}	$\delta(^{31}P\{^{1}H\})$	$\delta(^{1}H)$	$\delta(^{13}C)$
$[RhMnMe(CO)_2(\mu\text{-}CO)_2(dppm)_2][I]$ (**10b**)	2016(vs),[c] 1974(st), 1820(sh), 1798(vs)	60.1(m),[d] 30.4(dm, $^{1}J_{RhP}$=139Hz)	3.13(m, 4H, PCH_2P),[d] 0.92(dt, 3H, CH_3, $^{2}J_{RhH}$=2Hz, $^{3}J_{P(Rh)CH}$=11Hz)	
$[RhMn(C(O)Me)(CO)_2(\mu\text{-}CO)_2(dppm)_2]$-$[SO_3CF_3]$ (**11**)	2008(vs),[b] 1972(st), 1839(m), 1798(st) 1665(m) 2018(vs),[c] 1971(st), 1820(sh), 1797(st) 1655(m)	58.4(m),[d] 14.9(dm, $^{1}J_{RhP}$=162Hz)	3.14(m, 4H, PCH_2P),[d] 1.04(s, 3H, CH_3)	251.3(d, 1CO, $^{1}J_{RhC}$=28Hz),[c] 246.5(dt, $^{1}J_{RhC}$=20Hz, $^{2}J_{P(Mn)C}$=12Hz, 1CO), 240.9(dt, $^{1}J_{RhC}$=10Hz, $^{2}J_{P(Mn)C}$=18Hz, 1CO), 217.9(t, $^{2}J_{P(Mn)C}$=20Hz, 1CO), 215.8(t, $^{2}J_{P(Mn)C}$=18Hz, 1CO)
$[RhMn(CO)_3(\mu\text{-}H)(\mu\text{-}HFB)(dppm)_2]$-$[BF_4]$(**12**)		46.1(b),[j] 13.9(dm, $^{1}J_{RhP}$=90Hz)	3.81(m, 2H, PCH_2P),[j] -16.98(bd, hydride, $^{1}J_{RhH}$=15Hz)	232.4(t, $^{2}J_{P(Mn)C}$=29Hz, 1CO),[j] 228.8(m, 1CO), 184.4(dm, $^{1}J_{RhC}$=58Hz, 1CO)

Table 3.1. continued

Compound	IR,cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
$[RhMn(CO)_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}HFB)\text{-}(dppm)_2][BF_4]$(**13a**)		82.9(m),^{j} 32.0(dm, $^1J_{RhP}$=135Hz)	3.16(m, 2H, PCH_2P),^{j} -20.83(dtt, hydride, $^1J_{RhH}$=15Hz, $^2J_{P(Rh)H}$=14Hz, $^2J_{P(Mn)H}$=26Hz)	231.6(t, $^2J_{P(Mn)C}$=53Hz, 1CO),^{j} 217.2(m, 1CO), 186.2(dm, $^1J_{RhC}$=63Hz, 1CO)
$[RhMn(CO)_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}HFB)\text{-}(dppm)_2][CO_2CF_3]$(**13b**)		82.9(m),^{j} 32.0(dm, $^1J_{RhP}$=135Hz)	3.29(m, 2H, PCH_2P),^{j} 3.16(m, 2H, PCH_2P), -20.83(dtt, hydride, $^1J_{RhH}$=16Hz, $^2J_{P(Rh)H}$=12Hz, $^2J_{P(Mn)H}$=26Hz)	231.0(t, $^2J_{P(Mn)C}$=53Hz, 1CO),^{e} 217.2(m, 1CO), 185.8(dm, $^1J_{RhC}$=64Hz, 1CO)
$RhMn(CH_2{=}CC(O)Me)(CO)_2(\mu\text{-}CO)_2\text{-}(dppm)_2][SO_3CF_3]$ (**14**)		57.7(m),^{d} 22.4(dm, $^1J_{RhP}$=134Hz)	5.89(dt, $^3J_{RhCCH}$=3Hz, $^4J_{PRhCCH}$=2Hz, 1H, $CH_2{=}C$),^{d} 5.42(t, $^4J_{PRhCCH}$=2Hz, 1H, $CH_2{=}C$), 3.22(m, 2H, PCH_2P), 3.10(m, 2H, PCH_2P), 1.20(s, 3H, CH_3)	249.7(dm, $^1J_{RhC}$=32Hz, 1CO),^{d} 237.8(dt, $^1J_{RhC}$=13Hz, $^2J_{P(Mn)C}$=15Hz, 1CO), 218.5(t, $^2J_{P(Mn)C}$=19Hz, 1CO), 217.4(t, $^2J_{P(Mn)C}$=18Hz, 1CO)

Table 3.1. continued

Compound	IR,cm^{-1}	NMR $\delta(^{31}P\{^1H\})$	 $\delta(^1H)$	 $\delta(^{13}C)$
[RhMn(<u>trans</u>-CH=CHC(O)Me)$(CO)_2$- (μ-CO)$_2$(dppm)$_2$][SO_3CF_3] **(15a)**	2036(st),^{b} 1974(vs), 1845(w), 1815(st), 1654(m) 2026(vs),^{c} 1984(st), 1838(sh), 1809(st), 1654(m)	58.8(m),^{d} 24.3(dm, $^1J_{RhP}$=134Hz)	7.99(dt, 1H$_\alpha$, $^3J_{HCCH}$=17Hz, $^3J_{P(Rh)CH}$=7Hz),^{d} 5.32(d, 1H$_\beta$, $^3J_{HCCH}$=17Hz), 3.16(m, 4H, PCH_2P), 1.05(s, 3H, CH_3)	244.1(dt, $^1J_{RhC}$=22Hz, $^2J_{P(Mn)C}$=11Hz, 2CO),^{d} 217.4(t, $^2J_{P(Mn)C}$=17Hz, 2CO)
[RhMn(<u>trans</u>-CH=CHC(O)Me)$(CO)_2$- (μ-CO)$_2$(dppm)$_2$][BF_4] **(15b)**	2026(vs),^{c} 1982(st), 1830(sh), 1807(st) 1652(m)	58.8(m),^{d} 24.3(dm, $^1J_{RhP}$=134Hz)	8.00(dt, 1H$_\alpha$, $^3J_{HCCH}$=17Hz, $^3J_{P(Rh)CH}$=7Hz),^{d} 5.32(d, 1H$_\beta$, $^3J_{HCCH}$=17Hz), 3.16(m, 4H, PCH_2P), 1.04(s, 3H, CH_3)	244.1(dt, $^1J_{RhP}$=21Hz, $^2J_{P(Mn)C}$=12Hz, 2CO),^{d} 217.4(t, $^2J_{P(Mn)C}$=16Hz, 2CO)
RhMn$(CO)_4$(μ-HC=CC(O)Me)(dppm)$_2$ **(16)**		56.7(m),^{e} 15.7(dm, $^1J_{RhP}$=157Hz)	9.99(b, 1H, HC=C),^{e} 3.87(b, 2H, PCH_2P), 2.85(b, 2H, PCH_2P), 0.59(s, 3H, CH_3)	228.3(b, 1CO),^{e} 221.3(b, 1CO), 220.5(b, 1CO), 195.6(dt, $^1J_{RhC}$=58Hz, $^2J_{P(Rh)C}$=12Hz, 1CO)

Table 3.1. continued

Compound	IR,cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
RhMn(CO)$_3$(μ-CCHC(O)Me)(μ-CO)(dppm)$_2$ **(17a)**		67.7(m),^{e} 35.2(dm, $^1J_{RhP}$=170Hz)	6.59(t, 1H$_\beta$, $^4J_{P(Rh)CCH}$= 12Hz),^{e} 2.98(m, 2H, PCH$_2$P), 2.19(m, 2H, PCH$_2$P), 1.55(s, 3H, CH$_3$)	244.9(dt, $^1J_{RhC}$=15Hz, $^2J_{P(Mn)C}$=21Hz, 1CO),^{e} 229.5(t, $^2J_{P(Mn)C}$=13Hz, 1CO) 223.4(t, $^2J_{P(Mn)C}$=18Hz, 1CO), 206.2(dt, $^1J_{RhC}$=59Hz, $^2J_{P(Mn)C}$=20Hz, 1CO)
RhMn(CO)$_3$(μ-CCHC(O)Me)(μ-CO)-(dppm)$_2$(**17b**)	1964(w),^{d} 1907(st), 1857(vs), 1788(m)), 1597(st) 2002(sh),^{c} 1946(vs), 1887(st), 1801(m), 1600(w)	64.1(m),^{d} 23.1(dm, $^1J_{RhP}$=163Hz)	8.09(t, 1H$_\beta$, $^4J_{P(Rh)CCH}$= 7Hz),^{d} 3.28(m, 2H, PCH$_2$P), 2.46(m, 2H, PCH$_2$P), 0.62(s, 3H, CH$_3$)	242.0(dt, $^1J_{RhC}$=10Hz, $^2J_{P(Mn)C}$=18Hz, 1CO),^{d} 226.6(t, $^2J_{P(Mn)C}$= 17Hz, 1CO), 223.8(t, $^2J_{P(Mn)C}$=20Hz, 1CO), 207.6(dt, $^1J_{RhC}$=56Hz, $^2J_{P(Rh)C}$=20Hz, 1CO), 193.8(s, 1C, $\underline{C}$(O)CH$_3$), 146.8(s, 1C$_\beta$), 137.4(dtt, $^1J_{RhC}$=4Hz, $^2J_{P(M)C}$=19Hz, $^2J_{P(M')C}$= 4Hz, 1C$_\alpha$), 22.0(s, 1C, CH$_3$)

Table 3.1. continued

Compound	IR,cm^{-1}	NMR $\delta(^{31}P\{^1H\})$	 $\delta(^1H)$	 $\delta(^{13}C)$
$RhMn(CO)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CCHC(O)Me)\text{-}(dppm)_2$(**18**)	1937(st),[b] 1876(vs), 1790(m) 1942(st),[c] 1893(vs), 1808(m)	73.1(m),[d] 29.6(dm, $^1J_{RhP}$=175Hz)	3.08(m, 2H, PCH_2P),[d] 2.68(m, 2H, PCH_2P), 0.99(t, 3H, CH_3, $^5J_{P(Mn)OCCH}$=2Hz)	230.1(t, $^2J_{P(Mn)C}$=14Hz, 1CO),[d] 228.7(t, $^2J_{P(Mn)C}$=20Hz, 1CO), 206.2(dt, $^1J_{RhC}$=57Hz, $^2J_{P(Rh)C}$=15Hz, 1CO), 190.8(s, 1C, $\underline{C}(O)CH_3$), 140.1(s, $1C_\beta$), 138.3(tt, $^2J_{P(Mn)C}$=14.4Hz, $^2J_{P(Rh)C}$=4Hz, $1C_\alpha$), 23.8(s, 1C, CH_3)
$RhMn(CO)_3(\mu\text{-}CCHC(OH)Me)(\mu\text{-}CO)\text{-}(dppm)_2[BF_4]$ (**19**)		61.3(m),[h] 23.6(m)	9.30(b, 1H, OH),[f] 2.62(b, 2H, PCH_2P), 0.81(s, 3H, Me)	236.0(dt, $^1J_{RhC}$=20Hz, $^2J_{P(Mn)C}$=16Hz, 1CO),[h] 227.4(t, $^2J_{P(Mn)C}$=18Hz, 1CO) 220.9(t, $^2J_{P(Mn)C}$=20Hz, 1CO), 206.8(dt, $^1J_{RhC}$=56Hz, $^2J_{P(Mn)C}$=19Hz, 1CO)

Table 3.1. continued

Compound	IR,cm^{-1}	NMR δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C)
[RhMn(<u>cis</u>-CH=CHC(O)Me)(CO)$_2$-(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**20a**)	2015(st),[b] 1972(st), 1857(m), 1751(m), 1617(w) 2014(vs),[c] 1966(st), 1859(st), 1736(st), 1613(w)	58.0(m),[d] 25.3(dm, $^{1}J_{RhP}$=124Hz)	9.20(ddt, 1H$_\alpha$, $^{3}J_{HCCH}$=7.5Hz, $^{2}J_{RhCH}$=5Hz, $^{3}J_{P(Rh)CH}$=6Hz),[d] 6.42(dd, 1H$_\beta$, $^{3}J_{HCCH}$=7.5Hz, $^{3}J_{RhCCH}$=2.5Hz), 3.34(m, 2H, PCH$_2$P), 3.15(m, 2H, PCH$_2$P), 1.03(s, 3H, Me)	259.8(dqui, $^{1}J_{RhC}$=41Hz, $^{2}J_{P(Rh)C}$=$^{2}J_{P(Mn)C}$=9Hz, 1CO),[d] 231.9(dt, $^{1}J_{RhC}$=12Hz, $^{2}J_{P(Mn)C}$=13Hz, 1CO), 219.7(t, $^{2}J_{P(Mn)C}$=22Hz, 1CO), 218.0(t, $^{2}J_{P(Mn)C}$=15Hz, 1CO)
[RhMn(<u>cis</u>-CD=CHC(O)Me)(CO)$_2$-(μ-CO)$_2$(dppm)$_2$][CO$_2$CF$_3$] (**20b**)		57.6(m),[d] 25.1(dm, $^{1}J_{RhP}$=126Hz)	6.42(d, 1H$_\beta$, $^{3}J_{RhCCH}$=2.5Hz),[d] 3.35(m, 2H, PCH$_2$P), 3.13(m, 2H, PCH$_2$P), 1.03(s, 3H, CH$_3$)	
[RhMn(<u>cis</u>-CH=CDC(O)Me)(CO)$_2$-(μ-CO)$_2$(dppm)$_2$][CO$_2$CF$_3$] (**20c**)		57.8(m),[d] 25.2(dm, $^{1}J_{RhP}$=126Hz)	9.20(m, 1H$_\alpha$),[d] 3.35(m, 2H, PCH$_2$P), 3.13(m, 2H, PCH$_2$P), 1.04(s, 3H, CH$_3$)	

Table 3.1. continued

Compound	IR,cm^{-1}	NMR $\delta(^{31}P\{^1H\})$	 $\delta(^1H)$	 $\delta(^{13}C)$
$[RhMn(\eta^2\text{-}CHCH{=}C(O)Me)(CO)_3\text{-}(dppm)_2][SO_3CF_3]$ **(21a)**	1981(vs),^{b} 1934(st), 1820(st), 1987(st),^{c} 1939(st), 1818(m),	67.1(m),^{d} 25.7(dm, $^1J_{RhP}$=107Hz)	8.04(dt, $^3J_{HCCH}$=10Hz, $^3J_{P(Mn)CH}$=2.5Hz, 1H$_\beta$),^{d} 3.24(m, 2H, PCH_2P), 2.94(m, 2H, PCH_2P), 0.98(t, 3H, CH_3, $^5J_{P(Mn)OCCH}$=3Hz)	228.8(t, $^2J_{P(Mn)C}$=23Hz, 1CO),^{d} 225.0(t, $^2J_{P(Mn)C}$=17Hz, 1CO), 186.7(dt, $^1J_{RhC}$=80Hz, $^2J_{P(Rh)C}$=18Hz, 1CO)
$[RhMn(\eta^2\text{-}CDCH{=}C(O)Me)(CO)_3\text{-}(dppm)_2][CO_2CF_3]$ **(21b)**		67.0(m),^{d} 25.6(dm, $^1J_{RhP}$=107Hz)	7.91(t, $^3J_{P(Mn)CH}$=2.5Hz, 1H$_\beta$),^{d} 3.24(m, 2H, PCH_2P), 2.83(m, 2H, PCH_2P), 0.92(t, $^5J_{P(Mn)OCCH}$=3Hz, 3H, CH_3)	
$[RhMn(Z\text{-}C(Me){=}CHC(O)Me)(CO)_2\text{-}(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]$ **(22)**	2006(st),^{b} 1953(st), 1864(m), 1728(m), 1605(w) 2016(st),^{c} 1957(st), 1869(st), 1723(m), 1603(w)	58.1(m),^{d} 20.0(dm, $^1J_{RhP}$=125Hz)	6.30(s, 1H, H$_\beta$),^{d} 3.30(m, 2H, PCH_2P), 3.15(m, 2H, PCH_2P), 1.57(s, 3H, CH_3), 1.41(s, 3H, CH_3)	260.7(dtt, $^1J_{RhC}$=45Hz, $^2J_{P(Rh)C}$=$^2J_{P(Mn)C}$=8Hz, 1CO),^{d} 230.1(dt, $^1J_{RhC}$=5Hz, $^2J_{P(Mn)C}$=15Hz, 1CO), 220.0(t, $^2J_{P(Mn)C}$=17Hz, 1CO), 218.9(t, $^2J_{P(Mn)C}$=20Hz, 1CO)

Table 3.1. continued

Compound	IR,cm^{-1}	NMR δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C)
[RhMn(Me)(CO)$_3$(μ-η^1:η^2-CCH=C(O)Me)-(dppm)$_2$][SO$_3$CF$_3$] (**23**)		62.9(m),[e] 26.0(dm, $^1J_{RhP}$=101Hz)	3.40(b, 2H, PCH$_2$P),[e] 2.89(b, 2H, PCH$_2$P), 1.43(b, 3H, CH$_3$), 0.04(b, 3H, CH$_3$)	227.6(t, $^2J_{P(Mn)C}$=17Hz, 1CO),[e] 225.8(t, $^2J_{P(Mn)C}$=13Hz, 1CO), 193.2(dt, $^1J_{RhC}$=47Hz, $^2J_{P(Rh)C}$=16Hz, 1CO) 26.0(s, 1C, CH$_3$),[i] 20.4(m, 2C, PCH$_2$P), 9.0(db, $^1J_{RhC}$=27Hz, 1C, CH$_3$)
RhMn(η^2-MeC=CHC(O)Me)(CO)$_3$-(dppm)$_2$][SO$_3$CF$_3$] (**24**)		57.7(m),[i] 29.1(dm, $^1J_{RhP}$=127Hz)	6.04(b, 1H$_β$),[i] 3.70(b, 2H, PCH$_2$P), 3.44(b, 2H, PCH$_2$P), 1.44(b, 3H, CH$_3$), 0.72(b, 3H, CH$_3$)	231.0(t, $^2J_{P(Mn)C}$=27Hz, 1CO),[i] 229.7(t, $^2J_{P(Mn)C}$=15Hz, 1CO), 192.4(dt, $^1J_{RhC}$=49Hz, $^2J_{P(Rh)C}$=14Hz, 1CO), 29.6(s, 1C, CH$_3$)[f], 29.1(s, 1C, CH$_3$), 28.5(m, 2C, PCH$_2$P)
[RhMn(CO)$_3$(μ-η^1:η^1-MeC=CHC(O)Me)-(dppm)$_2$][SO$_3$CF$_3$] (**25**)	1993(st),[b] 1979(st), 1910(st), 1846(st), 1992(st),[c] 1926(st), 1862(vs)	58.2(m),[d] 24.2(dm, $^1J_{RhP}$=128Hz)	6.77(s, 1H$_β$),[d] 3.17(m, 2H, PCH$_2$P), 2.43(m, 2H, PCH$_2$P), 1.97(t, 3H, CH$_3$, $^5J_{P(Mn)OCCH}$=3Hz), 1.27(s, 3H, CH$_3$)	231.3(t, $^2J_{P(Mn)C}$=20Hz, 1CO),[d] 222.2(t, $^2J_{P(Mn)C}$=19Hz, 1CO), 190.4(dt, $^1J_{RhC}$=77Hz, $^2J_{P(Rh)C}$=15Hz, 1CO), 202.1(s, 1C, <u>C</u>(O)CH$_3$), 138.7(m, 1C$_α$), 36.0(s, 1C, CH$_3$), 25.7(s, 1C, CH$_3$)

[a] Abbreviations used IR: w = weak; m = medium; st = strong; vs = very strong. NMR: s = singlet; d = doublet; t = triplet; q = quartet; qui = quintet; m = multiplet; b = broad; or any combination. [b] Nujol mull. [c] CH$_2$Cl$_2$ solution. [d] 22°C. [e] -40°C. [f] -60°C. [g] -70°C. [h] -80°C. [i] -20°C. [j] 0°C.

Table 3.2. ^{19}F NMR Data for the Compounds.

Compounds	$\delta(^{19}F)^a$
$RhMn(CO)_3(\mu\text{-HFB})(\mu\text{-CO})(dppm)_2$ **(3b)**	-50.1(q, $^5J_{FF}=17Hz$, 3F),^{b} -51.1(q, $^5J_{FF}=17Hz$, 3F)
$RhMn(CO)_3(\mu\text{-HFB})(dppm)_2$ **(4b)**	-40.8(tq, $^4J_{P(Mn)CCF}=8Hz$, $^5J_{FF}=13Hz$, 3F),^{b} -49.0(ttq, $J_{P(Mn)F}=4Hz$, $^4J_{P(Rh)CCF}=6Hz$, $^5J_{FF}=13Hz$, 3F)
$RhMn(CO)_3(\mu\text{-}\eta^2\text{:}\eta^2\text{-HFB})(dppm)_2$ **(5b)**	-44.8(m),^{b}
$[RhMn(H)(CO)_4(\mu\text{-HFB})(dppm)_2]$- $[BF_4]$ **(6b·BF$_4$)**	-51.1(q, $^5J_{FF}=18Hz$, 3F),^{b} -51.8(q, $^5J_{FF}=18Hz$, 3F)
$[RhMn(CR{=}CHR)(CO)_2(\mu\text{-CO})_2(dppm)_2]$- $[BF_4]$ ($R=CF_3$) **(7b·BF$_4$)**	-51.1(q, $^5J_{FF}=12Hz$, 3F),^{c} -59.1(q, $^5J_{FF}=12Hz$, 3F)
$[RhMn(CO)_3(\mu\text{-H})(\mu\text{-HFB})(dppm)_2]$- $[BF_4]$**(11)**	-45.7(q, $^5J_{FF}=17Hz$, 3F),^{d} -55.7(q, $^5J_{FF}=17Hz$, 3F)
$[RhMn(CO)_3(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^2\text{-HFB})$- $(dppm)_2][BF_4]$**(12a)**	-45.8(m),^{d}

[a] see footnotes on Table 3.1 for abbreviations. [b] -40°C. [c] 22°C. [d] 0°C.

mL of CH_2Cl_2. A red crystalline solid was obtained in 70% yield and was stored under CO. Anal. Calcd. for $RhMnP_4O_8C_{60}H_{50}\bullet CH_2Cl_2$: C, 57.88; H, 4.14; Cl, 5.60. Found: C, 57.79; H, 4.16; Cl, 5.66.

(b) **[RhMn(CO)$_3$(μ-HFB)(μ-CO)(dppm)$_2$] (3b).** A CH_2Cl_2 solution of compound **4b** and **5b** (100 mg in 10 mL) was put under CO (10 psi). The solution was cooled to -78°C and stirred for 1 h. The color of the solution changed to orange from green and an orange solid precipitated out of the solution. 50 mL of hexane was added to precipitate the solid and the supernatant was removed by canula. The solid was dried by the rapid flow of CO and the solid was stored under CO. The solid was unstable in air toward the loss of CO therefore the elemental analysis was not attempted.

(c) **[RhMn(CO)$_3$(μ-DMAD)(dppm)$_2$] (4a).** To a THF solution of [RhMn(CO)$_4$-(dppm)$_2$] (**1**) (50 mg, 48 μmol in 10 mL) was added 8 μL of DMAD (65 μmol). Refluxing for 1 h yielded a black-purple solution. Recrystallization from CH_2Cl_2/hexane gave a black solid in 80% yield. Anal. Calcd. for $RhMnP_4O_7C_{49}H_{50}\bullet 0.6CH_2Cl_2$: C, 59.49; H, 4.29; Cl, 3.50. Found: C, 59.15; H, 3.76; Cl, 3.51. A CH_2Cl_2 solution containing **4a** could be obtained by dissolving the solid at -78°C.

(d) **[RhMn(CO)$_3$(μ-HFB)(dppm)$_2$] (4b).** 200 mg of compound **1** was placed in a Schlenk tube (100 mL) and put under vacuum. The tube was filled with hexafluoro-2-butyne at 1 atm pressure and 20 mL of CH_2Cl_2 was added. The solution was stirred for 24 h. Removal of the solvent in vacuo and recrystallization from CH_2Cl_2 (10 mL of Et_2O and 40 mL of hexane) gave a green crystalline solid (80%). Anal. Calcd. for $RhMnP_4F_6O_3C_{57}H_{44}$: C, 58.36; H, 3.75. Found: C, 57.92; H, 3.83. A CH_2Cl_2 solution of **4b** could be obtained by dissolving the solid at temperatures below 0°C.

(e) **[RhMn(CO)$_3$(μ-η^2:η^2-DMAD)(dppm)$_2$] (5a).** The crystalline solid of compound (**4a**) was dissolved in CD_2Cl_2 (5 mg in 0.5 mL) at room temperature. The

^{31}P and ^{1}H NMR showed the formation of the mixture of compound **5a** and compound **4a** in a ratio of about 0.2:1.

(f) [RhMn(CO)$_3$(μ-η^2:η^2-HFB)(dppm)$_2$] (5b). The crystalline solid of compound (**4b**) was dissolved in CD_2Cl_2 (5 mg in 0.5 mL) at room temperature. After 1 h the ^{31}P and ^{1}H NMR showed the formation of the mixture of compound **5b** and compound **4b** in a ratio of about 0.7:1.

(g) [RhMn(H)(CO)$_4$(μ-DMAD)(dppm)$_2$][BF$_4$] (6a). To a CD_2Cl_2 solution of compound **3a** (3 mg, 2.5 μmol in 0.5 mL, in an NMR tube) at -78°C was added 1 μL of $HBF_4 \bullet Et_2O$ (4.8 μmol). The compound was characterized by NMR at -80°C.

(h) [RhMn(H)(CO)$_4$(μ-HFB)(dppm)$_2$][BF$_4$] (6b). To a CD_2Cl_2 solution of compound **3b** (3 mg, 2.5 μmol in 0.5 mL, dissolved at -78°C under 10 psi of CO in an NMR tube) was added 2 μL of $HBF_4 \bullet Me_2O$ (16 μmol). The product was characterized by NMR at -40°C.

(j) [RhMn(C(COOMe)=CH(COOMe))(CO)$_2$(μ-CO)$_2$(dppm)$_2$][BF$_4$] (7a•BF$_4$). **Method (i).** To a CH_2Cl_2 solution of compound **3** (50 mg, 42 μmol in 10 mL) was added 7.3 μL of $HBF_4 \bullet Et_2O$ (42 μmol) causing an instant color change from red to yellow. After stirring for 1 h the solvent was removed and the residue was recrystallized from CH_2Cl_2/Et_2O. A yellow solid was obtained in 88% yield.

Method (ii). To a CH_2Cl_2 solution of [RhMn(CO)$_4$(μ-H)(dppm)$_2$][BF$_4$] (**2**) (50 mg, 44 μmol in 10 mL) was added 5.5 μL of DMAD (44 μmol). After stirring for 3 days the solvent was removed under vacuum and the residue was recrystallized from CH_2Cl_2/Et_2O. A yellow solid was obtained in 92% yield. Elemental analysis of the BF_4^- salt was not obtained; that of the $SO_3CF_3^-$ salt (**7a•SO$_3$CF$_3$**) is given below.

(k)[RhMn(C(COOMe)=CH(COOMe))(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (7a•-SO$_3$CF$_3$). To a CH_2Cl_2 solution of compound **3** (50 mg, 42 μmol in 10 mL) was added 3.8 μL of CF_3SO_3H (42 μmol) resulting in an immediate color change from red to yellow. After 1 h the solvent was removed and the residue was recrystallized from THF/Et$_2$O. A yellow solid was obtained in 87% yield. Anal. Calcd. for RhMnSP$_4$F$_3$O$_{11}$C$_{61}$H$_{51}$: C, 55.05; H, 3.86. Found: C, 55.48; H, 4.54.

(l) [RhMn(C(CF$_3$)=C(H)(CF$_3$)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][BF$_4$] (7b•BF$_4$). To a CH$_2$Cl$_2$ solution of compound **3b** (50 mg, 42 μmol in 10 mL under 10 psi of CO at -78°C) was added 6 μL of HBF$_4$•Me$_2$O (49 μmol). After stirring for 0.5 h the solution was warmed to room temperature and was stirred for another 0.5 h. The solvent was removed and the residue was recrystallized from CH$_2$Cl$_2$/Et$_2$O. A yellow solid was obtained in 82% yield. Anal. Calcd. for RhMnP$_4$F$_{10}$O$_4$BC$_{58}$H$_{45}$ 0.4 CH$_2$Cl$_2$: C, 53.01; H, 3.46. Found: 52.92; H, 4.51. The amount of CH$_2$Cl$_2$ was established from the ^{1}H NMR spectrum in d$_8$-THF.

(m) [RhMn(CO)$_3$(μ-C(COOMe)=CH(COOMe))(dppm)$_2$][BF$_4$] (8a•BF$_4$). To a CD$_2$Cl$_2$ solution of isomers **4a** and **5a** (5 mg, 4 μmol in 0.5 mL in an NMR tube) was added 2 μL of HBF$_4$•Me$_2$O (16 μmol) at -78°C. The solution turned grey from black. The compound was characterized by NMR experiments at -80°C.

(n) [RhMn(CO)$_3$(μ-C(COOMe)=CH(COOMe))(dppm)$_2$] [CO$_2$CF$_3$] (8a•CO$_2$-CF$_3$). To a CD$_2$Cl$_2$ solution of isomers **4a** and **5a** (5 mg, 4 μmol in 0.5 mL in an NMR tube) was added 10 μL of CF$_3$CO$_2$H (130 μmol) at -78°C. The solution turned grey from black. The compound was characterized by NMR experiments at -80°C.

(o) [RhMn(C(Me)=CH$_2$)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (9a). 10 mL of allene (*ca.* 400 μmol) was syringed to a THF solution of [RhMn(CO)$_4$(μ-H)(dppm)$_2$][SO$_3$CF$_3$] (**2**) (50 mg, 42 μmol in 10 mL). The solution was refluxed for 6 h and cooled to ambient temperature resulting in the precipitation of a yellow solid. The supernatant was removed by syringe and the solid was washed with Et$_2$O. A yellow solid was obtained (yield 64%). Anal. Calcd. for RhMnC$_{58}$H$_{49}$O$_7$F$_3$P$_4$S: C, 56.68; H, 3.99. Found: C, 56.39; H, 3.99.

(p) Compound 9a and $[\mathrm{RhMn(CH_2CH{=}CH_2)(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]}$ (9b). A Schlenk tube containing 50 mg of compound **2** was filled with allene at *ca.* 1 atm. and 5 mL of CH_2Cl_2 was added. The solution was stirred for 4 d. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (76% yield). NMR characterization showed it to be an approximate 1:1 mixture of **9a** and the η^1-allyl product **9b**. Refluxing a mixture of **9a** and **9b** in THF for 3 h resulted in the transformation of **9b** to **9a**.

(q) $[\mathrm{RhMnMe(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]}$ (10a). To a CH_2Cl_2 solution of $[\mathrm{RhMn(CO)_4(dppm)_2}]$ (**1**) (100 mg, 96 μmol in 10 mL) was added 15 μL of $CF_3SO_3CH_3$ (133 μmol) and the mixture was stirred for 18 h. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid in 70% yield. Anal. Calcd. for $RhMnSP_4F_3O_7C_{56}H_{47}$: C, 55.91; H, 3.91. Found: C, 55.58; H, 3.80.

(r) $[\mathrm{RhMnMe(CO)_2(\mu\text{-}CO)_2(dppm)_2}]$ [I] (10b). To a CH_2Cl_2 solution of $[\mathrm{RhMn(CO)_4\text{-}(dppm)_2}]$ (**1**) (50 mg, 48 μmol in 10 mL) was added 50 μL of CH_3I (80 μmol). The solution was stirred for 18 h. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid in 82% yield.

(s) $[\mathrm{RhMn(C(O)Me)(CO)_4(dppm)_2][SO_3CF_3]}$ (11). A CH_2Cl_2 solution of $[\mathrm{RhMnMe(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]}$ (**10a**) (100 mg, 83 μmol in 5 mL) was put under CO (10 psi) and was stirred for 5 weeks. Removal of the solvent and recrystallization from THF/Et_2O gave a yellow solid in 76% yield. Anal. Calcd. for $RhMnSP_4F_3O_8C_{57}H_{47}$: C, 55.61; H, 3.82. Found: C, 56.25; H, 3.95.

(t) $[\mathrm{RhMn(CO)_3(\mu\text{-}H)(\mu\text{-}HFB)(dppm)_2][BF_4]}$ (12) and **$[\mathrm{RhMn(CO)_3(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^2\text{-}HFB)(dppm)_2][BF_4]}$ (13a).** 5 mg of $[\mathrm{RhMn(CO)_3(\mu\text{-}HFB)(dppm)_2}]$ (**4b**, 4 μmol) was dissolved in 0.5 mL of CD_2Cl_2 at -78°C to which 2 μL of $HBF_4{\bullet}Me_2O$(16 μmol) was added. These compounds were formed in ratio of *ca* 0.5:1, respectively, at 0°C and were characterized by NMR experiments.

(u) **[RhMn(CO)$_3$(μ-H)(μ-η^2:η^2-HFB)(dppm)$_2$][CO$_2$CF$_3$] (13b).** 5 mg of [RhMn(CO)$_3$(μ-HFB)(dppm)$_2$] (**4b**, 4 μmol) was dissolved in 0.5 mL of CD$_2$Cl$_2$ at -78°C to which 25 μL of CF$_3$CO$_2$H (16 μmol) was added. The compound was characterized by NMR experiments at 0°C.

(v) **[RhMn(C(C(O)Me)=CH$_2$)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (14).** To a CH$_2$Cl$_2$ solution of [RhMn(μ-H)(CO)$_4$(dppm)$_2$][SO$_3$CF$_3$] (**2**) (50 mg, 42 μmol in 5 mL) was added 100 μL 3-butyn-2-one (1279 μmol) and stirred for 5 days. Recrystallization from CH$_2$Cl$_2$/Et$_2$O gave a yellow mixture (86%) which contained [RhMn(<u>trans</u>-CH=CHC(O)-Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**15a**) and [RhMn(C(C(O)Me)=CH$_2$)(CO)$_2$-(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**14**) in a 1:1 ratio, as characterized by NMR experiments.

(w) **[RhMn(<u>trans</u>-CH=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (15a).** To a CH$_2$Cl$_2$ solution of isomers **17a** and **17b** (50 mg, 45 μmol in 5 mL under CO) was added 4.0 μL of CF$_3$SO$_3$H (1 equiv) followed by stirring for 0.5 h. The color changed from red to light yellow. Removal of the solvent and recrystallization from CH$_2$Cl$_2$/Et$_2$O gave a yellow solid (70%). Satisfactory elemental analyses could not be obtained owing to sample decomposition.

(x) **[RhMn(<u>trans</u>-CH=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][BF$_4$] (15b).** To a CH$_2$Cl$_2$ solution of isomers **17a** and **17b** (50 mg, 45 μmol in 5 mL under CO) was added 7.8 μL of HBF$_4$•Et$_2$O (85%, 1 equiv). The color changed from red to light yellow immediately. The solution was stirred for 0.5 h, followed by removal of the solvent and recrystallization from CH$_2$Cl$_2$/Et$_2$O to give a yellow solid (74%).

(y) **[RhMn(CO)$_4$(μ-HC=CC(O)Me)(dppm)$_2$] (16).** At -78°C 10 μL of 3-butyn-2-one (128 μmol) was added to a CD$_2$Cl$_2$ solution of [RhMn(CO)$_4$(dppm)$_2$] (**1**) (10 mg, 10 μmol in 0.5 mL) in an NMR tube. The compound was characterized by NMR experiments at -40°C.

(z) [RhMn(CO)$_3$(μ-C=CHC(O)Me)(μ-CO)(dppm)$_2$] (17a and 17b). To a CH$_2$Cl$_2$ solution of compound **1** (50 mg, 48 μmol in 5 mL) was added 8 μL of 3-butyn-2-one (102 μmol). The solution was stirred under CO for 1 h causing the color to change from light yellow to red. The solvent was reduced under a rapid flow of CO. The residue was recrystallized from CH$_2$Cl$_2$/Et$_2$O under a CO atmosphere and washed with 5 mL of Et$_2$O, yielding a red solid (86%). Anal. Calcd. for RhMnP$_4$C$_{58}$O$_5$H$_{48}$: C, 62.93; H, 4.34. Found: C, 62.02; H, 4.61.

(aa) [RhMn(CO)$_3$(μ-η^1:η^2-C=CHC(O)Me)(dppm)$_2$] (18). To a suspension of compound **1** (50 mg, 48 μmol in 5 mL of THF) was added 8 μL of 3-butyn-2-one (102 μmol) and the mixture was refluxed for 1 h. Removal of the solvent in vacuo and recrystallization from THF/hexane gave a red-brown crystalline solid (yield 90%). Anal. Calcd. for RhMnP$_4$C$_{57}$O$_4$H$_{48}$: C, 63.45; H, 4.45. Found: C, 63.46; H, 4.64.

(bb) [RhMn(CO)$_3$(μ-CCH=C(OH)Me)(μ-CO)(dppm)$_2$][BF$_4$] (19). To a CD$_2$Cl$_2$ solution of compound **1** (15 mg, 15 μmol in 0.5 mL in an NMR tube) under CO (10 psi) was added 3 μL of 3-butyn-2-one (38 μmol). The color changed from light yellow to red. The NMR tube was left for 3 h, then to this solution 3 μL of HBF$_4$•Me$_2$O (25 μmol) was added at -78°C. The compound was characterized by variable temperature NMR experiments.

(cc) [RhMn(*cis*-CH=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (20a). 50 mg of [RhMn(η^2-CHCHC(O)Me)(CO)$_2$(μ-CO)(dppm)$_2$][SO$_3$CF$_3$] (**21a**) (41 μmol) was dissolved in 5 mL of CH$_2$Cl$_2$ and stirred overnight under CO (10 psi). Removal of the solvent and recrystallization from CH$_2$Cl$_2$/Et$_2$O gave an orange solid (86%). Satisfactory elemental analyses could not be obtained owing to sample decomposition.

(dd) [RhMn(*cis*-CD=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][CO$_2$CF$_3$] (20b). To a CD$_2$Cl$_2$ solution of compound **18** (10 mg, 9 μmol in 0.5 mL) in an NMR tube was added 4 μL of CF_3CO_2D(52 μmol). The color changed from deep red-orange to orange immediately. The solution was put under CO (10 psi) for 12 h, followed by characterization by NMR.

(ee) [RhMn(cis-CH=CDC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][CO_2CF_3] (20c). To a CD_2Cl_2 solution of compound **1** (15 mg, 15 μmol in 0.5 mL) in an NMR tube was added 50 μL of 3-butyn-2-one (639 μmol, excess) at -78°. After 1 h a yellow suspension appeared. The ^{31}P NMR spectrum was run at -40°C and showed the presence of only compound **16**. 15 μL of CF_3CO_2D (195 μmol, excess) was added, causing the solution to turn clear yellow. The NMR spectroscopic characterization was carried out at both -40°C and room temperature. For the ^2H NMR spectrum 0.5 mL of CH_2Cl_2 was used as solvent instead of CD_2Cl_2.

(ff) [RhMn(η^2-CH=CHC(O)Me)(CO)$_2$(μ-CO)(dppm)$_2$][SO_3CF_3] (21a). To a CH_2Cl_2 solution of compound **18** (50 mg, 46 μmol in 5 mL) was added 4.1 μL of CF_3SO_3H (1 equiv). The color changed to orange from deep red-orange immediately. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave an orange compound (96%). Anal. Calcd. for $RhMnSP_4F_3O_7C_{58}H_{49}$: C, 56.68; H, 3.99. Found: C, 56.34; H, 3.85.

(gg) [RhMn(η^2-CD=CHC(O)Me)(CO)$_2$(μ-CO)(dppm)$_2$][CO_2CF_3] (21b). To a CD_2Cl_2 solution of compound **18** (10 mg, 9 μmol in 0.5 mL) in an nmr tube was added 4 μL of CF_3CO_2D (52 μmol). The color changed from deep red-orange to orange immediately. Characterization was by NMR. To obtain the ^2H NMR spectrum 0.5 mL of CH_2Cl_2 was used as solvent instead of CD_2Cl_2.

(hh) [RhMn(Z-C(Me)=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO_3CF_3] (22). To a CH_2Cl_2 solution of isomers **17a** and **17b** (50 mg, 45 μmol in 5 mL under CO) was added 5.0 μL of $CF_3SO_3CH_3$ (1 equiv.) followed by stirring for 1 h. Removal of the solvent in vacuo and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (72%). Anal. Calcd. for $RhMnP_4SF_3C_{60}H_{51}O_8$: C, 56.69; H, 4.02. Found: C, 56.66; H, 3.82.

(ii) **[RhMn(CH_3)(CO)$_3$(μ-η^1:η^2-CCHC(O)Me)(dppm)$_2$][SO_3CF_3] (23).** To a CD_2Cl_2 solution of [RhMn(CO)$_3$(μ-η^1:η^2-CCHC(O)Me)(dppm)$_2$] (**18**) (10 mg, 9 μmol in 0.5 mL) in an NMR tube was added 2 μL of $CF_3SO_3CH_3$ (17 μmol) at -78°C, causing the solution to turn from maroon to red. The compound was characterized by NMR experiments at -40°C.

(jj) **[RhMn(CO)$_3$(η^2-MeC=CHC(O)Me)(dppm)$_2$][SO_3CF_3] (24).** To a CD_2Cl_2 solution of [RhMn(CO)$_3$(μ-η^1:η^2-CCHC(O)Me)(dppm)$_2$] (**18**) (10 mg, 9 μmol in 0.5 mL) in an NMR tube was added 2 μL of $CF_3SO_3CH_3$ (17 μmol) at -78°C. The solution turn black after the solution was warmed up to -20°C. The compound was characterized by NMR experiments at -20°C.

(kk) **[RhMn(CO)$_3$(μ-η^1:η^1-MeC=CHC(O)Me)(dppm)$_2$][SO_3CF_3] (25).** To a CH_2Cl_2 solution of compound **18** (50 mg, 46 μmol in 5 mL) was added 5.2 μL of $CF_3SO_3CH_3$ (1 equiv) followed by stirring for 1 h. Removal of the solvent in vacuo and recrystallization from CH_2Cl_2/Et_2O gave a red crystalline solid (84%). Anal. Calcd. for $RhMnSP_4F_3O_7C_{59}H_{51}$: C, 57.00; H, 4.11. Found: C, 56.82; H, 4.25.

Reactions. (a) Reaction of compound 23 with CO. 50 mg of compound **18** (46 μmol) was dissolved in 10 mL of CH_2Cl_2 at -78°C to which 10 μL of $CF_3SO_3CH_3$ (85 μmol) was added, followed by stirring at -78°C for 1 h. The color changed to red from maroon. The solution was partially evacuated and put under CO (10 psi). The sample was left in the acetone-dry-ice bath overnight and slowly allowed to warm to room temperature. A yellow powder was obtained after recrystallization from Et_2O/CH_2Cl_2 (80% yield). It was shown to be compound **22** by ^{31}P and ^1H NMR spectra.

(b) Reaction of compound 24 with CO. To a CD_2Cl_2 solution of compound **18** (10 mg, 9 µmol in 0.5 mL) in nmr tube was added 2 µL of $CF_3SO_3CH_3$ (17 µmol) at -78°C. The ^{31}P and ^1H showed the formation of compound **24** at -20°C (black solution). To the solution 1 mL of CO was added by syringe. The sample was left in the acetone-dry-ice bath overnight and slowly allowed to warm to room temperature. The ^{31}P and ^1H NMR showed the presence of only compound **22**.

X-ray Data Collection. Red crystals of $[RhMn(CO)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C(H)C(O)\text{-}CH_3)(dppm)_2]\cdot(CH_3)_2CO$ (**18**$\cdot(CH_3)_2CO$) were grown by diffusion of Et_2O into an acetone solution of the complex. Several of these were mounted and flame sealed in glass capillaries under an atmosphere of the solvent vapor to minimize solvent loss. 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 $20.0° < 2\theta < 23.8°$. The monoclinic diffraction symmetry and the systematic absences ($h0\ell$, $h+\ell \neq 2n$; $0k0$, $k \neq 2n$) defined the space group as $P2_1/n$ (a non-standard setting of $P2_1/c$ [No. 14]).

Intensity data were collected at 22°C by using the $\theta/2\theta$ scan technique, covering reflections having indices of the form $\pm h$, $+k$, $+\ell$ to a maximum of $2\theta = 50°$. Of the 10259 data collected, 9709 were unique and of these 3980 were observed ($I \geq 3\sigma(I)$). Backgrounds were scanned for 25% of the scan width on either side of the scan. Three reflections were chosen as intensity standards and were remeasured after every 120 min of X-ray exposure. The intensities of these standards dropped by *ca.* 7.5% over the duration of data collection so a linear correction was applied to the data. The data were processed in the usual way, with a value of 0.04 for p employed to downweight intense reflections.[44,45] Absorption corrections were applied to the data according to the method of Walker and Stuart.[46] See Table 3.3 for crystal data and additional information on X-ray data collection.

Table 3.3. Crystallographic Data for Compound **18**.

formula	$C_{60}H_{54}MnO_5P_4Rh$
formula weight	1136.84
space group	$P2_1/n$ (a non-standard setting of $P2_1/c$ [No. 14])
unit cell parameters	
a (Å)	14.489 (1)
b (Å)	15.754 (2)
c (Å)	24.104 (2)
β (deg)	91.41 (1)
V ($Å^3$)	5501 (1)
Z	4
D(calcd) (g cm^{-3})	1.373
μ (cm^{-1})	6.756
diffractometer	Enraf-Nonius CAD4
temperature (°C)	23
radiation (λ (Å))	graphite-monochromated Mo K_α (0.71069)
crystal-detector distance (mm)	173
scan type	$\theta/2\theta$
scan rate (deg min^{-1})	1.73-6.71
scan width (deg)	$0.80 + 0.344\tan(\theta)$
maximum 2θ (deg)	50.0
total unique reflections	9960 (±h +k +l)
total observations (NO)	3980 ($Fo^2 \geq 3.0\sigma(Fo^2)$)
range of absorption correction factors	0.7792-1.1061
final no. params. varied (NV)	404
R^a	0.058
$R_w{}^b$	0.063
error in obs. of unit weight (GOF)^c	1.615

^{a} $R = \Sigma \mid |Fo| - |Fc| \mid / \Sigma |Fo|$. ^{b} $R_w = [\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2]^{1/2}$.

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

Structure Solution and Refinement. The structure of RhMn(CO)$_3$(μ-η^1:η^2-C=C(H)C(O)CH$_3$)(dppm)$_2$]•(CH$_3$)$_2$CO was solved in space group P2$_1$/n using standard Patterson and Fourier techniques. Full-matrix, least-squares refinements minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor $w = 4F_o{}^2/\sigma^2(F_o)^2$. Atomic scattering factors[47] and anomalous dispersion terms[48] were taken from the usual tabulations. All hydrogen atoms were observed but were generated at idealized calculated positions by assuming a C-H bond length of 0.95Å and the appropriate sp^2 or sp^3 geometry, except for the acetone hydrogens, which were not included. All hydrogens within the complex molecule were included in calculations with fixed, isotropic thermal parameters 20% greater than those of the attached atoms. Their positions were recalculated after every few cycles of refinement. In the final cycles of refinement the vinylidene hydrogen atom was allowed to refine, and was shown to be well behaved. There was no evidence of secondary extinction therefore no correction was applied.

The final model with 404 parameters varied converged to R = 0.058 and R$_w$ = 0.C63. In the final difference Fourier map the highest residuals (0.47-0.65 e/Å^3) were found in the vicinities of Rh and the phenyl group. The atomic coordinates and thermal parameters for selected atoms of compound **18** are given in Table 3.4 and selected bond lengths and angles are given in Table 3.5 Tables of fractional coordinates and thermal parameters for all atoms, and observed and calculated structure factor amplitudes can be obtained from Professor M. Cowie. We thank Dr. R. McDonald of the departmental Structure Determination Laboratory for technical assistance.

Kinetics for the Transformation of 4b to 5b. The green solid of isomer **4b** was dissolved in CD$_2$Cl$_2$ at -78°C (5 mg in 0.5 mL) in an NMR tube (at this

Table 3.4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Core Atoms of **18**.[a]

Atom[a]	x	y	z	B, Å^2 [b]
Rh	0.12279(5)	0.22450(5)	-0.08839(3)	2.89(2)*
Mn	0.1503(1)	0.34558(9)	-0.18423(6)	2.63(4)*
P(1)	0.2693(2)	0.1729(2)	-0.0932(1)	2.86(7)*
P(2)	0.3022(2)	0.3075(2)	-0.1827(1)	2.87(7)*
P(3)	-0.0338(2)	0.2241(2)	-0.1021(1)	3.17(7)*
P(4)	-0.0064(2)	0.3598(2)	-0.1923(1)	3.15(7)*
O(1)	0.1179(5)	0.2338(5)	0.0366(3)	5.9(2)*
O(2)	0.1604(5)	0.4233(4)	-0.0739(3)	4.3(2)*
O(3)	0.1902(5)	0.5187(4)	-0.2235(3)	5.4(2)*
O(4)	0.1438(4)	0.2967(4)	-0.2637(2)	3.5(2)*
C(1)	0.1205(7)	0.2327(6)	-0.0105(4)	3.6(3)*
C(2)	0.1547(6)	0.3825(6)	-0.1156(4)	3.5(3)*
C(3)	0.1741(7)	0.4495(6)	-0.2095(4)	3.5(3)*
C(4)	0.1251(6)	0.2231(6)	-0.1701(3)	2.6(2)*
C(5)	0.1166(7)	0.1732(6)	-0.2162(4)	3.8(3)*
C(6)	0.1272(6)	0.2185(7)	-0.2660(4)	3.8(3)*
C(7)	0.1203(8)	0.1777(8)	-0.3230(4)	5.7(4)*
C(8)	0.3251(6)	0.1983(6)	-0.1590(4)	2.7(3)*
C(9)	-0.0728(7)	0.2671(6)	-0.1701(4)	3.7(3)*
H(5)	0.098(6)	0.110(6)	-0.207(4)	2.8(24)

[a] Phenyl carbons and solvent atoms are given in the Supplementary material.

[b] Anisotropically-refined atoms are marked with an asterisk (*). Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian diplacement parameter, B_{eq}, defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 3.5. Selected Bond Lengths (Å) and Angles (deg) for **18**.

(a) Distances

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	P(1)	2.278 (2)	Mn	C(4)	1.995 (8)
Rh	P(3)	2.285 (2)	O(1)	C(1)	1.138 (8)
Rh	C(1)	1.883 (9)	O(2)	C(2)	1.196 (9)
Rh	C(4)	1.971 (7)	O(3)	C(3)	1.167 (9)
Mn	P(2)	2.282 (2)	O(4)	C(6)	1.26 (1)
Mn	P(4)	2.284 (3)	C(4)	C(5)	1.36 (1)
Mn	O(4)	2.065 (5)	C(5)	C(6)	1.41 (1)
Mn	C(2)	1.752 (9)	C(5)	H(5)	1.05 (8)
Mn	C(3)	1.783 (9)	C(6)	C(7)	1.52 (1)

(b) Angles

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P(1)	Rh	P(3)	156.17 (9)	O(4)	Mn	C(4)	78.1 (3)
P(1)	Rh	C(1)	96.6 (3)	C(2)	Mn	C(3)	90.9 (4)
P(1)	Rh	C(4)	84.7 (2)	C(2)	Mn	C(4)	99.4 (3)
P(3)	Rh	C(1)	95.9 (3)	C(3)	Mn	C(4)	169.8 (4)
P(3)	Rh	C(4)	84.0 (2)	Mn	O(4)	C(6)	114.3 (6)
C(1)	Rh	C(4)	176.7 (4)	Rh	C(1)	O(1)	176.8 (9)
P(2)	Mn	P(4)	169.6 (1)	Mn	C(2)	O(2)	166.6 (7)
P(2)	Mn	O(4)	86.5 (2)	Mn	C(3)	O(3)	176.9 (8)
P(2)	Mn	C(2)	93.4 (3)	Rh	C(4)	Mn	99.6 (4)
P(2)	Mn	C(3)	93.0 (3)	Rh	C(4)	C(5)	144.8 (7)
P(2)	Mn	C(4)	85.6 (2)	Mn	C(4)	C(5)	115.6 (6)
P(4)	Mn	O(4)	86.3 (2)	C(4)	C(5)	C(6)	113.1 (8)
P(4)	Mn	C(2)	93.5 (3)	C(4)	C(5)	H(5)	113 (4)
P(4)	Mn	C(3)	94.7 (3)	C(6)	C(5)	H(5)	134 (4)
P(4)	Mn	C(4)	85.6 (2)	O(4)	C(6)	C(5)	118.9 (8)
O(4)	Mn	C(2)	177.4 (3)	O(4)	C(6)	C(7)	117.7 (9)
O(4)	Mn	C(3)	91.7 (3)	C(5)	C(6)	C(7)	123.4 (9)

temperature no isomerization occurs) and the temperature of the NMR probe was set to the appropriate running temperature (20°, 25°, 30° or 35°C (corrected)). A beaker of water was prepared at the same temperature as the probe and the NMR tube was placed in this beaker for 1 min. The use of the bath ensured that the sample warmed to running temperature as soon as possible. The sample was placed into the NMR probe and the ^{19}F NMR spectra were obtained at regular intervals (6 min), starting from the time the sample was immersed into the warm water.

The transformation of **4b** to **5b** is a first-order system coming to equilibrium,[49] and can be represented as:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{1}$$

in which A and B represent **4b** and **5b**, respectively. From this, the expression:

$$-\ell n \frac{[B]_e - [B]}{[B]_e - [B]_o} = (k_1 + k_{-1})t \ , \tag{2}$$

can be obtained, where $[B]_o$, $[B]$ and $[B]_e$ are the concentrations of **5b** at $t = 0$, $t = t$ and $t = \infty$, respectively. Assuming $[B]_o = 0$, eqn. (2) simplifies to:

$$-\ell n(1 - {}^{[B]}/_{[B]_e}) = (k_1 + k_{-1})t \ . \tag{3}$$

The units of concentration used are mole fractions, and $[B]_e$ is obtained after the sample has sat at room temperature for 1 day then at the desired temperature for 0.5 h. Plots of $-\ell n(1 - {}^{[B]}/_{[B]_e})$ against t give the slope $k_1 + k_{-1}$. The ratio k_1/k_{-1} equals $[B]_e/(1-[B]_e)$. From $k_1 + k_{-1}$ and k_1/k_{-1} values of k_1 and k_{-1} can be calculated and are given in Table 3.6. Values of ΔH^{o*} and ΔS^{o*} were derived by the application of the transition state theory eqn. (4).

$$\ell n(k/T) = -\Delta H^{o*}/RT + (23.76 + \Delta S^{o*}/R) \tag{4}$$

Table 3.6. Forward and Reverse Rate Constants for the Reversible Conversion of **4b** to **5b**.

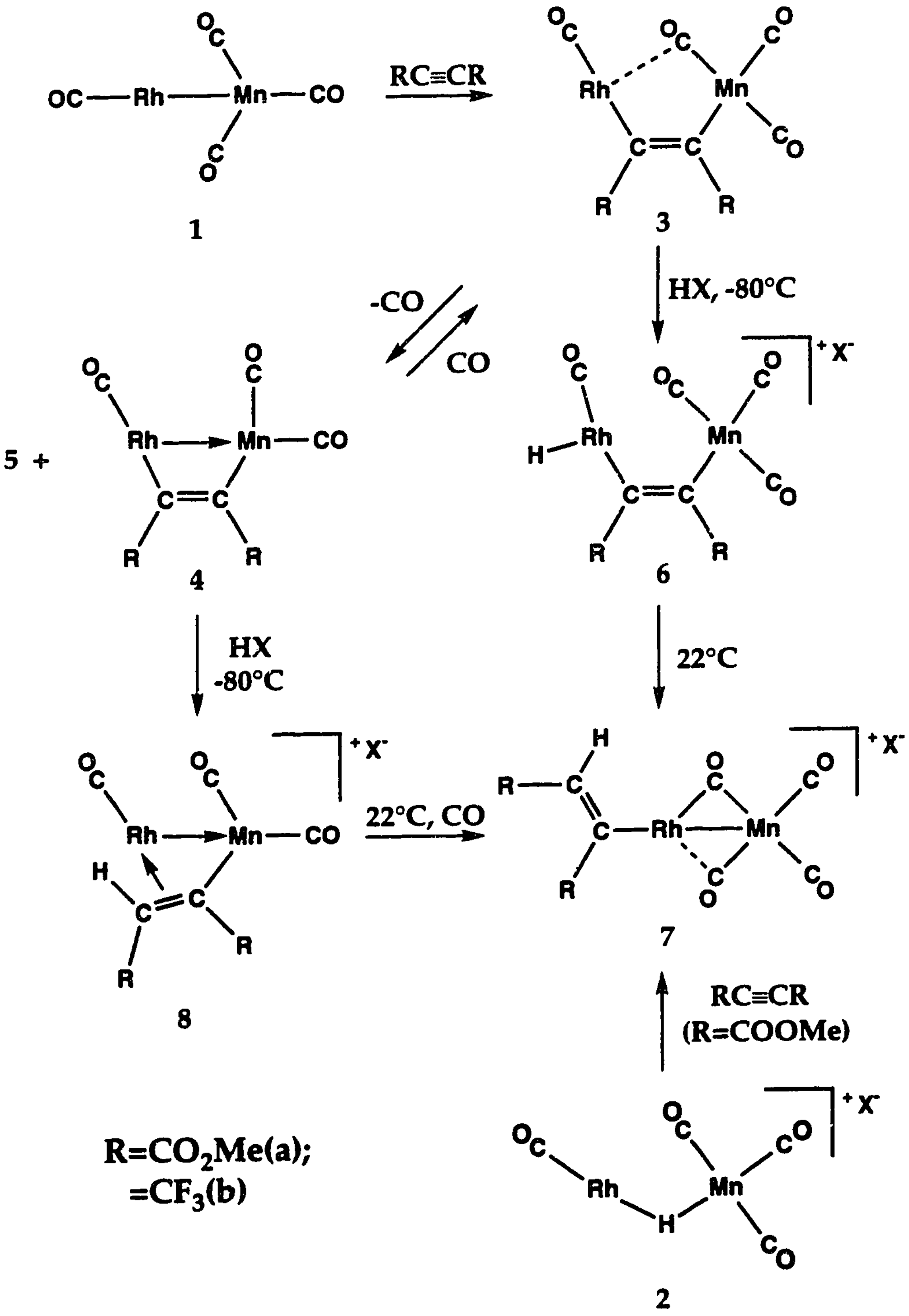
	Rate Constant	
Temperature (°C)	$k_1(s^{-1}) \times 10^4$	$k_{-1}(s^{-1}) \times 10^4$
20	1.10	1.53
25	2.22	3.08
30	4.42	6.22
35	8.03	11.47

Results and Discussion

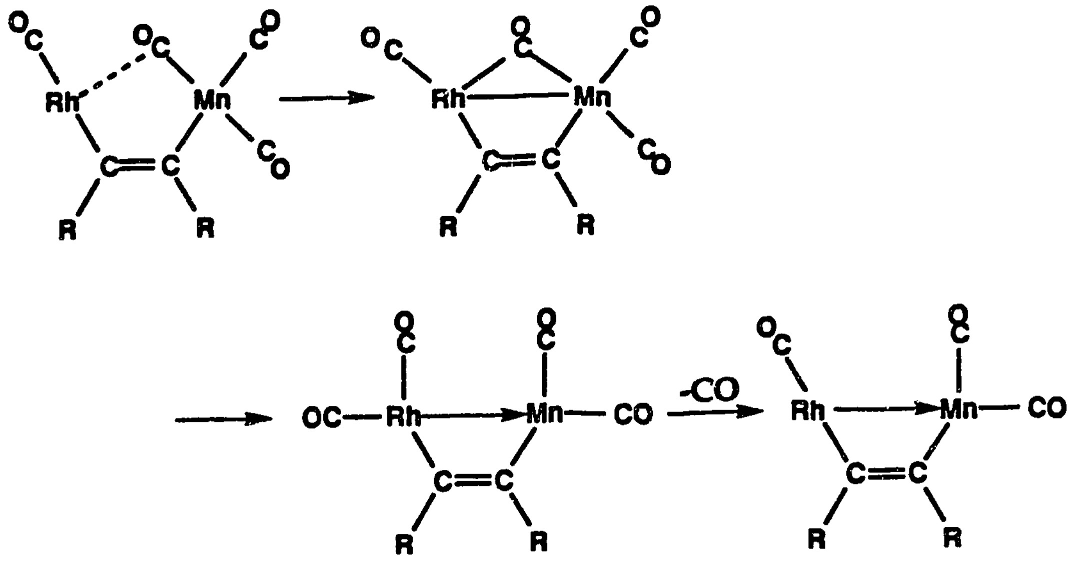
(a) Alkyne and Vinyl Species. The reaction of $[RhMn(CO)_4(dppm)_2]$ (**1**) with dimethyl acetylenedicarboxylate (DMAD) under CO yields the DMAD-bridged product $[RhMn(CO)_4(\mu\text{-DMAD})(dppm)_2]$ (**3a**), as was observed in the isoelectronic compounds, $[RhRe(CO)_4(\mu\text{-DMAD})(dppm)_2]$[50] and $[RhOs(CO)_4(\mu\text{-DMAD})(dppm)_2]^+$,[4] and spectral characterization of **3a** proceeded much as reported for these analogues. Although coordination of the alkyne perpendicular to the Rh-Mn axis was considered in **3a**, it was ruled out on the basis of the ^1H NMR spectrum, which showed two separate resonances for the DMAD methyl groups, which are in different environments by virtue of their proximity to either Rh or Mn; a perpendicular arrangement would have only one methyl signal. The $^{13}C\{^1H\}$ NMR spectrum of **3a** shows a resonance for the terminal carbonyl on Rh at δ 193.8 ($^1J_{Rh\text{-}C}$ = 57 Hz), two for the terminal carbonyls on Mn (δ 221.8, 223.5) and one corresponding to a semibridging carbonyl at δ 248.7, showing a weak interaction with Rh($^1J_{Rh\text{-}C}$ = 10 Hz). This semibridging interaction is substantiated by the low carbonyl stretch at 1727 cm^{-1} in the IR spectrum. The similarities in the spectroscopic parameters for **3a** (see Table 3.1) to those of the Rh/Re and Rh/Os analogues lead to the formulation shown in Scheme 3.1 (note that in the schemes the dppm groups above and below the plane of the drawing are usually omitted for clarity).

If the reaction of **1** with DMAD is carried out in the absence of CO a mixture of **3a** and two new species **4a** and **5a** is obtained. Refluxing this mixture in THF yields **4a** and **5a** and recrystallization yields only **4a**, as a black solid. A solution containing only **4a** can be prepared by dissolving the black solid in CH_2Cl_2 at –78°C. Upon gradually increasing the solution temperature to –40°C compound **5a** begins to appear, as shown by the $^{31}P\{^1H\}$ NMR spectra. At temperatures between 0° and

Scheme 3.1

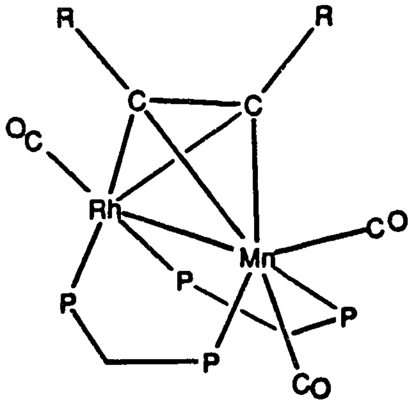

RC≡CR
HX, -80°C
-CO
CO
5 +
HX
-80°C
22°C
22°C, CO
RC≡CR
(R=COOMe)
R=CO$_2$Me(a);
=CF$_3$(b)
1
2
3
4
6
7
8

20°C an equilibrium mixture of **4a** and **5a** is present in an approximate 85:15 molar ratio. Both new products are isomers of formulation [RhMn(CO)$_3$(μ-DMAD)(dppm)$_2$], resulting from carbonyl loss from **3a**. The major isomer (**4a**) has the structure shown in Scheme 3.1, and is the species expected based on previous work with the related Rh/Re and Rh/Os systems; in particular the Rh/Os analogue [RhOs(CO)$_3$(μ-DMAD)(dppm)$_2$]$^+$ was previously characterized by an X-ray structure determination.[4] The ^{13}C{^{1}H} NMR spectrum of **4a** shows one carbonyl ligand on Rh and two on Mn, in addition to two singlets for the DMAD-carbonyl groups at δ 175.0 and 168.0, and two signals for the methyl groups at δ 50.3 and 50.1. Only one acetylenic carbon resonance was observed at δ 140.9 as a triplet of triplets, displaying coupling to both sets of ^{31}P nuclei; the other acetylenic resonance was not observed and appears to be obscured by phenyl resonances (non-isotopically-enriched DMAD was used so the signals due to DMAD are of low intensity). The ^{1}H NMR spectrum also displays two signals for the DMAD methyl groups consistent with a parallel DMAD coordination in which the two ends of the alkyne are inequivalent by virtue of their proximity to either Rh or Mn. A dative Rh→Mn bond is proposed to give Mn an 18-electron configuration, as was previously suggested for the Rh/Os analogue, in which the metal-metal interaction was supported by the X-ray study. Carbonyl loss from **3** probably occurs by transfer of the semibridging carbonyl to Rh, followed by CO loss from this metal. Concomitant with the transformation of this carbonyl from semibridging, to symmetrically bridging to terminal on Rh, is a change in the metal-metal bonding, from no bond in **3**, to a conventional Rh-Mn bond in the symmetrically CO-bridged intermediate, to a Rh→Mn dative bond in the last species, as shown below.



This shift of electron density from Rh to Mn accompanies the movement of the carbonyl's donor pair from Mn to Rh, and demonstrates how the adjacent metal (Rh) can assist in the labilization of a ligand from the normally inert, 18e center (Mn).

The minor isomer **5a** is proposed to have a perpendicular alkyne binding mode, shown below, as has been previously observed within the Co triad for $[Rh_2(CO)_2(\mu\text{-}\eta^2\text{-}PhC_2Ph)(dppm)_2]$,[51] $[Ir_2(CO)_2(\mu\text{-}\eta^2\text{-}DMAD)(dppm)_2]$,[6] a series of related dicobalt complexes,[52-58] as well as other dirhodium[59,60] and diiridium[61] systems. This proposed structure is based on the spectral data. The $^{31}P\{^1H\}$ NMR spectrum shows an AA'BB'X spin system in which the Mn-bound phosphorus nuclei resonate at δ 98.9; this is 47 ppm downfield from the related signal in **4a** in which a trans arrangement of phosphines is proposed. The resonance for the Rh-bound phosphorus nuclei is also somewhat downfield from that observed in **4a**. Both Mn-bound carbonyls display unusually high coupling (48 and 38 Hz) to the Mn-bound phosphorus nuclei, compared to values between 10 and 20 Hz when a trans diphosphine arrangement is involved, suggesting a geometry in which the CO and phosphines are at an angle other than 90°. Also unexpectedly the Rh-bound CO displays weak coupling to the Mn-bound phosphorus nuclei, presumably through the Rh-Mn bond. Only one signal is observed in the $^{13}C\{^1H\}$ NMR spectrum corresponding to the two equivalent DMAD carbonyls (δ 176.0) and another for the two methyl groups. In addition the ^1H NMR spectrum also shows only one resonance for both methyl groups. These data support the perpendicular orientation of the alkyne, which would result in both ends of the alkyne being chemically equivalent.



5a (R = CO_2Me); **5b** (R = CF_3)

Although the perpendicular coordination mode of the alkyne and the concomitant *cis* -diphosphine arrangement seems clear, the resulting geometry at Mn, regarding the positions of the carbonyls is still ambiguous.

All routes to **4a** and **5a** invariably yield these species in a constant ratio in solution, suggesting an equilibrium between the two. This has been confirmed by spin-saturation-transfer experiments at 60°C in which saturation of the signal for the Mn-bound phosphorus nuclei of one isomer results in a substantial intensity decrease

(>60%) for the corresponding signal of the other isomer. Although reversible conversion of one alkyne-bridged mode to the other has been reported upon ligand gain or loss,[62,63] we know of only one other study in which such a reversible transformation in alkyne-bonding modes occurs with no change in the number of ligands; this conversion from a dimetallacyclobutene structure to the perpendicular binding mode for $[Cp^*(CO)_2Re]_2(\mu\text{-DMAD})$ was induced upon photolysis and was reversed upon heating.[64] However the facility of this reversible change in alkyne binding mode (**4a** $\rightleftharpoons$ **5a**) is unprecedented. At ambient temperature spin-saturation transfer between **4a** and **5a** was not observed because the exchange rate is too slow.

The reaction of **1** with hexafluoro-2-butyne (HFB) leads to a series of HFB-bridged complexes **3b**, **4b** and **5b**, exactly analogous to the DMAD-bridged compounds discussed, and are again shown in Scheme 3.1 ($R = CF_3$). These products show very similar spectroscopic properties to their DMAD analogues. The major difference lies in the relative proportions of isomers **4** and **5**. Whereas isomer **5a**, having the perpendicular alkyne bridge was the minor isomer for DMAD, both isomers **4b** and **5b** are present in comparable amounts with HFB. The ^{19}F NMR spectra (see Table 3.2) conveniently differentiate between the parallel and perpendicular alkyne binding modes, with the parallel isomer **4b** showing two multiplet resonances for the inequivalent CF_3 groups while **5b** displays only one multiplet resonance for the chemically equivalent CF_3 groups. Carrying out ^{19}F NMR experiments on **4b** with selective and broad-band ^{31}P-decoupling shows that the fluorine resonance at δ −40.8 couples to only the Mn-bound phosphorus atoms so is assigned to the CF_3 group adjacent to Mn, whereas the signal at δ −49.0 surprisingly couples to all phosphorus nuclei. In addition, the two CF_3 groups display a mutual coupling of 13 Hz-typical for a cis arrangement. The single ^{19}F resonance in **5b** collapses to a singlet upon decoupling the Rh-bound phosphorus nuclei, but shows no apparent coupling to the Mn-bound ends of the diphosphines, suggesting a stronger binding to Rh. Although the coordinatively unsaturated **4b** immediately reverts to **3b** at –40°C under CO, **5b** remains unreacted at this temperature, consistent with the coordinatively saturated formulation for this species. The electronic effect of substituting DMAD by the better π-accepting HFB group[65] shows up in the greater lability of the fourth carbonyl in **3b**. Therefore the tetracarbonyl species [$RhMn(CO)_4(\mu$-HFB)$(dppm)_2$] (**3b**) is only observed under CO at -40°C, otherwise the tricarbonyl isomers are the only species observed. In none of the alkyne-bridged species described was a C≡C stretch visible in the IR spectra.

The isomerization of **4b** to **5b** is less facile than for the DMAD analogue; whereas conversion of **4a** to **5a** was observed at –40°C, that for **4b** to **5b** did not occur appreciably until temperatures near 0°C. Even at 60°C exchange between **4b** and **5b** was too slow to be detected by spin-saturation transfer experiments. However over the temperature range between 20°C and 35°C this conversion can be conveniently monitored by ^{19}F NMR. Figure 3.1 shows the changes in ^{19}F NMR spectra that occur as **4b** slowly converts to **5b** at 20°C. For this first-order system coming to equilibrium the forward and reverse rate constants (k_1 and k_{-1}; see Table 3.6) can be obtained,[49] and from the transition-state theory (T = 20, 25, 30, 35°C), values for ΔH^* and ΔS^* for the forward (23.3 kcal mol^{-1}, 2.9 cal K^{-1} mol^{-1}) and reverse (23.6 kcal mol^{-1}, 4.7 cal K^{-1} mol^{-1}) reactions can be obtained. Although the corresponding kinetic study was not carried out for the conversion between the DMAD analogues **4a** and **5a**, the more facile conversion at lower temperatures

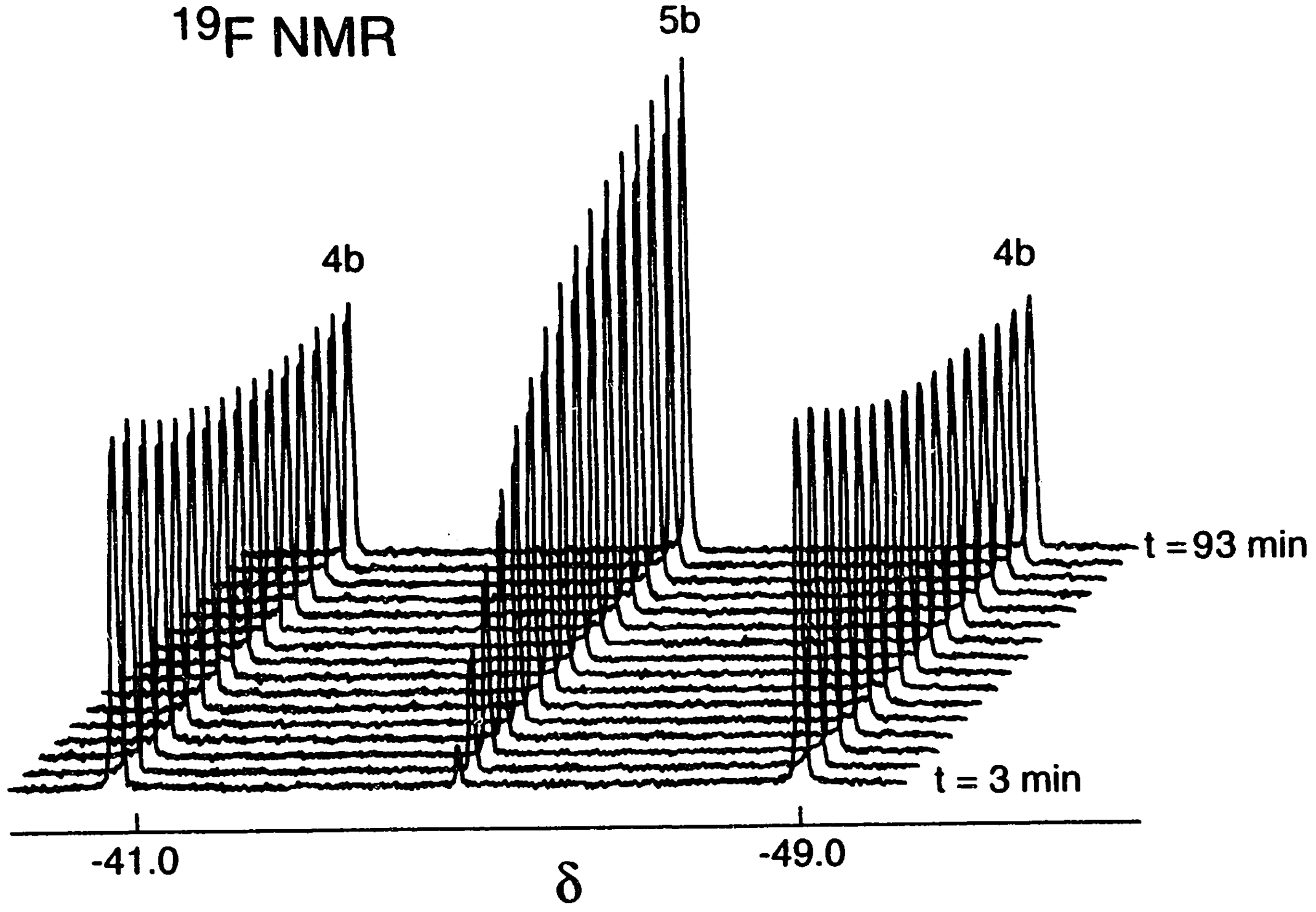


Figure 3.1. ^{19}F NMR spectra (at 376.5 MHz) at 20°C showing the conversion of compound **4b** to **5b** over a 90 min period; the spectra were acquired at 6 min intervals.

indicates a lower barrier to rotation. This presumably reflects the stronger binding of HFB by virtue of its better π-accepting ability.

Addition of protic acids to **3a** at -80°C results in protonation at Rh to yield $[RhMnH(CO)_4(\mu\text{-DMAD})(dppm)_2][X]$ (X = BF_4 (**6a**)). The hydride resonance, at δ -14.3 in the ^1H NMR spectrum, displays coupling to Rh of 38 Hz and to the phosphorus nuclei on Rh, confirming its terminal coordination to this metal. All other spectroscopic data (see Table 3.1), including the observation of two resonances for the DMAD methyl protons support the structure shown. The observed protonation at only one metal is in contrast to the protonation of the metal-metal bond in the related compound $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ (dmpm = $Me_2PCH_2PMe_2$) to give a hydride-bridged species.[8]

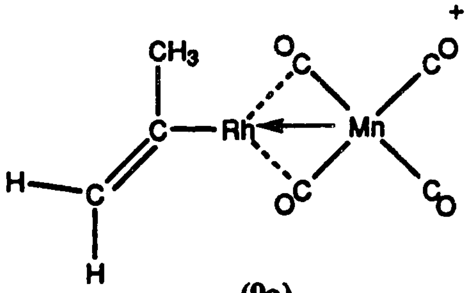
Upon warming, compound **6a** transforms to the vinyl complex **7a**. The $^{13}C\{^1H\}$ NMR spectra for the BF_4^- salt show four separate carbonyl resonances. The low-field signal, at δ 243.4, displays coupling of 29 Hz to Rh and 8 Hz to the Mn-bound phosphines, so is formulated as a bridging carbonyl. The resonance at δ 235.6 displays coupling to Rh and to the Mn-bound phosphines, both of 14 Hz, so is formulated as semibridging, whereas the remaining two carbonyls are terminally bound to Mn, as shown in Scheme 3.1. It appears that the weaker interaction of the semi-bridging carbonyl with Rh results from repulsion of this group by a methoxycarbonyl substituent of the terminal vinyl group, with the conventionally bridged carbonyl adjacent to the hydrogen on the β-carbon. Such a proposal presumes that there is no facile rotation about the Rh-vinyl bond. The vinylic proton of **7a** (X = BF_4 or SO_3CF_3) is observed at *ca.* δ 4.4 and displays coupling of 2 Hz to Rh, suggesting that the vinyl group is bound to Rh. In any case, with no other ligand bound terminally to Rh the vinyl group must be terminally bound to this metal. The

IR spectra of **7a** show two terminal-carbonyl stretches, two corresponding to bridged carbonyls, between 1809 and 1854 cm^{-1}, and a strong band due to the ester carbonyl groups and a weak stretch at *ca.* 1585 due to the C=C bond of the vinyl moiety.

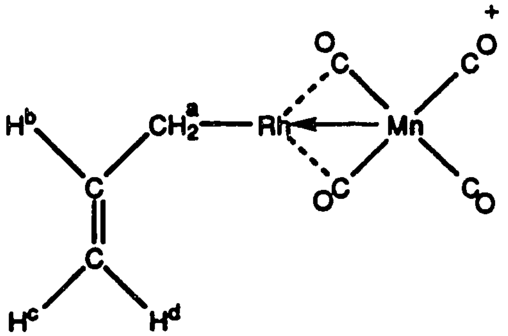
Protonation of the HFB-bridged species **3b** again parallels that involving the DMAD-bridged analogue, yielding at low temperature, the hydrido intermediate **6b**, which rearranges to the vinyl species **7b** at ambient temperature. In **7a** (R = CO_2Me) our spectroscopic data could not differentiate between a cis or trans arrangement of CO_2Me groups about the vinylic C=C bond, so we assumed a cis arrangement, as normally observed in such migratory insertions.[66-70] Having CF_3 substituents we are now able to establish a cis arrangement based on ^{19}F-^{19}F coupling constants. In **7b** this coupling ($^5J_{F-F}$ = 12 Hz) is typical of a cis arrangement,[71-74] and compares well to the values of 13 and 18 Hz observed in **3b** and **6b**, respectively.

Compound **7a** can also be prepared by the reaction of the hydride-bridged species, $[RhMn(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ (**2**) with DMAD, via migratory insertion. A very similar vinyl product, $[RhMn(C(Me){=}CH_2)(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]$ (**9a**), containing an isopropenyl group that is terminally bound to Rh, can be prepared by the insertion of allene ($H_2C{=}C{=}CH_2$) into the metal-hydride bond of the above hydride-bridged complex in refluxing THF. A similar transformation was previously observed in a closely related Rh/Os complex and this isopropenyl product was structurally characterized by an X-ray study.[75] Compound **9a** shows four carbonyl resonances in the $^{13}C\{^1H\}$ NMR with two at low field corresponding to bridging groups, displaying 20 Hz coupling to Rh and 11 Hz coupling to the phosphorus nuclei on Mn. On the basis of this coupling pattern and the magnitude of the Rh coupling these carbonyls are assigned as semibridging. The assignment of two bridging and two terminal carbonyls is also supported by the IR data. In the ^1H NMR spectrum, two separate resonances are observed for the inequivalent vinyl protons of **9a** and a singlet for the three methyl protons.

Surprisingly, if the reaction of **2** with allene is carried out at room temperature



(9a)



(9b)

for several days **9a** is obtained together with another species (**9b**) in approximately equal proportions. This new species can be shown to be the isomer [RhMn($CH_2CH{=}CH_2$)$(CO)_2$(μ-$CO)_2$($dppm)_2$][SO_3CF_3] containing an η^1-allyl group. The $^{13}P\{^1H\}$ NMR resonances of **9a** and **9b** are quite similar, and although the $^{13}C\{^1H\}$ NMR spectrum of **9b** has only two carbonyl resonances, corresponding to two equivalent semi-bridging and two equivalent terminal carbonyls, the chemical shifts and coupling constants are similar to those for **9a**. However the ^1H NMR spectra of the two isomers are quite distinct, showing four different resonances for the allyl group. The resonance at δ 2.73, corresponding to the two methylene protons adjacent to Rh, shows 8 Hz coupling to the Rh-bound phosphorus nuclei as well as 6 Hz coupling to H^b on the adjacent carbon. The slight broadening of this resonance obscures the expected 2 Hz coupling of these protons to Rh (see for example compound **10**). The three olefinic protons resonate at δ 5.30, 3.70 and 2.63, with the low-field signal appearing as a shoulder on the solvent peak (the poor solubility of **9b** in $CHCl_3$ or THF precluded the use of these solvents). Protons H^b and H^d were shown to be mutually trans, based on the 17 Hz coupling between them and this value can be compared with the 10 Hz coupling between H^b and H^c which is consistent with a cis arrangement. Other than the isomeric hydrocarbyl ligands, the only substantial difference between **7** and **9** is that the latter has two semibridging carbonyls instead of one being bridging and the other semibridging. Refluxing a mixture of **9a** and **9b** in THF results in the disappearance of **9b** with a corresponding increase in the concentration of the thermodynamic product **9a**.

The formation of both **9a** and **9b** from allene and the hydride-bridged compound **2** is presumed to proceed via an allene-hydride intermediate, with allene coordinated at Rh (although this intermediate was not observed). These results support the earlier proposals[34,76-78] of allene-hydride intermediates being involved in the isomerization of isopropenyl to η^3-allyl groups. In our system this conversion is reversed, with the isopropenyl species being thermodynamically favored. The stability of the allyl group over the isopropenyl in the previous studies is presumably due to the η^3-binding mode of the former. We assume that this mode is not favored in our system owing to steric repulsions that would result involving the dppm phenyl groups above and below the equatorial plane of the metals. That being the case, we propose that when only the η^1-binding mode of an allyl is considered, the isopropenyl isomer is favored owing to a stronger metal-carbon bond involving the sp^2 carbon rather than the sp^3 carbon of the η^1-allyl group. In another report involving interconversion between an η^1-allyl and a vinyl group, the vinyl group was again favored.[79]

The prototype in this series, having an organic group (CH_3) σ-bound to Rh can be prepared either by the addition of methyl triflate to **1**, yielding $[RhMn(CH_3)(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]$ (**10a**), or by the addition of MeI to **1** to give the analogous iodide salt, $[RhMn(CH_3)(CO)_2(\mu\text{-}CO)_2(dppm)_2][I]$ (**10b**). All spectroscopic data (Table 3.1) support a structure like those proposed for **7** and **9**, with the methyl group terminally bound to Rh, exactly as observed in the Rh/Re analogue, which was characterized by an X-ray structure determination.[80] The $^{31}P\{^1H\}$ NMR and $^{13}C\{^1H\}$ NMR spectra of **10** are very closely comparable to those of **9b**, and the ^1H NMR spectrum of **10** shows the expected triplet of doublets for the methyl resonance, displaying 11 Hz coupling to the two Rh-bound phosphorus nuclei and 2 Hz coupling to Rh. This terminal binding of a methyl group to Rh has now been observed in a number of related mixed-metal binuclear systems,[9, 80-82] and all display closely comparable spectroscopic parameters, adding further support for our formulation for the closely related isopropenyl (**9a**) and η^1-allyl (**9b**) products.

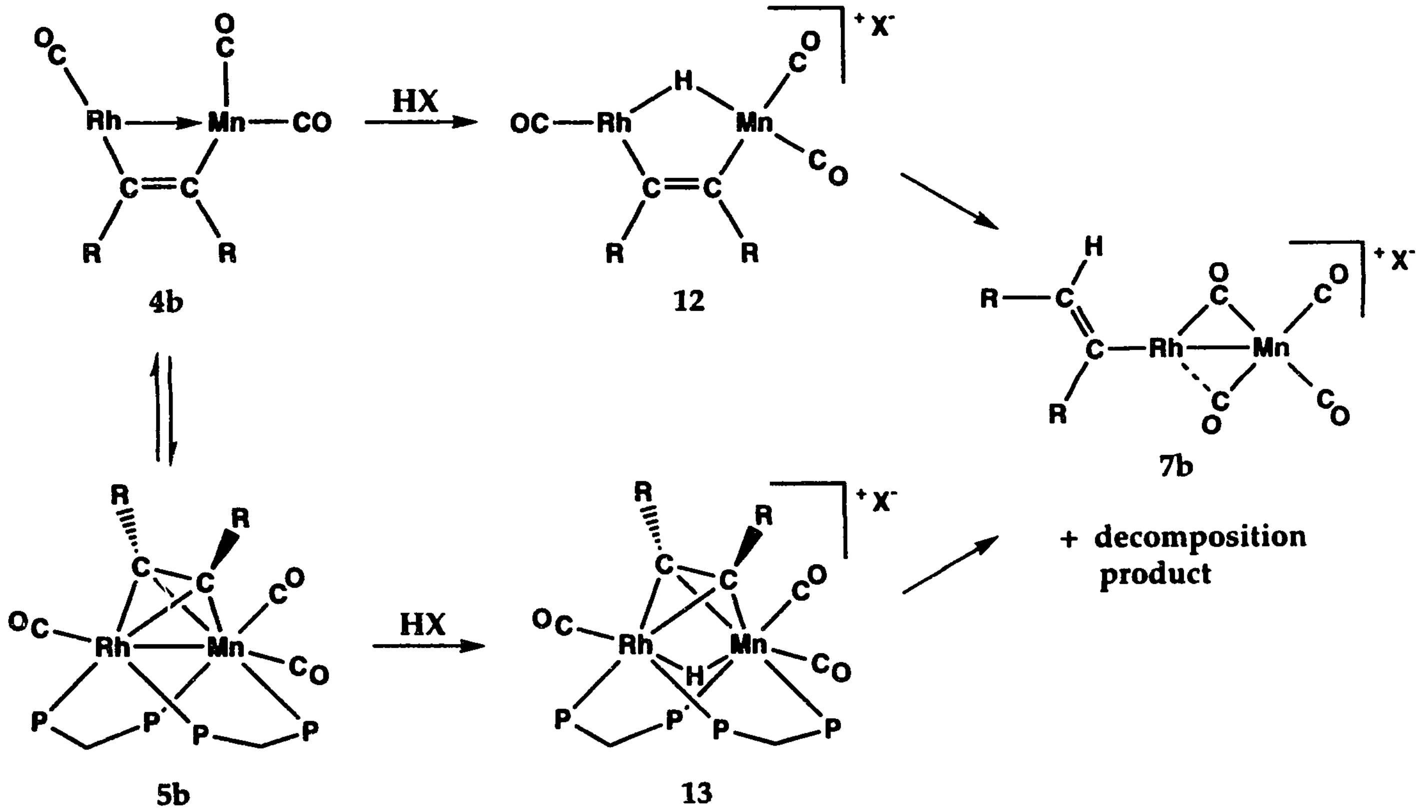
Reaction of **10a** with CO results in a migratory insertion to give the acyl species $[RhMn(C(O)CH_3)(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]$ (**11**). The ^1H NMR signal for the methyl group appears as a singlet at δ 1.04 when ^{12}CO is used or as a doublet ($^2J_{CH} = 5$ Hz) when ^{13}CO is used. In the $^{13}C\{^1H\}$ NMR the acyl carbon appears as a low-field doublet with 28 Hz coupling to Rh. Migratory insertion has resulted in a subtle change in the bridging carbonyls such that one shows stronger coupling to Rh (20 Hz) than the other (10 Hz), suggesting a strong and a weak semibridging interaction. Substitution of the methyl by the poorer donor acyl group means that there is less need for π back donation from Rh. However it is not clear why the bridging interactions should be asymmetric rather than two identical but weaker semibridging interactions. There appears to be no compelling steric argument, as for the related vinyl species.

The alkyne-bridged tricarbonyl species **4a** also can be protonated, but in this case, even at -80°C no metal-hydride is observed. Instead, an unstable species,

$[RhMn(CO)_3(\mu\text{-}C(CO_2Me)=C(H)CO_2Me)(dppm)_2][X]$ (**8a**) containing what is proposed to be a bridging vinyl moiety, is obtained. Unfortunately the presence of paramagnetic impurities, resulting from decomposition of **8a**, has led to broad resonances and the signal due to the vinylic hydrogen was not observed in the ^1H NMR spectrum. Upon warming **8a**, compound **7a** was obtained (as the tetrafluoroborate salt), together with several unidentified products, some of which are presumably the source of the extra carbonyl needed in the transformation of **8a** to **7a**. Whether **8a** has the structure shown in Scheme 3.1, or the related structure in which the vinyl moiety is σ-bound to Rh and π-bound to Mn could not be determined. The interaction of the vinyl π bond with either Rh or Mn is required to give the metals a 16 or 18e configuration, respectively. An analogous vinyl binding mode was previously proposed in related dirhodium[1k,8,83] and dimanganese[84] complexes. Compound **8** readily transforms to **7** upon addition of CO.

Although protonation of the species (**5a**) having the perpendicularly bound DMAD group could not be followed owing to its very low abundance, the protonation of both isomers **4b** and **5b**, having parallel and perpendicular HFB groups, respectively, was possible since both are present in comparable amounts. Starting with **4b**, the addition of $HBF_4{\bullet}Me_2O$ at -78°C does not result in a reaction until temperatures near 0°C are reached, at which point substantial amounts of **5b** have appeared. At 0°C and higher two hydride-bridged products **12** and **13** are obtained corresponding to protonation of the Rh-Mn bonds in **4b** and **5b**, respectively, as shown in Scheme 3.2. Compounds **12** and **13** are isomers of $[RhMn(CO)_3(\mu\text{-}H)(\mu\text{-}HFB)(dppm)_2][X]$ having either a parallel (**12**) or perpendicular (**13**) alkyne orientation, as in the respective precursors. The more abundant isomer **13** is assumed to have a perpendicular alkyne orientation based on the similarity of its spectral

Scheme 3.2



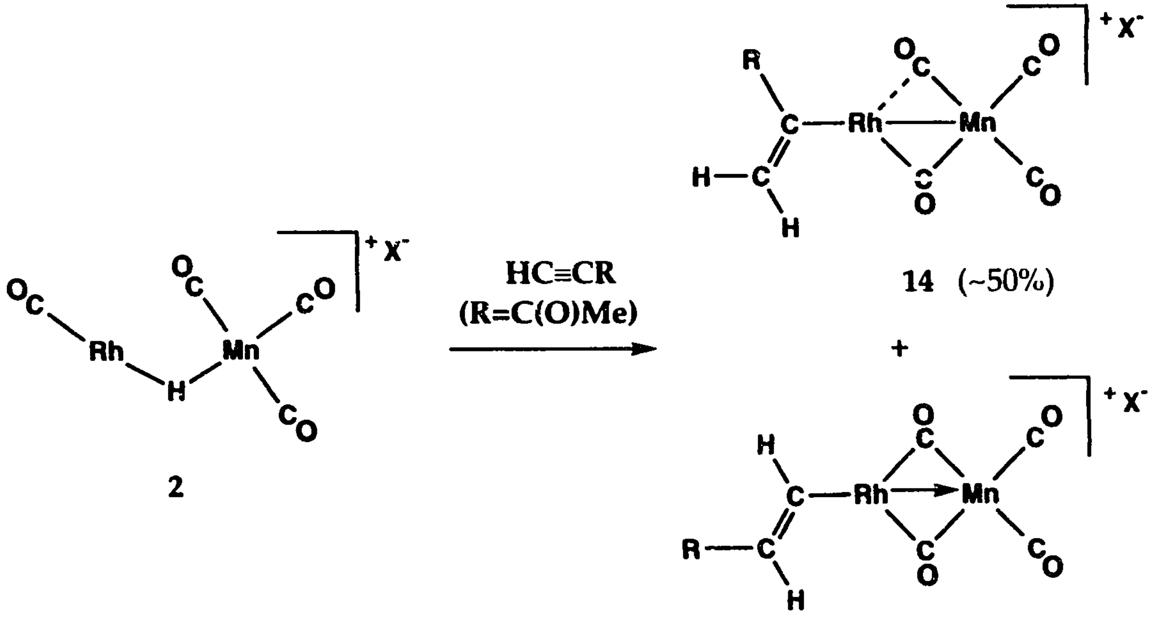
$R{=}CF_3$

parameters with those of **5b**. In particular **13** shows only one resonance for the CF_3 groups, whereas two resonances are observed in **12** owing to the chemical inequivalence of the two ends of the alkyne. The appropriate selective and broad-band decoupling experiments show that the hydrides in both **12** and **13** couple to Rh ($^1J_{Rh}$ = 15 Hz) and to all four phosphorus nuclei, confirming their bridging assignments. Although both isomers **12** and **13** are obtained upon protonation with $HBF_4{\bullet}Me_2O$, only **13** is obtained if trifluoroacetic acid is used.

After several hours at ambient temperature both **12** and **13** transform to the vinyl complex **7b**, together with unidentified species which are presumably the source of the additional carbonyl needed in the transformation of the tricarbonyl precursors to the tetracarbonyl product.

The hydride-bridged species **2** (as the triflate salt) also reacts with the terminal alkyne, 3-butyn-2-one, to give two isomers of the vinyl compound $[RhMn(C_2H_2C(O)Me)(CO)_4(dppm)_2][SO_3CF_3]$ (**14** and **15**), in approximately equal proportions, as shown in Scheme 3.3. These isomers differ mainly in the stereochemistry of the vinyl C=C bond, depending on whether alkyne insertion yields the products having a geminal (**14**) or trans arrangement (**15**) of vinyl hydrogens. In isomer **15** the trans vinyl hydrogens resonate at δ 7.99 and 5.32 for H_α and H_β, respectively, in the ^1H NMR spectrum. The 17 Hz coupling between these protons is consistent with a trans arrangement, and in addition H_α shows coupling ($^3J_{P(Rh)\text{-}H}$ = 7 Hz) to the two Rh-bound phosphorus nuclei. The $^{13}C\{^1H\}$ NMR spectrum for this isomer shows two carbonyl resonances, one corresponding to two bridging groups (δ 244.1, $^1J_{Rh\text{-}C}$ = 22 Hz) and the other corresponding to two terminal groups (δ 217.4)

Scheme 3.3



HC≡CR
(R=C(O)Me)

2

14 (~50%)

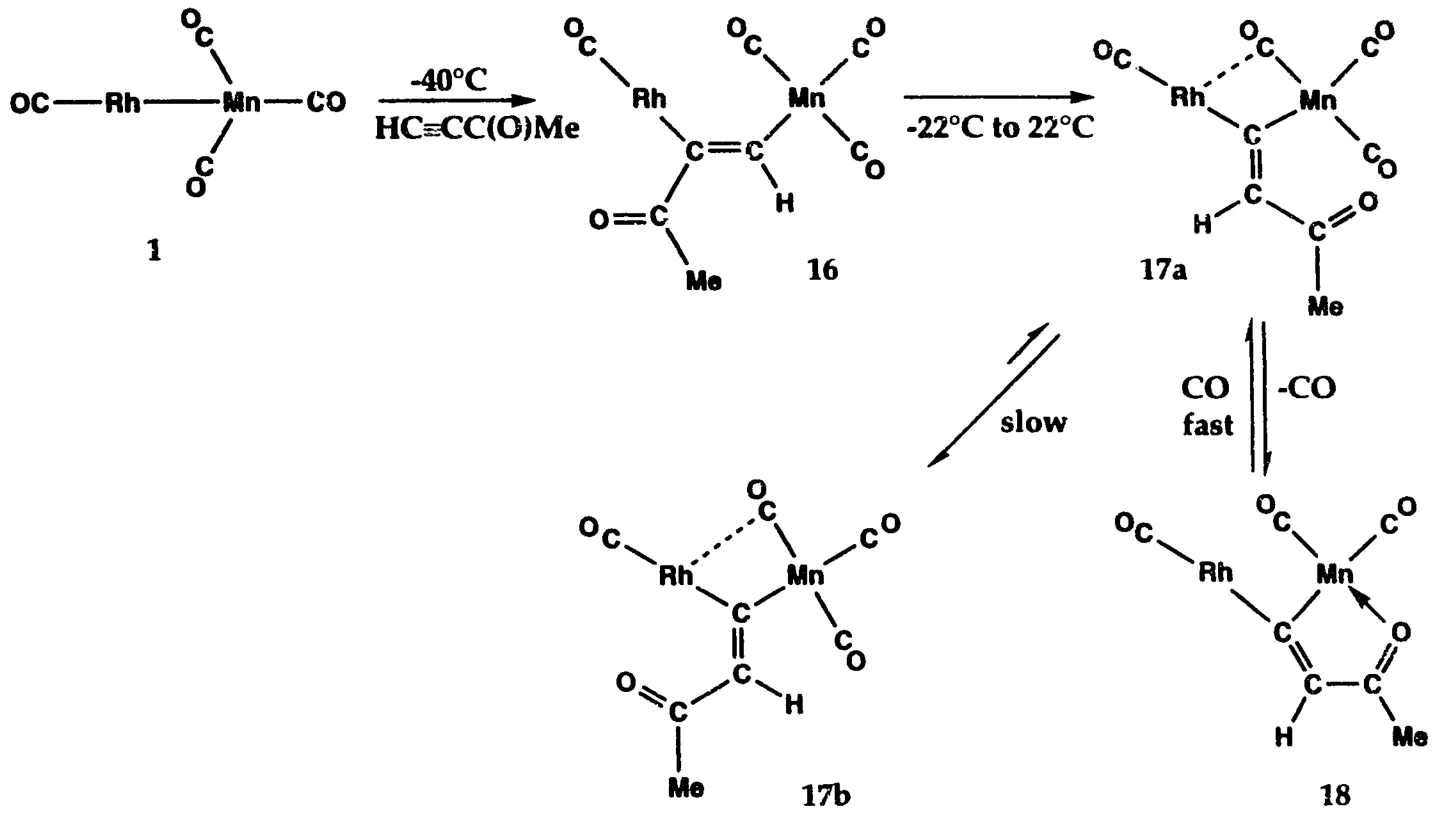
15 (~50%)

bound to Mn. The slightly smaller Rh-C coupling observed for the bridging carbonyls (compared to that for the symmetrically bridged CO in **14**) suggests asymmetric bridges for these groups, with stronger binding to Mn. In addition to the four carbonyl stretches (two terminal, two bridging) in the IR spectrum, the ketonic stretch is observed at 1654 cm^{-1}. For the other isomer (**14**) the geminal protons on the β-carbon of the vinyl group appear at δ 5.89 and 5.42 in the ^{1}H NMR spectrum. Both protons show coupling of 2 Hz to the Rh-bound phosphorus nuclei, and the lower-field signal also displays 3 Hz coupling to Rh. No coupling between the geminal protons is observed. Isomer **14** differs subtly from **15** in the natures of the carbonyl groups, displaying four carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectrum. The lowest-field signal (δ 249.7) shows coupling of 32 Hz with Rh, suggesting a conventional, bridged geometry, whereas the signal at δ 237.8 displays coupling to Rh of only 13 Hz, indicating that it is semibridging. Again we suggest that this difference is steric in origin, in which the bulkier -C(O)Me group on the α-carbon forces the adjacent carbonyl away from Rh, weakening the Rh-CO interaction. This is compensated for by a stronger interaction between Rh and the other carbonyl, as reflected in the larger $^1J_{Rh\text{-}C}$ value for this carbonyl.

These subtle structural differences between **14** and **15** demonstrate how adjacent metal centers can "tune" the electron distributions within the complex to changes in ligand binding modes. In **14** one carbonyl is semibridging while the other is symmetrically bridging, having a weak and strong interaction with Rh, respectively. In **15** the strengthening of the semibridging interaction with Rh is compensated for by a weakening of the other Rh-CO interaction such that both bridging carbonyls are asymmetrically bound. These changes in carbonyl binding modes, with each carbonyl being a one-electron donor to each metal for the symmetrically or asymmetrically bridged CO's or a two-electron donor to Mn in the semibridging CO,[85] are accompanied by a change in the nature of the Rh-Mn bond as shown in Scheme 3.3. Although such bonding descriptions are formalisms, they do demonstrate how the polarity of a metal-metal bond can change to compensate for changes in ligand binding.

(b) Vinylidene Complexes. As a continuation of our studies into the reactivities of alkynes at two metal centers we have also investigated reactions of **1** with terminal alkynes, with the goal of inducing alkyne-to-vinylidene transformations. Those alkynes not having strongly electron-withdrawing substituents, such as acetylene, phenylacetylene and propyne, do not react with **1**, even when present in a large excess for extended periods of time. However 3-butyn-2-one, having an electron-withdrawing -C(O)Me substituent, reacts readily with **1**, even at -40°C. The first species observed at this temperature is the alkyne-bridged product, $[RhMn(CO)_4(\mu\text{-}HC{\equiv}CC(O)Me)(dppm)_2]$ (**16**). All the NMR spectroscopic data (^1H, ^{13}C, ^{31}P) are very similar to that of compound **3**, therefore **16** is assigned an analogous structure, having a conventional alkyne bridge as shown in Scheme 3.4. The major difference between the two appears to be that the semibridging interaction of one carbonyl in **3** is either substantially weaker or not present in **16**, therefore the low-field carbonyl resonance in the ^{13}C NMR spectrum is at higher field than in **3**, more consistent with a terminal CO (δ 228.3 compared to 248.7), and shows no resolvable coupling to Rh. In the ^1H NMR spectrum the acetylenic hydrogen appears at δ 9.99, but shows no coupling to either Rh or the phosphorus nuclei. The absence of coupling involving the acetylenic hydrogen makes it impossible to unambiguously determine whether the alkyne unit is bound as shown in Scheme 3.4, or whether it has the opposite orientation in which the C(O)Me moiety is adjacent to Mn (we favor the

Scheme 3.4



orientation as shown since we would expect to observe Rh coupling in the other case). The orientation shown should be sterically favored, having the less encumbered end of the alkyne adjacent to the more crowded $Mn(CO)_3P_2$ end of the complex, but would be less favorable for the subsequent oxidative addition into the alkyne C-H bond, a presumed step in the conversion to vinylidene-bridged species.[20,37]

Upon warming solutions of **16**, two new compounds **17a** and **18** start to appear at *ca.* -20°C while warming to *ca.* 0°C results in the appearance of a third species **17b**. By ambient temperature compounds **17b** and **18** are the major species with **17a** being present in only *ca.* 10% of **17b**. Compound **17a** and **17b** are isomers of the vinylidene-bridged species, $[RhMn(CO)_4(\mu\text{-}CC(H)C(O)Me)(dppm)_2]$, differing only in the orientations of the substituents on the vinylidene β-carbon. The major isomer (**17b**) shows four carbonyl resonances in the $^{13}C\{^1H\}$ NMR; the high-field signal corresponds to a carbonyl which is terminally bound to Rh($^1J_{Rh\text{-}C}$ = 56 Hz), the intermediate two are terminally bound to Mn, and the low-field carbonyl is primarily bound to Mn with a semibridging interaction with Rh($^1J_{Rh\text{-}C}$ = 10 Hz). For this isomer the ^{13}C resonances for the carbons within the vinylidene unit could be obtained using unenriched alkyne. The alpha carbon appears at δ 137.4 and displays coupling to Rh of 4 Hz and to all phosphorus nuclei–one pair with 19 Hz coupling and one pair with 4 Hz coupling. Since overnight data acquisition on a 400 MHz instrument (for which we do not have appropriate heteronuclear decoupling capabilities) was necessary to observe these signals, no ^{31}P-decoupling experiments could be carried out so we do not know whether the larger coupling is to the Rh- or the Mn-bound phosphorus nuclei. However, the surprisingly small coupling to Rh suggests that the Rh-C_α interaction may be weak leading us to propose that coupling to the Rh-bound phosphines will also be weak. The chemical shift for C_α in our

RhMn compounds appears to be anomalous compared to other bridging vinylidenes,[15] in which these carbons invariably resonate downfield from δ 230. Even the complex [Cp(P^{i}Pr$_3$)Rh(μ-CO)(μ-CCH$_2$)Mn(CO)Cp],[86] having the same metal combination as our compounds, has the C$_\alpha$ resonance at δ 279, in the typical region. However in related vinylidene-bridged complexes of Rh and Ir we routinely observe chemical shifts for C$_\alpha$ upfield of δ 150,[11,13] with some even as high-field as δ 100. In addition compound **18**, which also has a high-field shift for C$_\alpha$ has been structurally characterized, confirming the vinylidene formulation (*vide infra*). The ^{13}C signals for C$_\beta$, the ketonic carbonyl, and the methyl group appear at δ 146.8, 193.8 and 22.0, respectively, and ^{13}C APT experiments support these assignments. The ^{1}H resonance for the methyl group of **17b** appears as a singlet at δ 0.62 and the vinylidene hydrogen appears as a triplet at δ 8.09, displaying coupling to the Rh-bound phosphorus nuclei of 7 Hz, as shown by the appropriate heteronuclear decoupling experiments. The minor isomer (**17a**) has very similar spectroscopic properties to **17b** with the major difference being in the ^{1}H NMR resonance for the vinylidene hydrogen which appears at δ 6.59, again showing coupling (12 Hz) to the Rh-bound phosphorus nuclei. It can be seen that **17b** is the thermodynamically favored isomer based on steric considerations with the more bulky C(O)Me substituent being directed away from the more crowded Mn center. In the IR spectrum the ketonic carbonyl stretch is observed at 1600 cm^{-1}.

The third species present (**18**) is shown (vide infra) to be a tricarbonyl species resulting from carbonyl loss from **17**. With this is mind an equilibrium mixture of only **17a** and **17b** (in *ca.* 10:90 molar ratio) can be prepared by allowing **16** to warm up in the presence of CO and conversely **18** results as the sole species by refluxing **17a** and **17b** in THF under an N$_2$ flush. Rearrangement of **17a** to **17b** is shown to be slow compared to CO attack on **18**, with **17a** appearing as the only species at -40°C with slow equilibration to the 10:90 mix of isomers as the temperature is raised to 20°C. Based on the structure established for **18** (*vide infra*), the structure of isomer **17a**, which is formed rapidly upon reaction of **18** with CO, can be assigned as shown. Rearrangement to give the thermodynamic product (**17b**), by rotation about the vinylidene unit, occurs slowly. Although rotation about the C=C bond in terminal vinylidene is apparently facile,[20] a similar rotation in vinylidene-bridged complexed appears less common, but has been observed.[12, 87]

The $^{13}C\{^1H\}$ NMR spectrum of **18** confirms the tricarbonyl formulation displaying three equal intensity carbonyl resonances, with one bound terminally to Rh and two bound terminally to Mn. The C_α resonance of the bridging vinylidene unit appears at δ 138.3 and is coupled to all four phosphorus nuclei. Surprisingly, no coupling to Rh is observed (although it should be recalled that this coupling in **17b** was only 4 Hz). Resonances for C_β, the ketonic carbon and the methyl carbon appear as singlets at δ 140.1, 190.8 and 23.8, respectively. Again ^{13}C APT experiments support these assignments. The ^1H NMR spectrum is unexceptional, apart from the methyl resonance which shows 2 Hz coupling to the Mn-bound phosphorus nuclei; the vinylidene-proton resonance was not observed and is presumably obscured by phenyl resonances. It is also significant that no stretch for the ketone carbonyl was observed in the IR spectrum. This fact and the ^{31}P-coupling to the methyl protons in the ^1H NMR suggests that coordination of the ketonic oxygen to Mn occurs to occupy the coordination site vacated by CO in the transformation from **17a**. This coordination mode has previously been noted in related vinylidene-bridged dimanganese compounds,[84,88,89] and has been confirmed in the present study by the X-ray structure determination of **18**, as shown in Figure 3.2.

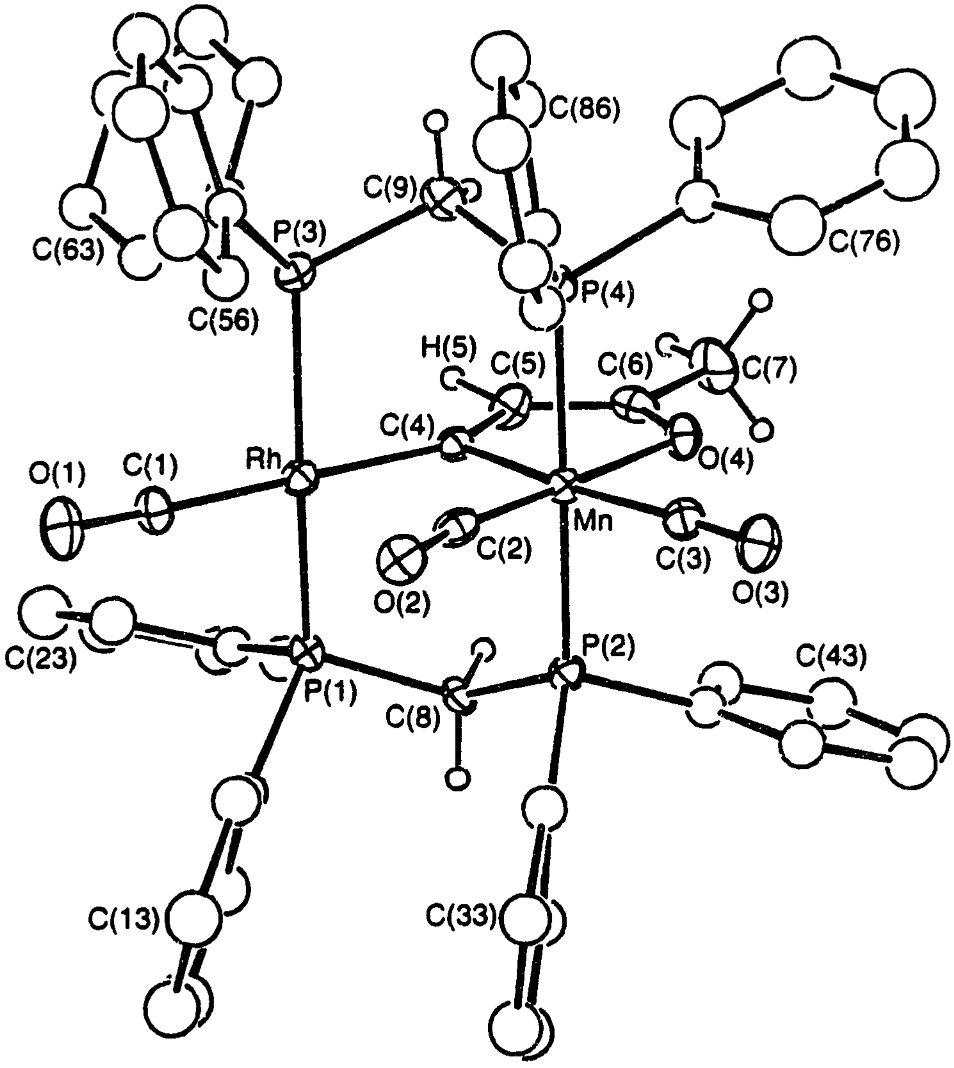


Figure 3.2. A perspective view of [RhMn(CO)$_3$(μ-η^1:η^2-CC(H)-C(O)Me)(dppm)$_2$] (**18**) showing the numbering scheme. Thermal ellipsoids are shown at the 20% level except for hydrogens which are shown artificially small or are omitted for phenyl groups. The numbering of the phenyl carbons starts at the ipso carbon and works sequentially around the ring.

Compound **18** crystallizes with one equiv of acetone, which has the expected geometry and displays no unusual contacts with the complex molecule. The bridging diphosphines have the common trans geometry at both metal centers, and all parameters within these units are normal. At rhodium the geometry is square planar, having the vinylidene bridge opposite a carbonyl, whereas at Mn the geometry is distorted octahedral, having the carbonyls opposite the vinylidene unit and the dative bond from the ketonic carbonyl group. The major distortions from an idealized octahedral geometry result from the bite of the bidentate ligand, which gives rise to a C(4)-Mn-O(4) angle of 78.1(3)° within the 5-membered metallacycle. Within this metallacycle the bond lengths suggest delocalized bonding. Although no single parameter is substantially different than that expected for a localized bonding model, all differ in the direction expected for delocalization. Therefore, the C(4)-C(5) distance (1.36(1)Å) is slightly longer than that expected (1.34Å) when conjugated with a ketone group, the C(5)-C(6) distance (1.41(1)Å) is shorter than expected (1.464Å) for a single bond between conjugated olefin and ketone moieties, and the C(6)-O(4) distance (1.26(1)Å) is also longer than expected for a C=O bond in this environment (1.22Å).[90] By contrast the C(6)-C(7) distance is exactly as expected for a $C(sp^2)$-$C(sp^3)$ bond in a ketone.[90] In addition all angles within the metallacycle are consistent with sp^2 hybridization of the carbon and oxygen atoms, keeping in mind the slight strain within the ring. The Mn-C(4) and Mn-O(4) distances are essentially as expected.[84,86,88,89]

Although the lack of coupling of the vinylidene C_α nucleus to Rh, together with the smaller coupling of C_α to the Rh-bound phosphorus nuclei than to those on Mn, suggests a weaker interaction of the vinylidene unit with Rh, this does not manifest itself in the structural parameters. Therefore the Rh-C(4) distance is actually shorter than Mn-C(4) (1.971(7) *vs.* 1.995(8)Å), in spite of an opposite prediction based on the covalent radii of the metals. The Rh-Mn separation (3.030(1)Å) is significantly longer than the single bond (2.667(1)Å) in [Cp(P^{i}Pr$_3$)Rh(μ-CO)(μ-CCH$_2$)Mn(CO)Cp],[86] consistent with the absence of a metal-metal bond. However the Rh-C(4)-Mn angle, of 99.6 (4)°, is more acute than expected, and there seems to be no reason that the Rh-Mn distance could not expand to allow an undistorted sp^2 geometry at C(4). This suggests that the two metals are drawn together. Such a compression of the nominally non-bonded metal-metal separation has been noted in a related system, induced by a weak semi-bridging carbonyl interaction.[43] The carbonyl group C(2)O(2) in **18** is bent away from Rh slightly, consistent with a semi-bridging interaction, giving a Mn-C(2)-O(2) angle of 166.6(7)°, but the long Rh-C(2) contact (2.618(8)Å) suggests that this interaction is weak at best.

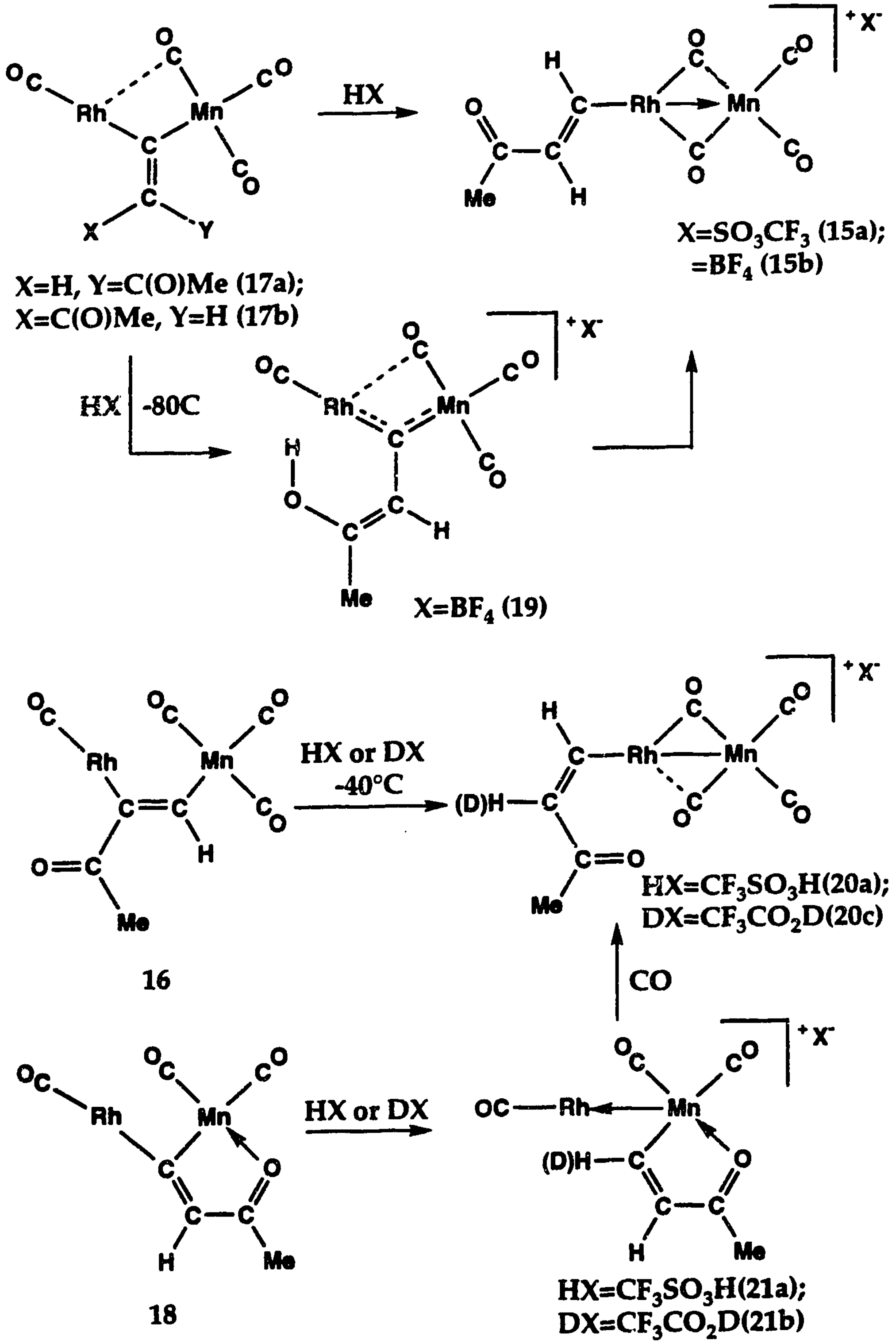
The vinylidene unit is not perpendicular to the Rh-Mn vector but is skewed substantially towards Mn, as shown by the Rh-C(4)-C(5) and Mn-C(4)-C(5) angles of 144.8 (7)° and 115.6(6)°, respectively. Presumably this skewing occurs to accommodate coordination of the ketonic oxygen at the sixth site, giving Mn the octahedral geometry. This offers further support that Rh is being drawn in the direction of C(2) since movement in the opposite direction would give less distortion at C(4). A similar skewing of a bridging vinylidene unit has been observed in related complexes in which the vinylidene forms part of a five-membered metallacycle ring.[84,86,88,89]

In an attempt to detect the interconversion of compounds **17a** and **17b**, spin-saturation transfer experiments were attempted by irradiating the ^{31}P resonance corresponding to the Mn-bound phosphines in **17b**. No change in the resonances of **17a** was noted, presumably because exchange is too slow. However, when this experiment is carried out by irradiating the corresponding resonance (δ 73.1) of compound **18** in a sealed NMR tube, a decrease in intensity of 80% was noted in the appropriate resonance (δ 67.7) of **17a**. This indicates that reversible CO loss from **17a** and concomitant coordination of the ketonic carbonyl occurs readily in solution.

(c) **Vinylidene Reactivity.** (i) **Protonation.** Having isolated and characterized the vinylidene-bridged complexes **17** and **18**, it was of interest to investigate their reactivities. In particular we were interested in the transformation of the vinylidene bridges to substituted vinyl moieties, either by protonation or alkylation. It was felt that the square planar Rh(I) center could be basic enough to react with electrophiles such as H^+ and CH_3^+, and that the resulting rhodium-hydride and rhodium-alkyl moieties might undergo migratory insertion with the bridging vinylidene units. Protonation of a mixture of **17a** and **17b** gives only one species at ambient temperature – the vinyl complex, [RhMn(*trans*-CH=C(H)C(O)Me)$(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]$ (**15a**), as shown in Scheme 3.5. This product is analogous to compound **7**, described earlier, in which the vinyl group is terminally bound to Rh, and is the same species as one isomer obtained in the reaction of **2** with HC≡CC(O)Me (see Scheme 3.3). The trans geometry for **15a** is as expected if the initial protonation were to occur at the vacant site on Rh, adjacent to the vinylidene unit in **17b**. Significantly, no species corresponding to a cis arrangement of vinyl hydrogens is observed, even though both isomers **17a** and **17b** were initially present.

At temperatures between -80° and -40°C protonation of **17** yields an intermediate **19** in between 5% and 20% yield, which then transforms to **15**, even at these low temperatures. Owing to the presence of **17a**, **17b** and **15**, together with impurities (ether, excess acid, etc.) not all the proton resonances of **19** could be

Scheme 3.5



X=H, Y=C(O)Me (17a);
X=C(O)Me, Y=H (17b)

$X=SO_3CF_3$ (15a);
$=BF_4$ (15b)

$X=BF_4$ (19)

16

HX=CF_3SO_3H(20a);
DX=CF_3CO_2D(20c)

18

HX=CF_3SO_3H(21a);
DX=CF_3CO_2D(21b)

identified. In the ^1H NMR spectrum of **19** a low-field signal at δ 9.30, one of the dppm-methylene resonances at δ 2.62, and the methyl resonance at δ 0.81 were observed. The vinyl-hydrogen resonance and the second dppm-methylene resonance were not identified. Significantly, no evidence of a hydride resonance was observed. Compound **19** is assigned as the enol intermediate $[RhMn(CO)_3(\mu\text{-}CC(H){=}C(OH)Me)(\mu\text{-}CO)(dppm)_2][BF_4]$ on the basis of the broad low-field ^1H signal which appears to be typical for an enol proton.[91] Keto-enol tautomerism generally occurs via deprotonation and reprotonation and the alternative site.[92] Whether the Rh center or the anion of the acid functions as the base is not known, although as noted, no high-field ^1H signal, that would indicate proton transfer to the metal, was observed.

Protonation of the alkyne-bridged precursor (**16**) yields the vinyl species **20**, in which the major difference with **15** is a cis arrangement of the vinyl hydrogens. The ^1H NMR spectrum of **20** shows the vinyl protons at δ 9.20 (H_α) and 6.42 (H_β) with mutual coupling of 7.5 Hz, consistent with the cis arrangement shown in Scheme 3.5. Additional coupling of H_α to Rh ($^2J_{Rh\text{-}H}$ = 5 Hz) and to the Rh-bound phosphorus nuclei of 6 Hz is also observed. In addition, the β-hydrogen also shows coupling to Rh of 2.5 Hz. Subtle differences in the $^{13}C\{^1H\}$ NMR spectrum, compared to **15**, show a carbonyl resonance at δ 259.8 with relatively strong coupling to Rh (41 Hz) as well as equal coupling to all four phosphorus nuclei, indicating a conventionally bridged CO, another at δ 231.9 couples weakly to Rh (12 Hz) and two other higher field resonances for the terminal carbonyls on Mn. The difference in the two bridged carbonyls of **20** may result from steric interactions, as proposed previously in **7** and **14a**, in which the geminal arrangement of the CO_2Me or C(O)Me group and Rh on C_α forces one of the bridged carbonyls away from Rh. Confirmation of the vinyl hydrogen assignments comes from reaction of **16** with CF_3CO_2D to give [RhMn(*cis*-

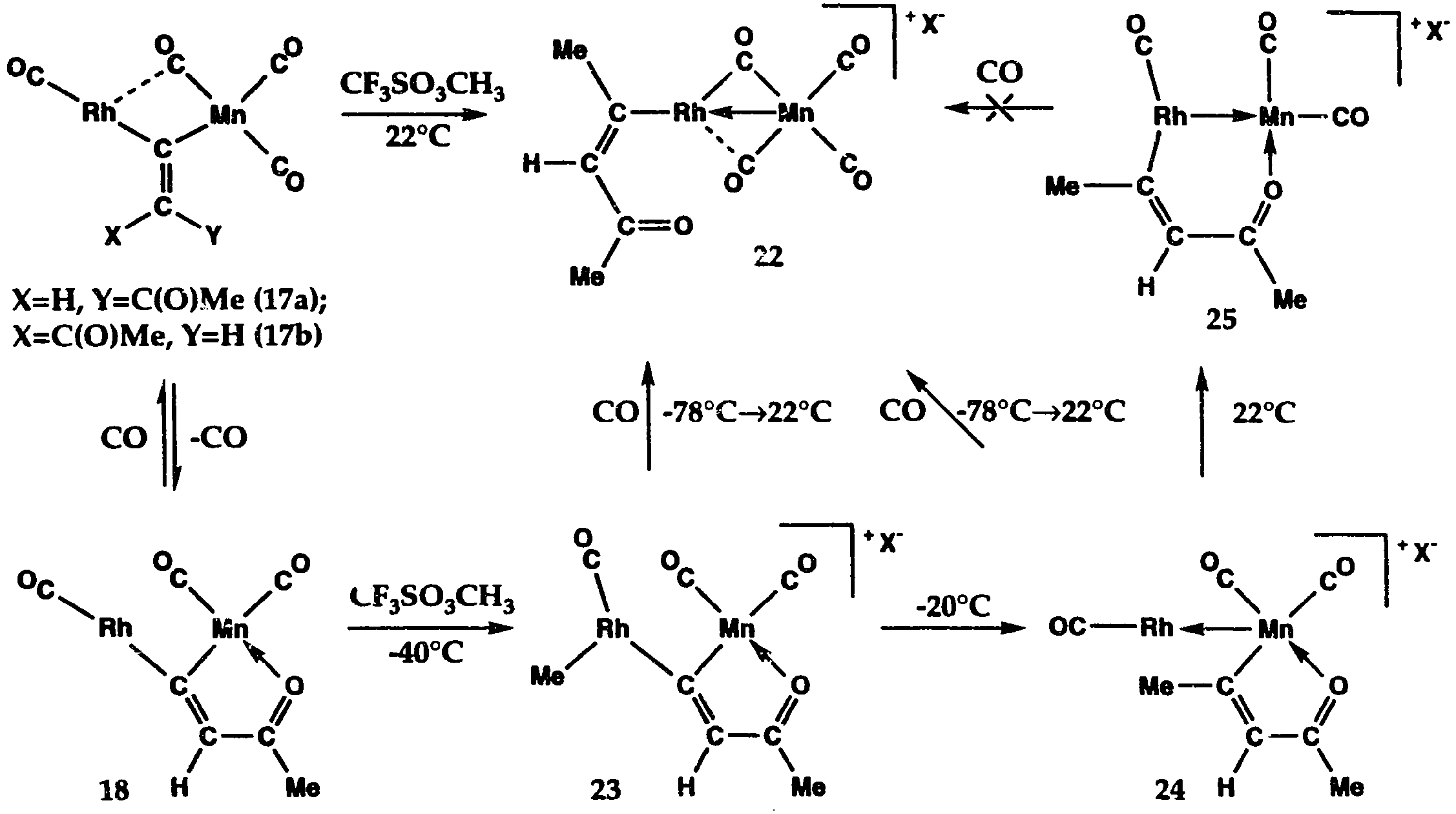
$CH=C(D)C(O)Me)(CO)_2(\mu\text{-}CO)_2(dppm)_2][CF_3CO_2]$; as expected the signal for the β-hydrogen is absent in the ^1H NMR spectrum, but appears in the ^2H NMR. Similarly species **20** having deuterium incorporated into the α position can be prepared (*vide infra*) giving the expected NMR results. The generation of a *cis*-vinyl species **20** from the *cis*-dimetallated olefinic precursor **16** is unexpected since rotation about the C=C bond has apparently occurred, such that the originally cis H_α and C(O)Me groups are now in a mutually trans arrangement. It is not clear how this occurs.

Protonation of th[illegible]ene species **18** yields the vinyl product [RhMn-(η^2-CH=C(H)C(O)M[illegible]n)$_2$][SO_3CF_3] (**21**), in which the vinyl group chelates the Mn atom, [illegible]rough C_α and the ketone oxygen. Although no metal-hydride species was observed, **21** is the anticipated product of protonation of **18** at Rh followed by hydrogen transfer to C_α accompanied by cleavage of the Rh-C_α bond. As was observed in **18**, which also has a 5-membered metallacycle involving Mn, the methyl resonance in the ^1H NMR spectrum of **21** displays coupling to the Mn-bound ^{31}P nuclei ($^5J_{P\text{-}H}$ = 3 Hz). The resonance for H_α is not observed, being obscured by phenyl resonances, however H_β appears at δ 8.04, showing 10 Hz coupling to H_α and [illegible].5 Hz coupling to the phosphorus nuclei on Mn. The magnitude of $H_\alpha H_\beta$ coupling is in line with a cis arrangement, which is also required by the chelated structure. If the protonation is carried out using CF_3CO_2D the product having deuterium in the α position is obtained and this signal is observed in the ^2H NMR at δ 7.66 (confirming the proposal that this resonance in the ^1H NMR spectrum is obscured by phenyl protons). As expected, no deuterium-hydrogen coupling is observed between the vinylic H and D atoms; H_β displays coupling (2.5 Hz) to only the ^{31}P nuclei on Mn. Unlike all species in which the ketonic carbonyl is not coordinated, but like the precursor (**18**), the IR spectrum of **21** shows no ketonic carbonyl stretch. Compound **21** can be transformed to **20** under CO. Thus replacing the donor bond from the ketone oxygen by a carbonyl group is also accompanied by migration of the vinyl group from Mn to Rh with concomitant transfer of the CO from Rh to Mn. This was the route used to generate **20** having deuterium incorporation at the α position (*vide supra*).

It is significant that protonation of the vinylidene-bridged species **17** and **18** has *not* yielded carbyne-bridged products as frequently occurs by attack of electrophiles at the β-carbon.[15] Instead the products obtained are consistent with the intervention of a Rh-hydride intermediate (although no such intermediate was observed). The formation of vinyl products via protonation of vinylidene complexes parallels an earlier study by Werner,[93] in which no metal-hydride species were detected, and is an interesting contrast to other work by the Werner group in which metal-hydride species rearranged by 1,3-hydride transfer to give carbynes.[37,41] Even though no metal-hydride species were observed in this part of our study, the formation of vinyl rather than carbyne products leads us to propose that they result from migratory insertion involving the vinylidene and hydride groups.

(ii) **Alkylation.** Reaction of the vinylidene-bridged isomers **17a** and **17b** with methyl triflate yields [RhMn(MeC=C(H)C(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**22**) as the sole observed product over the temperature range from -80° to 22°C. Unlike protonation, which yields a vinyl group in which the proton ends up on the α-carbon *cis* to the C(O)Me group, the methyl carbocation ends up *trans* to C(O)Me to give a product that is analogous to **20** rather than **15** (see Scheme 3.6). This analogy to **20** carries through to the binding of the bridging CO's, in which one is semi-bridging while the other is conventionally bridging, presumably for the reasons discussed

Scheme 3.6



CF₃SO₃CH₃
22°C
22
CO
25
X=H, Y=C(O)Me (17a);
X=C(O)Me, Y=H (17b)
CO
-CO
CO -78°C→22°C
CO -78°C→22°C
22°C
18
CF₃SO₃CH₃
-40°C
23
-20°C
24

earlier. The ^{1}H NMR spectrum of **22** shows the methyl signals as singlets at δ 1.57 and 1.41 and the vinyl hydrogen at δ 6.30. The arrangement shown about the vinyl C=C bond is supported by proton NOE experiments which indicate that the vinyl proton has a positive NOE effect with both sets of methyl protons, whereas the two methyl groups show no NOE effect with each other. If **22** results from an undetected Rh-methyl intermediate followed by migratory insertion with the vinylidene group, it would appear that isomer **17a** is the favored target, since this isomer would yield the appropriate stereochemistry at the double bond. Attack at Rh in this isomer, as opposed to the more predominant **17b**, would appear to be steric in origin with the larger C(O)Me substituent blocking attack at Rh in the latter.

The tricarbonyl, vinylidene-bridged **18** also reacts with methyl triflate, but in this case a couple of key intermediates can be detected at low temperature. At -60°C the first intermediate observed, $[RhMnCH_3(CO)_3(\mu\text{-}CC(H)C(O)Me)(dppm)_2][SO_3CF_3]$ (**23**) is a metal-alkyl species having the methyl group bound to Rh as shown in Scheme 3.6. This is the first complex in this study in which an alkyl unit is adjacent to a vinylidene unit, and as suggested earlier,[34] such species are unusual. In the ^{1}H NMR spectrum of **23** the resonance for the Rh-bound methyl group is broad, obscuring the expected 2-3 Hz coupling to Rh. However the $^{13}C\{^1H\}$ NMR study shows the broad methyl resonance at δ 9.0 with coupling of 27 Hz to Rh, clearly indicating a direct bond between the two. In addition, the ^{13}C chemical shift for this methyl group is at higher field than the alkyne-bound methyl group, falling in the range observed for other Rh-methyl complexes.[94] The methyl group of the C(O)Me moiety appears as a broad singlet at δ 26.0 in the $^{13}C\{^1H\}$ NMR spectrum with no obvious coupling to the Mn-bound phosphines, as was noted in the related metallacycles (**18**, **21**). It is noteworthy that upon reaction with CH_3^+ the value of

$^{1}J_{Rh-P}$ drops from 175 Hz in **18** to 101 Hz in **23**, consistent with an increase in oxidation state from +1 to +3.[95] An analogous drop (from 155 to 104 Hz) was observed upon protonation of **3** to give **6**, a product that is rather similar in formulation to **23**.

Upon warming a solution of **23** to -40°C a transformation to [RhMn(CO)$_3$(η^2-MeC=C(H)C(O)Me)(dppm)$_2$][SO$_3$CF$_3$] (**24**), occurs in which migration of the methyl group from Rh to the vinylidene ligand occurs, apparently yielding the chelated vinyl complex. The ^{13}C{^{1}H}NMR spectrum shows two Mn-bound (δ 227.6, 225.8) and one Rh-bound (δ 193.2, $^{1}J_{Rh-C}$ = 47 Hz) carbonyls, in addition to singlets for the methyl groups at δ 29.6 and 29.1 The lack of coupling of these methyl groups to phosphorus or Rh and the downfield shift from that observed for the Rh-CH$_3$ group in **23** suggests that the methyl group now resides on the transformed vinyl moiety Unfortunately, attempts to verify the geometry of the vinyl group in **24** by NOE experiments failed. The migratory insertion of the bridged vinylidene and methyl groups in **23** to give the vinyl moiety in **24** is unprecedented. This transformation can be regarded as reductive elimination from the Rh^{+3} center in **23** to give Rh^{+1} in **24**, and is supported by the increase in the value of $^{1}J_{RhP}$ that is observed (to 127 Hz in **24**). In the ^{1}H NMR spectrum the methyl resonances appear as singlets at δ 1.44 and 0.72 and the vinyl proton appears at δ 6.04.

Under a CO atmosphere both **23** and **24** transform to **22**. This product was well characterized and offers support for the formulation of **24**. Furthermore the transformation of **23** to **22** offers an additional example of migratory insertion of the bridging vinylidene group and the methyl group to give a substituted vinyl species. It may be that alkylation of **17** proceeds via intermediate **23**, since compounds **7a** and

18 were shown earlier to be in equilibrium. Alkylation to yield **23** would then be followed by attack of the CO initially lost from **17a**.

At ambient temperature compound **24** is unstable, even in the absence of CO, and gives a new species, $[RhMn(CO)_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}MeC{=}C(H)C(O)Me)(dppm)_2]\text{-}[SO_3CF_3]$ (**25**) in which the chelated vinyl moiety appears to adopt a bridging arrangement. In the $^{13}C\{^1H\}$ NMR spectrum the three carbonyl resonances are not unlike those of **24**, apart from the larger $^1J_{RhC}$ value (77 Hz) for **25**. The ketonic carbon is observed at δ 202.1, the vinyl C_α carbon is a complex multiplet at δ 138.7 and the methyl singlets appear at δ 36.0 and 25.7. Since the alkyne used in the preparation of **25** was not isotopically enriched overnight data acquisition was required. ruling out heteronuclear decoupling experiments. For this reason we were unable to resolve coupling of C_α to Rh. In the ^1H NMR spectrum one methyl group (δ 1.97) displays 3 Hz coupling to the Mn-bound phosphines, reminiscent of the coupling observed in **18** and **21** in which the ketone oxygen is coordinated to Mn. Although compound **24**, containing the chelating vinyl ketone group, reacts with CO displacing the ketone oxygen and causing migration of the vinyl group to Rh, compound **25** is inert to CO. Presumably in **24** the ketone oxygen is labile owing to the strain within the 5-membered metallacycle. Migration of the vinylic carbon to Rh in **25** generates a 6-membered metallacycle in which the intraligand strain is much less, resulting in decreased lability of the ketone oxygen.

Summary and Conclusions

The product resulting from the reaction of either of the internal, activated alkynes, DMAD or HFB, with $[RhMn(CO)_4(dppm)_2]$ is hardly unusual, having the alkyne coordinated parallel to the metal-metal bond, as is frequently observed in dppm-bridged species.[1c,4,96] However, the facile loss of CO that occurs from the coordinatively saturated Mn center is unusual in that it demonstrates two interesting ways in which saturation can be maintained at this center by virtue of the close proximity of Rh. In one isomer carbonyl loss is accompanied by formation of a dative Rh→Mn bond in which Rh utilizes its filled d_{z^2} orbital for donation to Mn, whereas in the second, rotation of the alkyne to a perpendicular orientation occurs with formation of a conventional metal-metal bond. This system is unique in demonstrating reversible interconversion of the two alkyne bonding modes, which occurs with unprecedented ease; we know of no other system in which both isomers are observed simultaneously.

Protonation of all alkyne-bridged products at ambient temperature yields a series of vinyl complexes while at low temperatures observation of metal-hydride intermediates is possible. In the alkyne-bridged complexes without a Rh-Mn bond, protonation appears to occur at Rh, followed by transfer to the alkyne. However, in the Rh-Mn bonded species protonation at the metal-metal bond occurs. Although in this latter case the hydride and alkyne groups are on opposite faces of the dimer, appearing not to be well placed for subsequent migratory insertion, movement of the hydride between the metals to the opposite face of the complex has been shown to be facile,[8] so that the observed structure appears to present no appreciable barrier to vinyl formation. These vinyl complexes also result from the reaction of the alkyne with the hydride-bridged complex $[RhMn(CO)_4(\mu\text{-}H)(dppm)_2][X]$. This hydride species also reacts with allene to give two isomers of $[RhMn(C_3H_5)(CO)_4(dppm)_2]$-$[X]$ having either a methyl vinyl or an η^1-allyl group σ-bound to Rh; the first results from transfer of the hydride ligand to a terminal carbon of allene while the second is a result of H-transfer to the central carbon. The vinyl species is thermodynamically favored, presumably because of the stronger Rh-C σ-bond involving an sp^2 carbon rather than an sp^3 carbon. This observation of both tautomeric forms resulting from the reaction of allene with a metal-hydride is unusual and presents strong support for the involvement of an allene-hydride intermediate in the interconversion between allyl and vinyl complexes.

When reaction of **1** with the terminal alkyne 3-butyn-2-one is monitored at low temperature the expected product having the alkyne coordinated parallel to the metals is observed. However upon warming to ambient temperature this species undergoes a 1,2-hydrogen shift to give a vinylidene-bridged product, [RhMn(CO)$_4$(μ-CC(H)C(O)Me)(dppm)$_2$] (**17**), and loss of one carbonyl from Mn is facilitated by a donor bond from the ketone oxygen of the vinylidene group to yield [RhMn(CO)$_3$(μ-η^1:η^2-CC(H)C(O)Me)(dppm)$_2$] (**18**).

Although protonation of a vinylidene ligand generally occurs at the β-carbon, the C(O)Me substituent on this carbon appears to lower its nucleophilicity such that Rh is the more basic site and protonation here is favored, followed by transfer to the α-carbon. Although no metal-hydride species were observed, these proposals are supported by the stereochemistry of the resulting vinyl groups. In the low temperature protonation of **17** the only intermediate observed appears to have resulted from protonation at the ketone oxygen to give an enol moiety. It is not clear how transfer of this proton to the α-carbon occurs, although transfer first to Rh appears feasible and reasonable.

The reaction of the vinylidene-bridged species, **17** and **18** with methyl triflate yields the corresponding vinyl products in which the carbocation has again ended up on the α-carbon, again suggesting primary attack at Rh, followed by migration to the vinylidene groups. In the case of the tricarbonyl species **18**, the unusual vinylidene-bridged methyl complex [RhMn(CH$_3$)(CO)$_3$(μ-η^1:η^2-CC(H)C(O)Me)(dppm)$_2$]-[SO$_3$CF$_3$] is observed at -60°C, and is shown to have the methyl group coordinated to Rh. Upon warming, this species undergoes a migratory insertion of the methyl and vinylidene ligands to give a tricarbonyl vinyl species in the absence of CO or a tetracarbonyl vinyl species in the presence of CO. These appear to be the only clearly defined examples involving the migratory insertion of a bridged vinylidene group; even examples involving terminal vinylidenes are not common.

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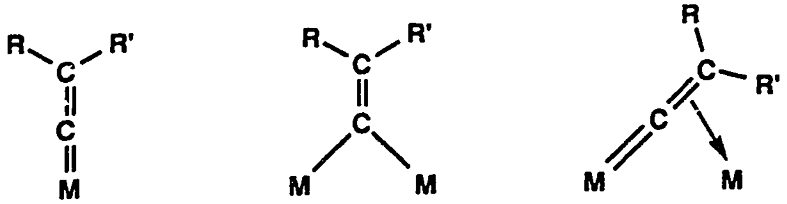
Chapter 4

Alkyne Transformations at Diiridium Centers– Alkyne-to-Vinylidene Isomerization

Introduction

Vinylidene ($:C{=}CH_2$) is an unstable tautomer of acetylene, which can be stabilized by coordination to one or more metal centers.[1,2] Since the first vinylidene complex was established, only 28 years ago,[3] interest in this fascinating group has grown dramatically, and its close analogy to the ubiquitous carbonyl ligand[2] suggests that a rich chemistry will continue to develop for vinylidene and its derivatives. Parallels between the carbonyl and vinylidene groups show up clearly in their coordination chemistry, in which vinylidene can function as either a terminal or a bridging group;[1,2] in addition the bridged vinylidene can be either symmetrically bridging or bound in a side-on manner (μ-η^1:η^2)[1,4], much as is observed for carbonyls.[5] This ability to function as either a terminal or bridging group has led to a strategy in which vinylidene-bridged heterobinuclear complexes are prepared through the reaction of a terminal-vinylidene complex with an unsaturated metal fragment.[6]

Much of the recent interest in vinylidene ligands focuses on their involvement in C-C bond-forming reactions.[1,7-18] Based on evidence of vinylidene species on the surface of Fischer-Tropsch catalysts[19] a mechanism for hydrocarbon chain growth, Vinylidene Binding Modes



Terminal

Symmetric Bridging

μ-η^1:η^2 Bridging

resulting from surface-bound vinylidene species has been presented.[20] Vinylidene groups have also been attracting attention for applications in organic synthesis[21,22] and in alkyne polymerization, for which vinylidenes are suggested as polymerization initiators.[10]

In a recent paper[23] it was reported that the vinylidene-bridged species [$Ir_2I_2(CO)_2(\mu$-$CCH_2)(dppm)_2$] reacted with excess acetylene to yield products which were proposed to have a bridging vinylidene and a bridging acetylene group on opposite faces of the complex. Since the diiodo vinylidene-bridged precursor is coordinatively saturated, it was suggested that I^- loss was occurring during the reaction so it appeared that removal of I^- should lead to unsaturation which might make preparation of these mixed alkyne-vinylidene species more facile. It also appeared that the preparation of bis-vinylidene species should be possible starting from coordinatively unsaturated mono-vinylidene precursors. In this chapter we report the preparation of cationic vinylidene-bridged species starting from either [$Ir_2(CO)_2(\mu$-$I)(dppm)_2$][X] or [$Ir_2I_2(CO)_2(\mu$-$CC(H)R)(dppm)_2$], and discuss some of the subsequent reactions of these products.

Experimental Section

General Procedures. Purified argon and carbon monoxide were obtained from Linde and allene from Matheson. The 99% carbon-13-enriched carbon monoxide was purchased from Isotec Inc and the 99% carbon-13-enriched acetylene from Cambridge Isotope Laboratories. All gases were used as received. Diethylether, THF and hexane were dried over Na-benzophenone ketyl whereas CH_2Cl_2 was dried by P_2O_5 and MeOH by magnesium metal; all solvents were distilled under argon before use. The perdeuterated methylene chloride was dried over molecular sieves and deoxygenated by repeated freeze-pump-thaw cycles. The compounds, phenylacetylene, silver tetrafluoroborate, methyllithium, tetrafluoroboric acid–dimethyl etherate, triflic acid, methyl triflate, t-butyl isocyanide, were used as received from Aldrich, potassium iodide was purchased from BDH Chemicals. Reactions were routinely conducted under Schlenk conditions. Ammonium hexachloroiridate (IV) was purchased from Victoria Precious Metals. Compounds, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) (**1**)[24] and $[Ir_2I_2(CO)_2\text{-}(\mu\text{-}CC(H)R)(dppm)_2]$ (R=H (**8**), Ph (**9**))[23] were prepared as previously reported. Unless otherwise noted, solvent removal, during purification of products, was performed under vacuum.

All routine NMR experiments were conducted on a Bruker AM-400 Spectrometer, whereas the $^{13}C\{^{31}P\}$ NMR experiments were conducted on a Bruker AM-200 spectrometer (this capability is not available on our AM-400 instrument). For all NMR experiments CD_2Cl_2 was used as solvent. IR spectra were recorded either on a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer as solids (Nujol mull or CH_2Cl_2 cast) or CH_2Cl_2 solutions. Elemental analyses were performed by the microanalytical service within the department. The spectral data for all compounds are given in Table 4.1.

Table 4.1. Spectroscopic Data for the Compounds[a]

Compound	IR,cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][SO_3CF_3]$ **(2)**	1971(st)^c	10.4(t, $^2J_{P(Ir)C}$=5Hz)^d	4.67(m, 4H, PCH_2P)^d	166.8(qui. CO, $^2J_{P(Ir)C}$=5Hz)^d
$[Ir_2(\eta^2\text{-}C_2H_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)\text{-}(dppm)_2][SO_3CF_3]$ **(3)**	1966(vs),^{b} 1824(m), 1660(w)	-4.4(ddm, P^1, $^2J_{P^1(Ir)C^t}$=14Hz, $^2J_{P^1(Ir)C^{bri}}$=4Hz),^{g} -13.2(dm, P^2, $^2J_{P^2(Ir)C^{bri}}$=4Hz)	4.98(dd, 1H_b, $^1J_{CH_b}$=234Hz, $^2J_{CCH_b}$=24Hz, $\underline{H}_bCCH_a$),^{g} 4.11(m, 2H, PCH_2P), 3.90(m, 2H, PCH_2P), 3.42(dd, 1H_a, $^1J_{CH_a}$=237Hz, $^2J_{CCH_a}$=26Hz, $H_bCC\underline{H}_a$)	187.7(ddm, $C^{bri}O$, $^2J_{C^{bri}(Ir)C^t}$=10Hz, $^2J_{C^{bri}(Ir)C_a}$=7.5Hz),^{g} 179.0(dt, C^tO, $^2J_{C^{bri}(Ir)C^t}$=10Hz, $^2J_{P^1(Ir)C^t}$=14Hz), 75.2(dd, C_a, $^1J_{C_aC_b}$=102Hz, $^2J_{C^{bri}(Ir)C_a}$=7.5Hz), 62.0(d, C_b, $^1J_{C_aC_b}$=102Hz)
$[Ir_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}I)(dppm)_2]\text{-}[SO_3CF_3]$ **(4·SO$_3$CF$_3$)**	1949(st),^{b} 1588(w) 1963(st),^{c} 1587(w)	-7.9(dt, $^2J_{C\alpha(Ir)P}$= 7Hz, $^2J_{C(Ir)P}$= [illegible]Hz)^d	4.63(m, 2H, PCH_2P),^{d} 3.92(m, 2H), PCH_2P) 3.72(d,$^1J_{C\beta H}$ =161Hz, CCH_2)	219.6(dtm, $^1J_{C\alpha C\beta}$=65Hz, $^2J_{C\alpha(Ir)C}$=9Hz, $\underline{C}CH_2$),^{d} 181.7(dquin, $^2J_{C\alpha(Ir)C}$=9Hz, $^2J_{P(Ir)C}$=8Hz, CO), 129.9(d, $^1J_{C\alpha C\beta}$=65Hz, $C\underline{C}H_2$)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C{^{1}H})
[Ir$_2$(CO)$_2$(μ-CCH$_2$)(μ-I)(dppm)$_2$]-[BF$_4$] (**4·BF$_4$**)		-7.9(d, $^2J_{Ca(Ir)P}$ =7Hz)^d	4.60(m, 2H, PC[illegible]), 3.92(m, 2H), PCH$_2$P), 3.72(d, $^1J_{C\beta}$[illegible] =161Hz, CC[illegible]2)	219.6(dqui, $^1J_{C\alpha C\beta}$=65Hz, $^2J_{P(Ir)C\alpha}$=7Hz, $\underline{C}$CH$_2$),^{d} 129.9(d, $^1J_{C\alpha C\beta}$=65Hz, C$\underline{C}$H$_2$)
[Ir$_2$(η^2-PhCCH)(CO)(μ-I)(μ-CO)-(dppm)$_2$][SO$_3$CF$_3$] (**5a**)		-2.7(ddm, P^1, $^2J_{P^1(Ir)C^1}$=14Hz, $^2J_{P^1(Ir)C^{bri}}$=4Hz),^{h} -10.8(dm, P^2, $^2J_{P^2(Ir)C^{bri}}$=4Hz)	4.30(s, 1H, PhCC$\underline{H}$),^{h} 3.92(m, 2H, PCH$_2$P), 3.81(m, 2H, PCH$_2$P)	190.2(dquin, 1C^{bri}O, $^2J_{C^{bri}(Ir)C^1}$=8Hz, $^2J_{P^1(Ir)C^{bri}}$= $^2J_{P^2(Ir)C^{bri}}$=4Hz),^{h} 179.2(dt, 1C^{1}O, $^2J_{C^{bri}(Ir)C^1}$=8Hz, $^2J_{P^1(Ir)C^1}$=14Hz)
[Ir$_2$(η^2-PhCCH)(CO)(μ-I)(μ-CO)-(dppm)$_2$][SO$_3$CF$_3$] (**5b**)	1977(w),^{b} 1965(vs), 1810(st)	-4.7(ddm, P^1, $^2J_{P^1(Ir)C^1}$=15Hz, $^2J_{P^1(Ir)C^{bri}}$=4Hz),^{d} -19.1(dm, P^2, $^2J_{P^2(Ir)C^{bri}}$=4Hz)	5.39(s, 1H, PhCC$\underline{H}$),^{d} 4.20(m, 2H, PCH$_2$P), 3.88(m, 2H, PCH$_2$P)	188.3(dquin, 1C^{bri}O, $^2J_{C^{bri}(Ir)C^1}$=11Hz, $^2J_{P^1(Ir)C^{bri}}$= $^2J_{P^2(Ir)C^{bri}}$=4Hz),^{d} 179.2(dt, 1C^{1}O, $^2J_{C^{bri}(Ir)C^1}$=11Hz, $^2J_{P^1(Ir)C^1}$=15Hz)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR		
		δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C{^{1}H})
[$Ir_2(CO)_2$(μ-CC(H)Ph)(μ-I)(dppm)$_2$] [SO_3CF_3] **(6)**	1972(vs),^{b} 1589(w) 1968(vs),^{c} 1590(w)	-5.2(m),^{d} -8.5(m)	5.08(s, 1H, CC(<u>H</u>)Ph),^{d} 4.54(m, 2H), PCH_2P), 3.90(m, 2H) PCH_2P),	220.7(m, <u>C</u>C(H)Ph),^{d} 182.5(t, $^{2}J_{P(Ir)C}$=15Hz, CO), 181.5(t, $^{2}J_{P(Ir)C}$=15Hz, CO), 129.2(s, C<u>C</u>(H)Ph)
[Ir_2(η^2-H_2CCCH_2)(CO)(μ-I)(μ-CO)- (dppm)$_2$][SO_3CF_3] **(7a·SO$_3$CF$_3$)**	1965(st),^{b} 1801(st) 1978(st),^{c} 1815(m)	-7.1(m),^{d} -10.5(m)	5.95(m, 1H),^{d} 5.34(m, 1H), 4.30(m, 2H), 4.01(m, 2H), 1.33(m, 2H)	189.9(dquin, 1CO),^{d} 179.9(dt, 1CO)
[Ir_2(η^2-H_2CCCH_2)(CO)(μ-I)(μ-CO) (dppm)$_2$][I] **(7a·I)**	1963(st),^{b} 1801(m) 1983(st),^{c} 1819(m)	-6.9(m, P^{1}),^{d} -10.4(m, P^{2})	5.93(dt, 1H$_a$, $^{2}J_{gem}$=2.4Hz, $^{4}J_{HaHc}$=3.4Hz, $(H_c)_2$CCC<u>H</u>$_a$H$_b$),^{d} 5.33(dt, 1H$_b$, $^{2}J_{gem}$=2.4Hz, $^{4}J_{HbHc}$=3.4Hz, $(H_c)_2$CCCH$_a$<u>H</u>$_b$), 4.29(m, 2H, PCH_2P), 4.08(m, 2H, PCH_2P), 1.31(ddt, 2H$_c$, $^{3}J_{P2(Ir)CHc}$=7Hz, (<u>H</u>$_c$)$_2$CCCH$_a$H$_b$)	189.9(dquin, C^{bri}O, $^{2}J_{C^1(Ir)C^{bri}}$=8Hz),^{d} $^{2}J_{P(Ir)C^{bri}}$=6.5Hz 179.9(dt, C^{1}O, $^{2}J_{C^1(Ir)C^{bri}}$=8Hz, $^{2}J_{P^1(Ir)C^1}$=14Hz)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR		
		δ($^{31}P\{^{1}H\}$)	δ(^{1}H)	δ($^{13}C\{^{1}H\}$)
[$Ir_2(\eta^2-H_2CCCH_2)(CO)(\mu-I)(\mu-CO)-(dppm)_2][SO_3CF_3]$ **(7b·SO$_3$CF$_3$)**	1921(st),^{b} 1760(st)	-7.2(m),^{d} -8.2(m)	5.26(m, 1H, $(H_c)_2CC\underline{C}\underline{H}_aH_b$),^{d} 4.27(m, 2H, PCH_2P), 4.05(m, 2H, PCH_2P), 2.70(m, 2H, $(\underline{H}_c)_2CCCH_aH_b$)	190.4(dquin, $C^{bri}O$. [illegible]$(Ir)C^{bri}$=10Hz, $^{2}J_{P(Ir)C^{bri}}$=6Hz),^{d} 179.9(dt, $C^{t}O$, $^{2}J_{C^{t}(Ir)C^{bri}}$=10Hz, $^{2}J_{P(Ir)C^{t}}$=12Hz)
[$Ir_2(\eta^2-H_2CCCH_2)(CO)(\mu-I)(\mu-CO)-(dppm)_2][I]$ **(7b·I)**		-7.1(m),^{d} -8.1(m)	5.25(m, 1H, $(H_c)_2CC\underline{C}\underline{H}_aH_b$),^{d} 4.28(m, 2H, PCH_2P), 4.10(m, 2H, PCH_2P), 2.67(m, 2H, $(\underline{H}_c)_2CCCH_aH_b$)	
[$Ir_2I_2(CO)_2(\mu-CCH_3)(dppm)_2]-[SO_3CF_3]$ **(10·SO$_3$CF$_3$)**		-14.7(m),^{g} -20.3(m)	4.78(m, 2H),^{g} 4.56(m, 2H), 4.00(d, 3H, $^{1}J_{C\beta H}$=128Hz)	

Table 4.1. continued

Compound	IR,cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[Ir_2I_2(CO)_2(\mu\text{-}CCH_3)(dppm)_2]$-$[BF_4]$ **($10\cdot BF_4$)**		-14.9(m, P^1),^{g} -20.3(m, P^2)	4.73(m, 2H, PCH_2P),^{g} 4.51(m, 2H, PCH_2P), 3.99(d, 3H, $^1J_{C\beta H}$=128Hz, CCH_3)	409.1(dd, $^1J_{C\alpha C\beta}$=23Hz, $^2J_{C\alpha(Ir)C^2}$=23Hz, $\underline{C}_\alpha C_\beta H_3$),^{g} 179.0(dt, $^2J_{C\alpha(Ir)C^2}$=23Hz, $^2J_{P^2(Ir)C^2}$=15Hz, C_2O), 166.5(t, $^2J_{P^1(Ir)C^1}$=10Hz, C_1O), 68.5(d, $^1J_{C\alpha C\beta}$=23Hz, $C_\alpha\underline{C}_\beta H_3$)
$[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}H)(dppm)_2]$-$[SO_3CF_3]$ **($11\cdot SO_3CF_3$)**	2066(st),^{b} 2020(st), 1605(w) 2081(st),^{c} 2028(st), 1594(w)	-21.2(m),^{d} -48.2(m)	8.18(d, 1H, $^2J_{gem}$=7Hz),^{d} 5.02(m, 2H), 4.13(m, 2H), -12.47(b, 1H)	
$[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}H)(dppm)_2]$-$[BF_4]$ **($11\cdot BF_4$)**		-21.3(m),^{d} -48.2(m)	8.17(dd, 1H, $^1J_{C\beta H}$=156Hz, $^2J_{gem}$=7Hz), CCH_2),^{d} 5.01(m, 2H, PCH_2P), 4.12(m, 2H, PCH_2P), -12.48(b, 1H, hydrido)	187.5(ddqui, C_α $^1J_{C\alpha C\beta}$=70Hz, $^2J_{C\alpha(Ir)C}$=26Hz, $^2J_{P(Ir)C}$=7Hz, $\underline{C}CH_2$),^{d} 167.9(t, $^2J_{P(Ir)C}$=12Hz, CO), 166.3(dt, $^2J_{C\alpha(Ir)C}$=26Hz, $^2J_{P(Ir)C}$=9Hz, CO), 132.3(d, $^1J_{C\alpha C\beta}$=70Hz, C_β, $C\underline{C}H_2$)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C{^{1}H})
[Ir$_2$I(CN-t-Bu)(CO)$_2$(μ-CCH$_2$)(dppm)$_2$]- [SO$_3$CF$_3$] **(12)**	2184(st),^{c} 1990(sh), 1976(vs), 1585(w)	-20.4(m, P^1),^{d} -22.8(m, P^2)	6.75(d, 2H, $^1J_{C\beta H}$=157Hz, CCH$_2$),^{d} 6.05(m, 2H, PCH$_2$P), 4.49(m, 2H, PCH$_2$P), 0.89(s, 9H, CN-t-Bu)	188.3(ddqui, Cα $^1J_{C\alpha C\beta}$=67Hz, $^2J_{C\alpha(Ir)C^1}$=3Hz, $^2J_{P(Ir)C\alpha}$=5Hz, $\underline{C}$CH$_2$),^{d} 172.9(ddt, C^{1}O, $^3J_{C^1C^2}$=8Hz, $^2J_{C\alpha(Ir)C^1}$=3Hz, $^2J_{P^1(Ir)C^1}$=8Hz), 166.3(dt, C^{2}O, $^3J_{C^1C^2}$=8Hz, $^2J_{P^2(Ir)C^2}$=8Hz), 132.0(d,$^1J_{C\alpha C\beta}$=67Hz, Cβ, C$\underline{C}$H$_2$)
[Ir$_2$I(CO)$_3$(μ-CCH$_2$)(dppm)$_2$]- [SO$_3$CF$_3$] **(13)**	2060(st),^{c} 2015(vs), 1985(vs), 1586(w)	-21.2(m),^{d} -23.5(m)	6.88(dd, 1H, $^1J_{C\beta H}$=158Hz, $^2J_{gem}$=6Hz, CCH$_2$),^{d} 6.77(dd, 1H, $^1J_{C\beta H}$=158Hz, $^2J_{gem}$=6Hz, CCH$_2$), 5.56(m, 2H, PCH$_2$P), 4.43(m, 2H, PCH$_2$P)	188.3(ddm(dd), Cα $^1J_{C\alpha C\beta}$=67Hz, $^2J_{C\alpha(Ir)C}$=15Hz, $^2J_{P(Ir)C\alpha}$=7Hz, $\underline{C}$CH$_2$),^{d} 174.1(dt(dd), CO, $^2J_{C\alpha(Ir)C}$=15Hz, $^2J_{P(Ir)C}$=9Hz), 170.0(t(ddd), CO, $^2J_{P(Ir)C}$=9Hz), 162.4(t(ddd), CO, $^2J_{P(Ir)C}$=8Hz) 131.4(d, C$\underline{C}$H$_2$, $^1J_{C\alpha C\beta}$=67Hz)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR $\delta(^{31}P\{^1H\})$	 $\delta(^1H)$	 $\delta(^{13}C\{^1H\})$
$[Ir_2I(CO)_2(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)\text{-}(dppm)_2][SO_3CF_3]$ **($14{\cdot}SO_3CF_3$)**	2054(sh),^{b} 2040(st), 1592(w) 2051(sh),^{c} 2034(st), 1598(w)	-9.4(m, P^1),^{d} -33.0(m, P^2)	8.60(d, 1H, $^1J_{C_bH}$=146Hz, $HCC\underline{H}$),^{d} 8.53(s, 1H, $CC(\underline{H})Ph$), 4.46(m, 2H), PCH_2P), 2.87(m, 2H) PCH_2P)	177.3(t, $^2J_{P^1(Ir)C^1}$=6Hz, C^1O),^{d} 169.2(dt, $^2J_{C_b(Ir)C^2}$=30Hz, $^2J_{P^2(Ir)C^2}$=9Hz, C^2O), 133.8(ddtt, $^1J_{C_aC_b}$=60Hz, $^2J_{C_b(Ir)C^2}$=30Hz, $^2J_{P^2(Ir)C_b}$=11Hz, $^2J_{P^1(Ir)C_b}$=6.5Hz, $HC_a\underline{C}_bH$), 120.8(dqui, $^1J_{C_aC_b}$=60Hz, $^2J_{P^1(Ir)C_a}$=$^2J_{P^2(Ir)C_a}$= 7.5Hz, $H\underline{C}_aC_bH$)
$[Ir_2I(CO)_2(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)\text{-}(dppm)_2][BPh_4]$ **($14{\cdot}BPh_4$)**		-9.4(m),^{d} -33.0(m)	8.61(s),^{d} 8.54(s, 1H), 4.46(m, 2H), 2.81(m, 2H)	
$[Ir_2I_2(CO)_2(\mu\text{-}HCCH)\text{-}(\mu\text{-}CC(H)Ph)(dppm)_2]$ **(15)**	2027(vs),^{b} 1587(w) 2023(vs),^{c} 1590(w)	-29.9(m, P^1),^{d} -33.6(m, P^2)	9.55(dm, 1H, $^1J_{CH}$=146Hz, $\underline{H}CCH$),^{d} 9.00(dm, 1H, $^1J_{CH}$=146Hz, $HCC\underline{H}$), 8.41(s, 1H, $CC(H)Ph$), 4.83(m, 2H, PCH_2P), 2.87(m, 2H, PCH_2P)	173.0(dt, $^2J_{C_a(Ir)C^1}$=29Hz, $^2J_{P^1(Ir)C^1}$=5Hz, C^1O),^{d} 172.5(dt, $^2J_{C_b(Ir)C^2}$=28Hz, $^2J_{P^2(Ir)C^2}$=5Hz, C^2O), 147.7(ddtt, $^1J_{C_aC_b}$=53Hz, $^2J_{C^2(Ir)C_b}$=29Hz, $^2J_{P^2(Ir)C_b}$=9Hz, $^2J_{P^1(Ir)C_b}$=6.5Hz, $HC_a\underline{C}_bH$), 144.1(ddtt, $^1J_{C_aC_b}$=53Hz, $^2J_{C^1(Ir)C_a}$=29Hz, $^2J_{P^1(Ir)C_a}$=9Hz, $^2J_{P^2(Ir)C_a}$=6Hz, $H\underline{C}_aC_bH$)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C{^{1}H})
[$Ir_2I(CO)_3$(μ-HCCH)(μ-CC(H)Ph)-($dppm)_2$][SO_3CF_3] (**16**)	2092(st),^{c} 2052(st) 2046(st)	-20.3(m),^{d} -30.0(m)	9.91(m, 1H, HCC$\underline{H}$),^{d} 8.57(m, 1H, HCC$\underline{H}$), 4.73(m, 2H), PCH_2P), 3.03(m, 2H) PCH_2P)	171.6(t, $^{2}J_{P(Ir)C}$=5Hz, 1CO),^{d} 164.6(t, $^{2}J_{P(Ir)C}$=6Hz, 1CO), 162.8(t, $^{2}J_{P(Ir)C}$=5Hz, 1CO)
[$Ir_2(CO)_4$(μ-HCCH)(μ-CC(H)Ph)-($dppm)_2$][$SO_3CF_3]_2$ (**17**)	2101(st),^{c} 2067(st)	19.8(m),^{d} -20.6(m)	9.06(m, 1H, HCC$\underline{H}$),^{d} 8.70(b, 1H, CC($\underline{H}$)Ph) 8.31(m, 1H, HCC$\underline{H}$), 4.43(m, 2H), PCH_2P), 3.79(m, 2H), PCH_2P)	164.6(t, $^{2}J_{P(Ir)C}$=5Hz, 1CO),^{d} 163.4(t, $^{2}J_{P(Ir)C}$=6Hz, 1CO), 162.9(t, $^{2}J_{P(Ir)C}$=5Hz, 1CO) 162.6(t, $^{2}J_{P(Ir)C}$=5Hz, 1CO)
[$Ir_2I(CO)_2$(μ-HCCPh)(μ-CC(H)Ph)-($dppm)_2$][SO_3CF_3] (**18**)	2071(m),^{c} 1967(st)	-7.9(m),^{d} -36.1(m)	8.60(s, 1H, CC($\underline{H}$)Ph),^{d} 7.95(s, 1H, $\underline{H}$CCPh), 4.12(m, 2H, PCH_2P), 3.12(m, 2H, PCH_2P)	181.1(t, $^{2}J_{P(Ir)C}$=11Hz, CO),^{d} 162.9(t, $^{2}J_{P(Ir)C}$=8Hz, CO)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR δ(^{31}P{^{1}H})	 δ(^{1}H)	 δ(^{13}C{^{1}H})
[$Ir_2I(CCH_2)(CC(H)Ph)(CO)_2$- $(dppm)_2$][SO_3CF_3] **(19·SO_3CF_3)**	2065(m),^{b} 1991(st), 1580(w) 2064(m),^{c} 1989(st), 1577(w)	-7.8(dm, P^1, $^2J_{P^1(Ir)C^1}$=10Hz),^{g} -34.8(ddm, P^2, $^2J_{P^2(Ir)C\alpha}$=9Hz, $^2J_{P^2(Ir)C^2}$=9Hz)	8.20(d, 1H, $^4J_{C^1(Ir)CCH}$=4Hz, CC($\underline{H}$)Ph),^{d} 6.54(ddt, 1H, $^1J_{C\beta H}$=157Hz, $^2J_{gem}$=10Hz, $^4J_{P(Ir)CCH}$=2Hz, CCH_2), 6.04(ddt, 1H, $^1J_{C\beta H}$=157Hz, $^2J_{gem}$=10Hz, $^4J_{P(Ir)CCH}$=2Hz, CCH_2), 4.40(m, 2H, PCH_2P), 3.02(m, 2H, PCH_2P)	179.9(t, $^2J_{P^1(Ir)C^1}$=10Hz, C^1O),^{d} 174.6(ddt, $^1J_{C\alpha C\beta}$=64Hz, $^2J_{C\alpha(Ir)C^2}$=35Hz, $^2J_{P^2IrC\alpha}$=10Hz, $\underline{C}CH_2$), 174.3(m, $\underline{C}$C(H)Ph) 163.8(dt, $^2J_{C\alpha(Ir)C^2}$=35Hz, $^2J_{P^2(Ir)C^2}$=9Hz, C^2O), 143.9(s, C$\underline{C}$(H)Ph) 133.6(d, $^1J_{C\alpha C\beta}$=64Hz, $C\underline{C}H_2$)
[$Ir_2I(CCH_2)(CC(H)Ph)(CO)_2$- $(dppm)_2$][BF_4] **(19·BF_4)**		-8.0(m, P^1),^{d} -34.8(dm, P^2, $^2J_{P^2(Ir)C\alpha}$=10Hz)	8.20(s, 1H, CC($\underline{H}$)Ph),^{d} 6.54(ddt, 1H, CCH_2), 6.04(ddt, 1H, CCH_2), 4.39(m, 2H, PCH_2P), 2.08(m, 2H, P[illegible])	174.6(dt, $^1J_{C\alpha C\beta}$=64Hz, $^2J_{P^2IrC\alpha}$=10Hz, $\underline{C}CH_2$),^{d} 133.7(d, $^1J_{C\alpha C\beta}$=64Hz, $C\underline{C}H_2$)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR		
		δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C{^{1}H})
$[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)\text{-}(\mu\text{-}CC(H)Ph)(dppm)_2]$ **(20a)**	2027(st),^{c}	-32.3(m),^{d} -37.7(m)	9.19(d, 1H, $^1J_{C\beta H}$=153Hz, CCH_2),^{d} 9.16(d, 1H, $^1J_{C\beta H}$=153Hz, CCH_2), 4.65(m, 2H), PCH_2P), 2.45(m, 2H) PCH_2P)	171.9(dt, $^2J_{C\alpha(Ir)C}$=27Hz, $^2J_{P(Ir)C}$=7Hz, CO),^{g} 170.4(dt, $^2J_{C\alpha(Ir)C}$=27Hz, $^2J_{P(Ir)C}$=5Hz, CO), 143.3(d, $^1J_{C\alpha C\beta}$=61Hz, $C\underline{C}H_2$), 102.2(dtm, $^1J_{C\alpha C\beta}$=61Hz, $^2J_{C\alpha(Ir)C}$=27Hz, $\underline{C}CH_2$)
$[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)\text{-}(\mu\text{-}CC(H)Ph)(dppm)_2]$ **(20b)**	2009(st),[illegible]	9.6(m),^{i} -10.3(m), -31.3(m), -36.5(m)		174.7(dt, $^2J_{C\alpha(Ir)C}$=30Hz, $^2J_{P(Ir)C}$=8Hz, CO),^{g} 172.7(t, $^2J_{P(Ir)C}$=8Hz, CO), 133.0(d, $^1J_{C\alpha C\beta}$=61Hz, $C\underline{C}H_2$), 102.2(m, $\underline{C}CH_2$)
$[Ir_2I(CO)_3(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)\text{-}(dppm)_2][SO_3CF_3]$ **(21a)**	2094(st),^{c} 2050(st), 2034(sh)	-19.4(m, P^1),^{e} -33.3(m, P^2)	8.81(d, 1H, $^1J_{CbH}$=157Hz, CCH_2),^{g} 8.14(d, 1H, $^1J_{CbH}$=157Hz), CCH_2), 4.01(m, 2H, PCH_2P), 3.26(m, 2H) PCH_2P)	171.4(dt, $^2J_{C\alpha(Ir)C^2}$=31Hz, $^2J_{P^2(Ir)C^2}$=7Hz, C^{2}O),^{g} 166.7(t, $^2J_{P^1(Ir)C^1}$=6Hz,C^{1}O), 164.4(dt, $^2J_{C\alpha(Ir)C^1}$=21Hz, $^2J_{P^1(Ir)C^1}$=5Hz, C^{1}O), 141.9(d, $^1J_{C\alpha C\beta}$=60Hz, $C\underline{C}H_2$), 101.0(m, $\underline{C}CH_2$)

Table 4.1. continued

		NMR		
Compound	IR,cm^{-1}	$\delta(^{31}P\{^{1}H\})$	$\delta(^{1}H)$	$\delta(^{13}C\{^{1}H\})$
$[Ir_2I(CO)_3(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)\text{-}(dppm)_2][SO_3CF_3]$ **(21b)**		-20.7(m, P^1),[e] -30.7(m, P^2)	8.72(d, 1H, $^1J_{C\beta H}$=152Hz, CCH_2),[g] 8.18(d, 1H, $^1J_{C\beta H}$=152Hz, CCH_2), 4.26(m, 2H, PCH_2P), 3.26(m, 2H, PCH_2P)	170.0(dt, $^2J_{C\alpha(Ir)C^2}$=32Hz, $^2J_{P^2(Ir)C^2}$=7Hz, C^2O),[g] 166.2(t, $^2J_{P(Ir)C^1}$=9Hz, C^1O), 164.0(dt, $^2J_{C\alpha(Ir)C^1}$=22Hz, $^2J_{P^1(Ir)C^1}$=5Hz, C^1O), 142.8(d, $^1J_{C\alpha C\beta}$=60Hz, $C\underline{C}H_2$), 99.8(m, $\underline{C}CH_2$)
$[Ir_2(CO)_4(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)\text{-}(dppm)_2][SO_3CF_3]_2$ **(22)**	2101(st),[c] 2066(st)	-17.4(m),[d] -19.1(m)	8.19(t, 1H, $^4J_{C(Ir)CCH}$=5.5Hz, $CC(\underline{H})Ph$),[d] 7.94(dd, 1H, $^1J_{CH}$=148Hz, $^2J_{gem}$=2.5Hz, CCH_2), 7.82(dd, 1H, $^1J_{CH}$=148Hz, $^2J_{gem}$=2.5Hz, CCH_2), 4.60(m, 2H), PCH_2P), 3.90(m, 2H) PCH_2P)	165.8(dt, $^2J_{C\alpha(Ir)C}$=26Hz, $^2J_{P(Ir)C}$=6Hz, 1CO),[d] 165.7(dt, $^2J_{C\alpha(Ir)C}$=26Hz, $^2J_{P(Ir)C}$=6Hz, 1CO), 164.7(t, $^2J_{P(Ir)C}$=6Hz, CO), 164.1(t, $^2J_{P(Ir)C}$=7Hz, CO), 142.6(d, $^1J_{C\alpha C\beta}$=61Hz, $C\underline{C}H_2$), 98.2(dtqui, $^1J_{C\alpha C\beta}$=61Hz, $^2J_{C\alpha(Ir)C}$=26Hz, $^2J_{P(Ir)C\alpha}$=8Hz, $\underline{C}CH_2$)

Table 4.1. continued

Compound	IR,cm^{-1}	NMR		
		δ(^{31}P{^{1}H})	δ(^{1}H)	δ(^{13}C{^{1}H})
[$Ir_2(CH_3)_2(CO)_2(\mu$-$CCH_2)$-(μ-CC(H)Ph)(dppm)$_2$] (**23**)		-10.7(m, P^1),^{d} -12.8(m, P^2)	-0.45(t, 3H, $^3J_{P^2(Ir)CH}$=4.5Hz, CH$_3$),^{d} -0.92(t, 3H, $^3J_{P^1(Ir)CH}$=4.5Hz, CH$_3$)	177.9(dt, $^2J_{C\alpha(Ir)C}$=26Hz, $^2J_{P(Ir)C}$=9Hz, 1CO),^{d} 177.5(t, 1CO, $^2J_{P(Ir)C}$=6Hz), 133.4(d, $^1J_{C\alpha C\beta}$=59Hz, C$\underline{C}$H$_2$), 106.0(m, $\underline{C}$CH$_2$)

[a] Abbreviations used IR: w = weak; m = medium; st = strong; vs = very strong. NMR: s = singlet; d = doublet; t = triplet; q = quartet; qui = quintet; m = multiplet; b = broad; or any combination; bri = bridging. In all samples, except where noted in the text, the NMR data are for ^{13}CO, ^{13}C=$^{13}CH_2$ and $H^{13}C\equiv^{13}CH$ groups, however IR results are for the natural abundace samples. [b] Nujol mull. [c] CH_2Cl_2 solution. [d] 22°C. [e] 0°C. [f] -20°C. [g] -40°C. [h] -60°C; [i] -80°C

Preparation of Compounds. (a) $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][SO_3CF_3]$ (2). To a CH_2Cl_2 solution of compound **1** (100 mg, 68 μmol in 5 mL) was added 7.8 μL of methyl triflate (68 μmol) causing the color of the solution to change from orange to burgundy immediately. Removal of the solvent and recrystallization from CH_2Cl_2/hexane gave a burgundy solid (yield 86%). The compound was very air sensitive and the elemental analysis was not attempted.

(b) $[Ir_2(\eta^2\text{-}HCCH)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (3). To a CH_2Cl_2 solution of compound **2** (100 mg, 67 μmol in 5 mL) was added 5 mL of acetylene (0.2 mmol) at -78°C causing the color of the solution to change from burgundy to yellow immediately. The solution was partially evacuated to remove excess acetylene and 30 mL of hexane was slowly added to the solution to precipitate a pale yellow solid (80%). The solid was found to be stable for short periods at room temperature however the CH_2Cl_2 solution was not stable at ambient temperature. Therefore the NMR sample was prepared at -78°C. Characterization was by NMR and IR spectroscopies.

(c) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ ($4 \cdot SO_3CF_3$). To a CH_2Cl_2 solution of compound **8** (100 mg, 67 μmol in 10 mL) was added 7.6 μL of $CF_3SO_3CH_3$ (67 μmol) and the solution was stirred for 1 h. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow crystalline solid (yield 90%). Anal. calcd for $Ir_2ISP_4F_3O_5C_{55}H_{46}$: C, 43.70; H, 3.05; I, 8.40. Found: C, 43.48; H, 2.91; I, 8.40.

(d) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CCH_2)(dppm)_2][BF_4]$ ($4 \cdot BF_4$). To a CH_2Cl_2 solution of compound **8** (50 mg, 34 μmol in 5 mL) was added 6.6 mg of $AgBF_4$ (34 μmol) and the solution was stirred for 15 min and filtered to remove AgI. Removal of the solvent from the yellow filtrate and recrystallization from CH_2Cl_2/Et_2O gave a yellow crystalline solid (yield 84%). Anal. calcd for $Ir_2IP_4F_4O_2BC_{54}H_{46}$: C, 44.75; H, 3.18. Found: C, 44.43; H, 3.12.

(e) $[Ir_2(\eta^2\text{-}HCCPh)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (5a and 5b). To a CD_2Cl_2 solution of compound 2 (10 mg, 7 µmol in 0.5 mL in an NMR tube) was added 3 µL of phenylacetylene (27 µmol) at -78°C. The solution turned to yellow from burgundy and the variable temperature NMR experiments were undertaken. These species were characterized by NMR and IR techniques, showing two isomers (**5a** and **5b**).

(f) $[Ir_2(\eta^2\text{-}HCCPh)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (5b). To a CH_2Cl_2 solution of compound **2** (50 mg, 34 µmol in 5 mL) was added 6 µL of phenylacetylene (54 µmol) at -78°C. The solution turned to yellow from burgundy and 30 mL of hexane was slowly added to the solution to precipitate the pale yellow solid (80%). The solid was found to be stable for short periods at room temperature however the CH_2Cl_2 solution was not stable at ambient temperature therefore the NMR sample was prepared at -78°C. Characterization was by NMR and IR spectroscopies, showing only **5b**.

(g) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (6). To a CH_2Cl_2 solution of compound **9** (100 mg, 64 µmol in 5 mL) was added 15 µL of $CF_3SO_3CH_3$ (128 µmol) and the solution was stirred for 0.5 h, resulting in a color change from yellow to orange. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow crystalline solid (yield 85%). Anal. calcd for $Ir_2ISP_4F_3O_5C_{61}H_{50}$: C, 46.15; H, 3.15. Found: C, 45.76; H, 3.03.

(h) $[Ir_2(\eta^2\text{-}H_2CCCH_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ ($7a\cdot SO_3CF_3$ and $7b\cdot SO_3CF_3$). To a CH_2Cl_2 solution of compound **2** (50 mg, 34 µmol in 5 mL) was added 5 mL of allene (0.2 mmol). The color of the solution changed from burgundy to light yellow immediately. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a pale yellow solid (yield 90%). The ^{31}P NMR showed a ratio of *ca* 2:1 of **7a•SO₃CF₃** and **7b•SO₃CF₃** respectively. Elemental analyses were not carried out on this species but were done instead for the iodide salts which have essentially identical spectroscopic parameters.

(i) **$[Ir_2(\eta^2\text{-}H_2CCCH_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (7a•I and 7b•I).** To a CH_2Cl_2 solution of compound **1** (50 mg, 34 μmol in 5 mL) was added 5 mL of allene (0.2 mmol). The solution was stirred for 1 h, during which time the yellow color of the solution lightened. Removal of the solvent and recrystallization from THF/Et_2O gave a pale yellow solid (yield 84%). The ^{31}P NMR showed a ratio of *ca* 10:1 of **7a•I** and **7b•I** respectively. Anal. calcd for $Ir_2I_2P_4O_2C_{55}H_{48}$: C 43.94; H, 3.20. Found: C, 44.58; H, 3.36.

(j) **$[Ir_2I_2(CO)_2(\mu\text{-}CCH_3)(dppm)_2][SO_3CF_3]$ (10•SO₃CF₃).** To a CD_2Cl_2 solution of compound **8** (10 mg, 7 μmol in 0.5 mL in an NMR tube) was added 1 μL of CF_3SO_3H (11 μmol) at -78°C. The compound was characterized by NMR experiments at -40°C.

(k) **$[Ir_2I_2(CO)_2(\mu\text{-}CCH_3)(dppm)_2][BF_4]$ (10•BF₄).** To a CD_2Cl_2 solution of compound **8** (5 mg, 3.4 μmol in 0.5 mL in an NMR tube) was added 1 μL of $HBF_4 \cdot Me_2O$(8 μmol) at -78°C. The NMR characterization was carried out at -40°C.

(l) **$[Ir_2I_2(CO)_2(\mu\text{-}H)(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (11•SO₃CF₃).** To a CH_2Cl_2 solution of compound **8** (50 mg, 34 μmol in 0.5 mL) was added 3 μL of CF_3SO_3H (34 μmol). Removal of the solvent and recrystallization from THF/Et_2O gave a yellow solid (yield 90%). Anal. calcd for $Ir_2I_2P_4SF_3O_5C_{55}H_{47} \cdot C_4H_8O$: C, 41.40; H, 3.22. Found: C, 41.27; H, 2.95. The presence of 1 equiv of THF was verified from the ^1H NMR spectrum.

(m) $[Ir_2I_2(CO)_2(\mu\text{-}H)(\mu\text{-}CCH_2)(dppm)_2][BF_4]$ (11•BF_4). To a CH_2Cl_2 solution of compound **8** (50 mg, 34 µmol in 0.5 mL) was added 4.2 µL of HBF_4•Me_2O (34 µmol). Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (yield 82%).

(n) $[Ir_2I(t\text{-}BuNC)(CO)_2(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (12). To a CH_2Cl_2 solution of compound **4a** (50 mg, 33 µmol in 5 mL) was added 5 µL of t-butyl isocyanide (43 µmol) and the solution was stirred for 0.5 h, during which time the yellow color lightened. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a pale yellow solid (yield 96%). Anal. calcd for $Ir_2ISP_4F_3O_5NC_{60}H_{55}$: C, 45.20; H, 3.45. Found: C, 45.12; H, 3.26.

(o) $[Ir_2I(CO)_3(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (13). A CH_2Cl_2 solution of compound **4a** (50 mg, 33 µmol in 5 mL) was put under CO (1 atmosphere) and the solution was stirred for 0.5 h, during which time the yellow color lightened. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a pale yellow solid (yield 90 %). An elemental analysis was not obtained for this compound owing to reversible CO loss regenerating **4•SO_3CF_3**.

(p) $[Ir_2I(CO)_2(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (14•SO_3CF_3). To a CH_2Cl_2 solution of compound **6** (100 mg, 63 µmol in 5 mL) was added 10 mL of C_2H_2 (0.4 mmol). The solution was allowed to stir for 24 h causing a color change from orange to brown. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a pale yellow solid (yield 82%). Anal. calcd for $Ir_2ISP_4F_3O_5C_{63}H_{52}$: C, 46.90; H, 3.23. Found: C, 46.88; H, 3.20.

(q) $[Ir_2I(CO)_2(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)(dppm)_2][BPh_4]$ (14•BPh_4). To a CH_2Cl_2 solution of compound **14•SO_3CF_3** (50 mg, 31 µmol in 5 mL) was added 5 mL of an acetone solution of $NaBPh_4$ (106 mg in 5 mL, 310 µmol) and the solution was stirred for 1 h. The solvent was removed and the residue was dissolved in 5 mL of CH_2Cl_2 and the solution was filtered. Removal of he solvent of the filtrate and recrystallization of the residue gave a yellow powder (yield 70%).

(r) **[$Ir_2I_2(CO)_2(\mu$-HCCH)(μ-CC(H)Ph)(dppm)$_2$] (15).** To a CH_2Cl_2 solution of compound **14•SO_3CF_3** (100 mg, 63 μmol in 5 mL) was added a solution of KI (130 mg, 783 μmol in a minimum volume of MeOH) causing the color to change from light orange to light yellow immediately. The solution was stirred for 0.5 h then the solvent was removed and the residue was dissolved in 5 mL of CH_2Cl_2 and the solution was filtered. The filtrate was washed by 3 × 5mL of deoxygenated water. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (yield 76%). Anal. calcd for $Ir_2I_2SP_4O_2C_{62}H_{52}$•$CH_2Cl_2$: C, 45.13; H, 3.22. Found: C, 44.76; H, 3.03. One equivalent of CH_2Cl_2 was verified from crystal structure determination.

(s) **[$Ir_2I(CO)_3(\mu$-HCCH)(μ-CC(H)Ph)(dppm)$_2$][SO_3CF_3] (16).** A CD_2Cl_2 solution of compound **14•SO_3CF_3** (15 mg, 10 μmol in 0.5 mL in an NMR tube) was put under CO (10 psi) and the NMR experiments were carried out. Removal of the CO atmosphere reversed the reaction.

(t) **[$Ir_2(CO)_4(\mu$-HCCH)(μ-CC(H)Ph)(dppm)$_2$][SO_3CF_3]$_2$ (17).** A CD_2Cl_2 solution of compound **14•SO_3CF_3** (15 mg, 10 μmol in 0.5 mL in an NMR tube) was put under CO (10 psi) and 2 μL of $CF_3SO_3CH_3$ (18 μmol) was added and the NMR experiments were undertaken. The iodomethane was observed in the ^1H NMR. Removal of CO caused the generation of unknown species at the cost of compound **17**.

(u) **[$Ir_2I(CO)_2(\mu$-HCCPh)(μ-CC(H)Ph)(dppm)$_2$][SO_3CF_3] (18).** To a CH_2Cl_2 solution of compound **6** (50 mg, 32 μmol in 5 mL) was added 1 mL of phenyl acetylene (8.92 mmol). The solution was allowed to stir for 3 days causing a color change from orange to burgundy. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a burgundy solid (yield 76%). The compound was not stable even in the solid owing to the slow loss of phenyl acetylene.

(v) **$[Ir_2I(CCH_2)(CC(H)Ph)(CO)_2(dppm)_2][SO_3CF_3]$ ($19{\bullet}SO_3CF_3$).** To a CH_2Cl_2 solution of compound **$4{\bullet}SO_3CF_3$** (100 mg, 66 μmol in 10 mL) was added 500 μL of phenylacetylene (4.46 mmol) and the solution was stirred for 2 days. The color changed gradually from yellow to deep burgundy. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a burgundy solid (yield 92%). Anal. calcd for $Ir_2ISP_4F_3O_5C_{63}H_{52}$: C, 46.90; H, 3.23. Found: C, 46.14; H, 3.12.

(w) **$[Ir_2I(CCH_2)(CC(H)Ph)(CO)_2(dppm)_2][BF_4]$ ($19{\bullet}BF_4$).** To a CH_2Cl_2 solution of compound **$4{\bullet}BF_4$** (50 mg, 35 μmol in 5 mL) was added 250 μL of phenylacetylene (2.23 mmol) and stirred for 24 h. The color changed from yellow to deep burgundy. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a burgundy solid (yield 86%).

(x) **$[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (20a and 20b).** To a CH_2Cl_2 solution of compound **$19{\bullet}SO_3CF_3$** (50 mg, 33 μmol in 5 mL) was added a solution of KI (100 mg in a minimum volume of MeOH, 602 μmol) causing the color to change from burgundy to yellow. After stirring for 0.5 h the solvent was removed, the residue was dissolved in 5 mL of CH_2Cl_2 and the solution was filtered. Removal of the solvent of the filtrate and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (yield 68%).

(y) **$[Ir_2I(CO)_3(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (21a and 21b).** A CD_2Cl_2 solution of compound **$19{\bullet}SO_3CF_3$** (15 mg, 10 μmol in 0.5 mL in an NMR tube) was put under CO (10 psi) for 1 h and the NMR experiments were carried out.

Removal of the CO atmosphere reversed the reaction.

(z) **[$Ir_2(CO)_4(\mu$-$CCH_2)(\mu$-$CC(H)Ph)(dppm)_2][SO_3CF_3]_2$(22).** A CD_2Cl_2 solution of compound **19•SO_3CF_3** (10 mg, 7 μmol in 0.5 mL in an NMR tube) was put under CO (10 psi) and 4 μL (36 μmol) of $CF_3SO_3CH_3$ was added and the NMR experiments were undertaken. Iodomethane was found in the ^1H NMR spectra. Removal of CO caused the transformation of compound 14 to unknown species.

(aa) [$Ir_2(Me)_2(CO)_2(\mu$-$CCH_2)(\mu$-$CC(H)Ph)(dppm)_2$] (23). To a CD_2Cl_2 solution of compound **19•SO_3CF_3** (25 mg in 0.5 mL in an NMR tube, 17 μmol) was added 50 μL of LiMe (1.4 M in Et_2O, 70 μmol) and NMR experiments were carried out. The ^{31}P NMR showed that 1 equiv compound **20** accompanies compound **23**.

X-ray Data Collection. (a) **[$Ir_2I_2(CO)_2(\mu$-$CC(H)Ph)(\mu$-$HCCH)(dppm)_2$] (15).** Crystals were obtained, with one equivalent of CH_2Cl_2 of crystallization, from CH_2Cl_2/Et_2O and mounted in capillaries. Unit cell parameters, at -65°C, were obtained from a least-squares analysis of 25 reflections in the range $20.1° \leqslant 2\theta \leqslant 23.9°$, which were accurately centered on an Enraf-Nonius CAD4 diffractometer. The systematic absences ($h0\ell$:$\ell \neq 2n$; $0k0$:$k \neq 2n$) defined the space group as $P2_1/c$ (No. 14).

Intensity data were collected on the CAD4 diffractometer at -65°C, employing the $\theta/2\theta$ scan technique in the bisecting mode up to $2\theta = 50°$. Peaks were collected using variable scan speeds (between 1.73 and 6.71 deg min^{-1}) with backgrounds scanned for 25% of the peak scan on either side of the peak. The intensities of three standard reflections were checked every 1 h of exposure time. No variation was observed so no correction was applied. A value of 0.04 was used for p^{25} and data were corrected for Lorentz and polarization effects and for absorption.[26] See Table

4.2 for additional information.

(b) $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (20b). Yellow crystals suitable for an X-ray diffraction study were grown from CH_2Cl_2/Et_2O, and one was wedged into a capillary which was flame sealed. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 18 reflections in the range $14.1° \leqslant 2\theta \leqslant 15.8°$, which were accurately centered on a Rigaku AFC7R diffractometer with graphite monochromated MoKα radiation and a 12 kW rotating anode generator. The systematic absences ($hk\ell$:$h+k+\ell \neq 2n$; $hk0$:$h \neq 2n$; 00ℓ:$\ell \neq 4n$) and the 4/m Laue symmetry defined the space group as $I4_1/a$ (No. 88).

Intensity data were collected on the Rigaku diffractometer at 22°C, employing the $\theta/2\theta$ scan technique in the bisecting mode up to $2\theta = 55°$, at scan speeds of 4.0 deg min^{-1}; weak reflections ($I<10\sigma(I)$) were rescanned up to three times and the counts accumulated. Stationary backgrounds were collected on each side of the reflection for a total duration of half of the time of the peak scan. The intensities of three standard reflections were measured every 150 reflections to monitor crystal and electronic stability; no significant variation was observed so no correction was applied. The data were processed in the usual manner assuming a value of 0.013 used for p to downweight intense reflections. Corrections for Lorenz and polarization effects and for absorption were made. See Table 4.2 for pertinent crystal data and details of intensity collection.

Structure Solution and Refinement. Both compounds were solved by a combination of Patterson and direct methods techniques to locate the Ir and I atoms, and all other atoms were located in subsequent difference Fourier maps. For compound **15** all hydrogens were located but were input in the idealized positions

Table 4.2. Crystallographic Data for Compound **15** and **20b**

Compound	**15**	**20b**
formula	$C_{63}H_{54}Cl_2I_2Ir_2O_2P_4$	$C_{62}H_{52}I_2Ir_2O_2P_4$
formula weight	1676.14	1591.20
space group	$P2_1/c$ (No. 14)	$I4_1/a$ (No. 88)
unit cell parameters		
a (Å)	15.799 (3)	30.407 (5)
b (Å)	18.029 (2)	–
c (Å)	21.126 (5)	13.065 (6)
β (deg)	99.48 (2)	–
V (Å^3)	5935 (4)	12079 (6)
Z	4	8
ρ(calcd) (g cm^{-3})	1.876	1.75
μ(cm^{-1})	57.3	55.8
diffractometer	Enraf-Nonius CAD4	Rigaku AFC7R
temperature (°C)	-65	22
radiation (λ [Å])	graphite-monochromated Mo K_α	(0.71069)
take-off angle (deg)	3.0	6.0
detector aperture (mm)	(3.00 + tanθ) horiz x 4.00 vert	3.0 x 3.0
crystal-detector distance (mm)	173	235
scan type	θ–2θ	θ–2θ
scan rate (deg min^{-1})	6.71–1.73	4.00
scan width (deg)	0.80 + 0.344tanθ	0.94 + 0.35tanθ
maximum 2θ (deg)	50.0	55.0
total unique reflections	10684 (±h +k +l)	7235 (+h +k +ℓ)
total observations (NO)	7406 ($F_o^2 \geq 3.0\sigma(F_o^2)$)	3730
range of absorption corrn. factors	0.85–1.21	0.83–1.20
final no. params. varied (NV)	441	305
R[a]	0.034	0.045
R_w[b]	0.040	0.050
error in obs. of unit weight (GOF)[c]	1.274	1.80

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

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

[c] $GOF = [\Sigma w(|F_o|-|F_c|)^2/(NO-NV)]^{1/2}$.

except for the phenyl vinylidene hydrogen which was allowed to refine. Although they were located, the hydrogens on the acetylene ligand did not refine well so were fixed at the idealized positions. In compound **20b** the vinylidene groups were disordered about the inversion center at $\frac{1}{2}$, $\frac{1}{2}$, 0. Attempts to refine the two half-occupancy, inversion-related phenyl rings allowing the phenyl carbons to refine individually resulted in a slightly distorted geometry for this group. It was therefore refined as a rigid group with a single thermal parameter refined for all carbon atoms. All hydrogen atoms, except on the disordered phenylvinylidene, were located but were input in idealized coordinates and assigned thermal parameters of 1.2 times those of the attached carbon.

Refinements were carried out using full-matrix, least-squares techniques[27,28] minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral atom scattering factors[29] and anomalous dispersion terms[30] used in structure solution were obtained from the usual sources. Both structures refined well as shown in Table 4.2. Atomic coordinates and isotropic thermal parameters for both compounds are given in Table 4.3 and 4.4.

Although the original data collection and structure solution for compound **20b** were carried out in our laboratory on the Enraf-Nonius CAD-4 diffractometer, the data reported were obtained at Molecular Structure Company on Rigaku AFC7R diffractometer in order to increase the ratio of observed reflections by using the rotating-anode diffractometer. For data acquisition and structure refinement we thank Drs. H. Liu, P.N. Swepston, J.M. Troup and B.R. Vincent at MSC.

Table 4.3. Atomic Coordinates and Thermal Parameters for the Core Atoms of Compound **15**.[a]

Atom	x	y	z	B, Å^2 [b]
Ir(1)	0.34732(2)	0.03235(1)	0.26634(1)	1.808(6)*
Ir(2)	0.20380(2)	-0.10432(2)	0.31382(1)	1.994(6)*
I(1)	0.47655(3)	0.13735(3)	0.30735(3)	3.04(1)*
I(2)	0.13086(4)	-0.17685(3)	0.40899(3)	4.27(1)*
P(1)	0.4502(1)	-0.0617(1)	0.27880(9)	2.04(4)*
P(2)	0.3159(1)	-0.1880(1)	0.3153(1)	2.39(5)*
P(3)	0.2332(1)	0.1152(1)	0.26892(9)	2.01(4)*
P(4)	0.1065(1)	-0.0065(1)	0.30832(9)	2.19(4)*
O(1)	0.3707(4)	0.0919(3)	0.1350(3)	4.0(2)*
O(2)	0.0741(4)	-0.2040(3)	0.2282(3)	4.3(2)*
C(1)	0.3597(5)	0.0647(4)	0.1807(4)	2.3(2)*
C(2)	0.1240(5)	-0.1656(4)	0.2576(4)	2.8(2)*
C(3)	0.3428(5)	0.0045(4)	0.3612(3)	2.3(2)*
C(4)	0.2885(5)	-0.0437(4)	0.3786(4)	2.4(2)*
C(5)	0.2558(4)	-0.0508(4)	0.2403(3)	2.0(2)*
C(6)	0.2277(5)	-0.0733(4)	0.1804(4)	2.8(2)*
C(7)	0.4044(4)	-0.1557(4)	0.2754(4)	2.5(2)*
C(8)	0.1295(4)	0.0681(4)	0.2550(3)	2.2(2)*

[a] Parameters for solvent molecule and phenyl rings are given as supplementary material.

[b] All atoms given were refined anisotropically. Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian diplacement parameter, B{eq}, defined as: $\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 4.4. Atomic Coordinates and Thermal Parameters for the Inner Core Atoms of Compound **20b**.[a]

Atom	x	y	z	B, Å^2 [b]
Ir	0.46133(2)	0.51955(2)	0.07445(4)	2.38(1)*
I	0.40802(4)	0.59642(3)	0.07318(9)	4.93(3)*
P(1)	0.5175(1)	0.5542(1)	0.1700(3)	2.73(7)*
P(2)	0.5904(1)	0.5164(1)	0.0306(3)	2.63(7)*
O(1)	0.4115(3)	0.4966(4)	0.2661(8)	5.4(3)*
C(1)	0.4283(4)	0.5047(5)	0.197(1)	4.4(4)*
C(2)	0.5000(4)	0.4638(4)	0.0559(9)	2.3(3)*
C(3)	0.4989(5)	0.4266(4)	0.103(1)	3.8(4)*
C(4)	0.5671(4)	0.5649(4)	0.0955(10)	2.7(3)*

[a] Phenyl carbons are given as supplementary material.

[b] See Table 4.3 for definition of B.

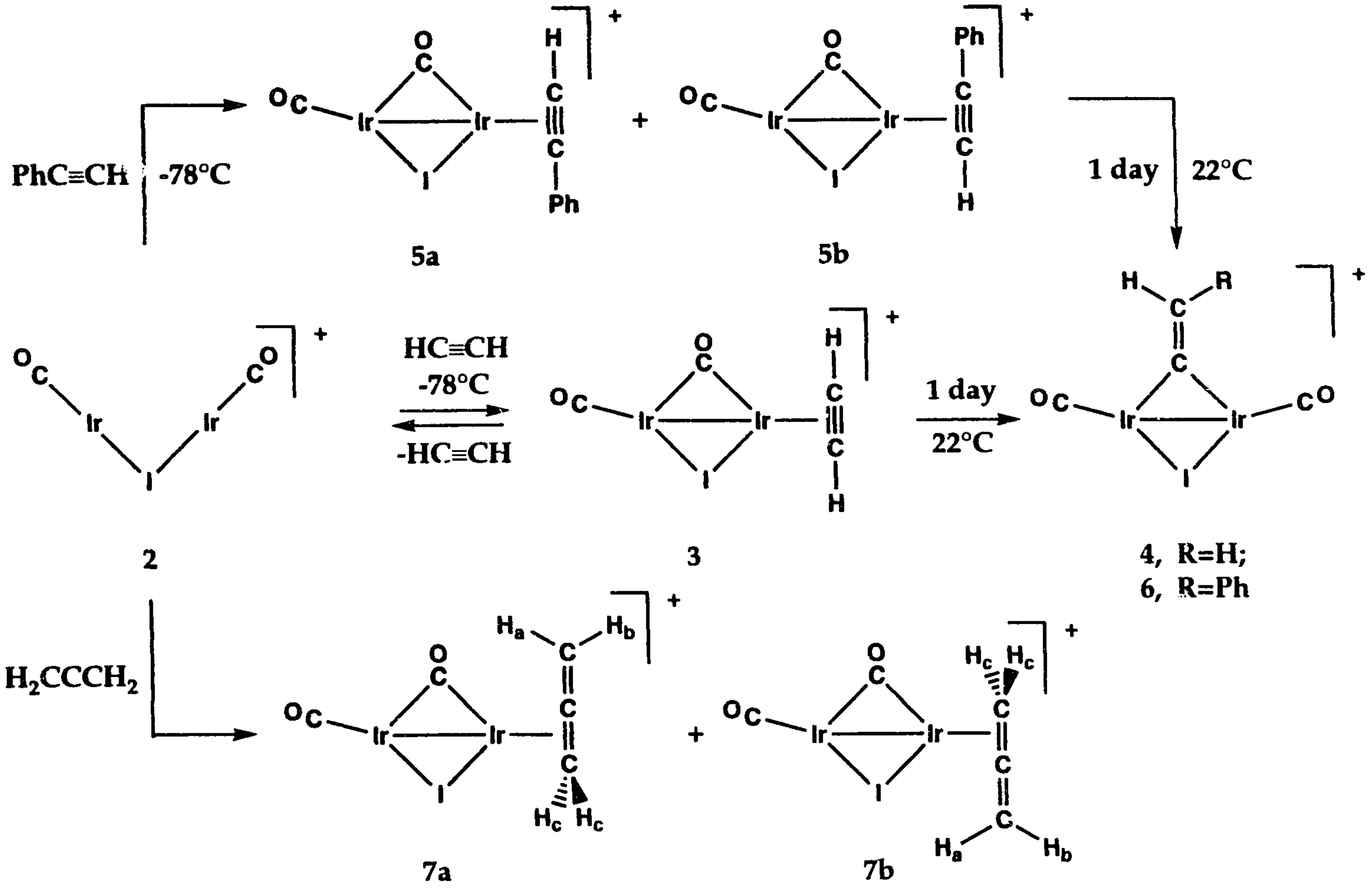
Results and Discussion

(a) Mono-Vinylidene Complexes. In a previous study of alkyne-to-vinylidene transformations at an "Ir_2" core[23] the majority of reactions carried out utilized the neutral diiodo species, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**), as precursor ; only preliminary studies were done with the closely related cationic A-frame, $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][X]$ (**2**). In this work, investigations of cationic vinylidene complexes were extended on the assumption that removal of an anionic ligand should generate a coordination site for additional substrate molecules. Using this strategy the reaction with additional alkynes should be capable of generating bis-vinylidene complexes, or alternately monovinylidene-alkyne complexes.

The cationic precursor (**2**) had been previously prepared by the reaction of **1** with an equivalent of the appropriate silver salt.[24] We now find that a more convenient preparation involves the reaction of **1** with methyl triflate, yielding **2** as the triflate salt, together with methyl iodide. Previous studies have demonstrated the coordination of CH_3^+ to an iodo ligand.[31] It is assumed that direct attack of CH_3^+ at an iodo ligand in **1** occurs, followed by CH_3I loss.

The reaction of **2** (as the triflate salt) with a 3-fold excess of acetylene at -80°C yields the cationic acetylene adduct **3** as shown in Scheme 4.1 (note that in all Schemes the dppm ligands above and below the plane of the drawing are omitted for clarity). This product can be isolated as a pale yellow solid at this temperature. The $^{13}C\{^1H\}$ NMR spectrum of **3** (at -40°C) shows two carbonyl signals at δ 179.0 and 187.7, and selective and broad-band ^{31}P decoupling experiments demonstrate a 10 Hz coupling between these carbonyls as well as coupling of the high-field carbonyl to the ^{31}P nuclei on one metal and coupling of the low field carbonyl to all four ^{31}P nuclei, identifying the former as terminal and the latter as bridging. The acetylenic carbons resonate at δ 75.2 and 62.0 with a mutual coupling of 102 Hz. This coupling is

Scheme 4.1


PhC≡CH
-78°C
5a
5b
1 day
22°C
2
HC≡CH
-78°C
-HC≡CH
3
4, R=H;
6, R=Ph
H₂CCCH₂
7a
7b

intermediate between those for ethylene (67.6 Hz) and acetylene (171.5 Hz),[32] consistent with the expected rehybridization upon coordination to a metal center. In the ^1H NMR spectrum the acetylenic protons resonate at δ 4.98 and 3.42 and, when $^{13}C_2H_2$ is used, display coupling to the attached carbons of 234 and 237 Hz, respectively. These values are close to that observed in acetylene (249 Hz)[32] suggesting little rehybridization of this group (although it appears that this parameter may not be as sensitive to changes at carbon as $^1J_{C\text{-}C}$). In the IR spectrum a stretch for the terminal carbonyl is observed at 1966 cm^{-1} while the bridging CO appears at 1824 cm^{-1}. A weak shoulder at 1660 cm^{-1} is identified as the alkyne C≡C stretch, which is significantly lower than that in the free acetylene (1974 cm^{-1}),[33] consistent with the significant change in C-C coupling constant noted above. This stretch is at higher frequency than values of *ca.* 1590 cm^{-1} reported later for vinylidene ligands in which rehybridization to sp^2, and bond-order reduction from three to two is complete. As expected for a low-valent, late transition metal, this alkyne, without electron-withdrawing substituents, is weakly bound,[34] as seen by the facile loss of acetylene from **3** under vacuum, even in the solid, which slowly develops a burgundy tinge, characteristic of **2**.

The structure proposed for compound **3** is analogous to that observed in the X-ray study of $[Ir_2(CO)(HFB)(\mu\text{-}S)(\mu\text{-}CO)(dppm)_2]$.[35] This is the structure expected for alkyne attack at the less sterically encumbered coordination site on the outside of the A-frame, remote from the adjacent metal. However, it is surprising that **3** has not rearranged to an alkyne-bridged product, since such rearrangements are usually extremely facile in these complexes.[36] It may be that the energy needed to rearrange the position of the bulky iodo ligand is too unfavorable. Compound **3** is also isoelectronic with the series of tricarbonyl A-frames derived from CO addition to **2** and its analogues.[24,37]

In the absence of excess acetylene, compound **3** rearranges to the vinylidene-bridged **4** after 24 h at ambient temperature. Although no intermediates were observed in this transformation it appears that it is not a trivial process since the 1,2-hydrogen shift is accompanied by a reshuffling of the vinylidene and a carbonyl ligand to give the symmetric **4**. The $^{13}C\{^{1}H\}$ NMR spectrum shows the vinylidene C_{α} and C_{β} resonances at δ 219.6 and 129.9, and the coupling between these nuclei (65 Hz) is consistent with a C=C double bond, comparing well to the value for ethylene (67.6 Hz).[32] C_{α} also displays coupling to all four phosphorus nuclei (7 Hz) and to both carbonyls (8 Hz, ^{13}CO-enriched), confirming its bridging nature. One resonance for both carbonyls is observed at δ 181.7, displaying coupling to C_{α} (^{13}C-enriched vinylidene) in addition to being virtually coupled to all four phosphorus nuclei. The ^{1}H NMR spectrum shows the vinylidene protons at δ 3.72, with coupling (in the $^{13}C_2H_2$ sample) to the β carbon of 161 Hz, which is again close to that in ethylene (156.4 Hz),[32] but substantially different from that noted in the acetylene adduct **3**. In the IR spectrum only one carbonyl stretch is observed (1949 cm^{-1}, Nujol) together with a weak band at 1588 cm^{-1} (1536 cm^{-1} in the $^{13}C{=}^{13}CH_2$ sample) corresponding to the vinylidene C=C stretch. Compound **4** was obtained as the $SO_3CF_3^-$ or the BF_4^- salt, starting from compound **2** having the appropriate anion, and both salts display identical spectroscopic parameters for the cations indicating that these anions behave as innocent, non-coordinating counterions.

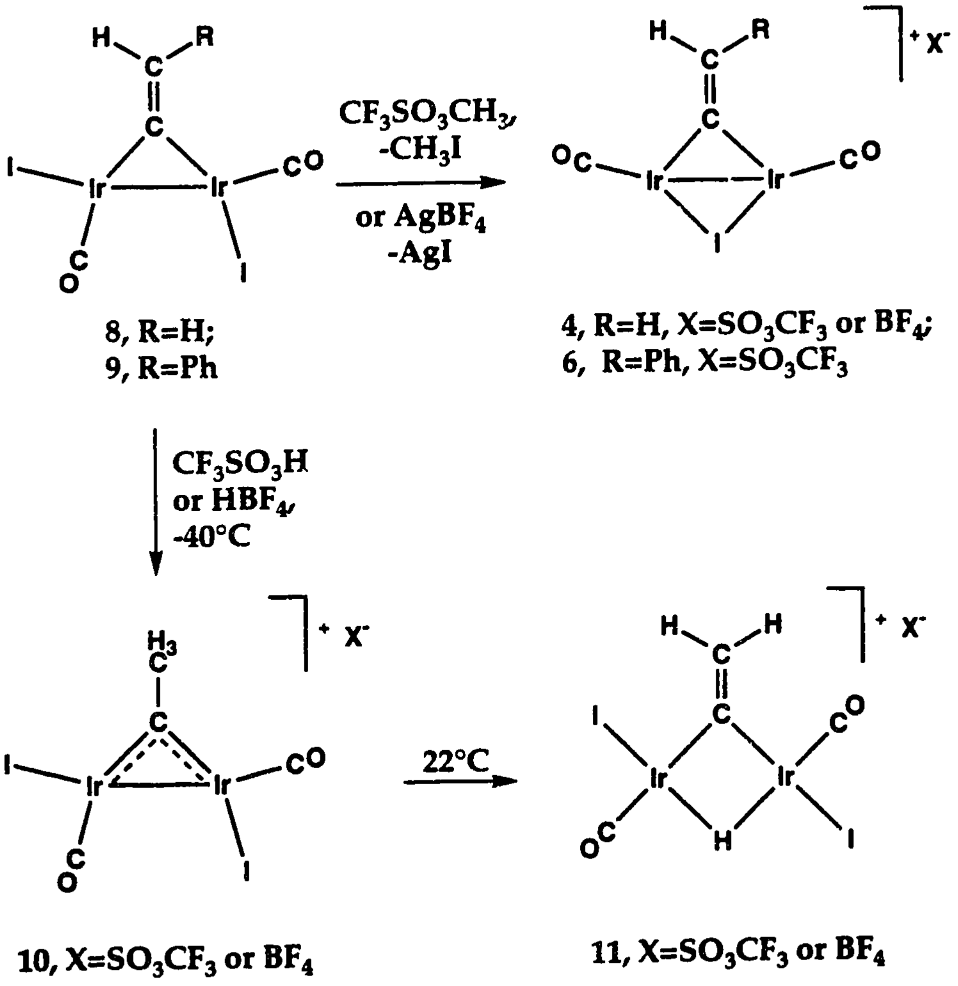
Extending this chemistry to include unsymmetrical, terminal alkynes, such as phenylacetylene, gives similar chemistry, except yielding two isomers of $[Ir_2(CO)(HC{\equiv}CPh)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (**5a**, **5b**) at -60°C, as shown in Scheme 4.1. The existence of two isomers presumably results from the differing orientations of the unsymmetrical alkyne, in which the phenyl substituent faces the bridging iodo (**5a**) or carbonyl (**5b**) groups. All spectroscopic parameters for these isomers closely resemble those of **3**, supporting the structural assignments. At -60°C **5a** is dominant (*ca.* 5:2 mole ratio), however as the temperature is raised to ambient, this isomer disappears leaving only **5b**. It is assumed that this is the thermodynamically favored isomer on the basis of less repulsion of the phenyl substituent with the smaller carbonyl ligand, as opposed to the large iodo group. At ambient temperature compound **5b** slowly transforms into several (four or more) intermediates which in turn, after 24 h, transform into **6**, the phenylvinylidene-bridged analogue of **4**. Unfortunately, these intermediates were never present in large enough quantities, and were always present as a complex mixture, so could not be identified. However, at least one of these intermediates displays a high-field resonance in the ^1H NMR spectrum, suggesting the involvement of a hydride-acetylide species, as has been observed in other acetylene-to-vinylidene rearrangements.[23,38-41] The presence of several intermediates is consistent with our earlier hypothesis that this transformation from a terminally bound alkyne to a bridging vinylidene in **4** and **6** must require several steps.

An allene product, $[Ir_2(CO)(C_3H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][X]$ (**7**), analogous to the alkyne species **3** and **5**, is obtained in the reaction of **2** with allene at ambient temperature. As was observed with phenylacetylene, two isomers, **7a** and **7b**, are obtained in *ca.* 5:1 ratio. It is proposed that the major isomer (**7a**) has the uncoordinated CH_2 moiety aimed towards the carbonyl rather than the iodo ligand, in the more favorable steric orientation, whereas this unit is closer to I in **7b**. For the major isomer a terminal (δ 179.9) and a bridging (δ 189.9) carbonyl is identified in the $^{13}C\{^1H\}$ NMR spectra, based on their coupling to the appropriate ^{31}P nuclei, and this assignment is substantiated by the IR spectrum which shows a terminal and a bridging (1983, 1819 cm^{-1}, CH_2Cl_2) carbonyl stretch. The ^{1}H NMR spectrum shows the allene protons at δ 5.93, 5.33 and 1.31 in a 1:1:2 intensity ratio, respectively. The high-field signal, corresponding to the protons on the coordinated CH_2 group display coupling to two phosphorus nuclei ($^3J_{PH}$ = 7 Hz) and to each of the other allene protons ($^4J_{H_aH_c} = {}^4J_{H_bH_c}$ = 3.4 Hz). In addition, the inequivalent protons on the unbound end of the allene (H_a, H_b) show geminal coupling of 2.4 Hz. For the less abundant isomer **7b** the spectroscopic data in Table 4.1 are very similar to those of **7a**. The subsequent chemistry of these allene adducts, with regards C-H activation or condensation reactions has not yet been investigated.

In an attempt to probe the reactivity of the bridging vinylidene moiety in the previously reported complexes, $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ (R = H (**8**), Ph (**9**)),[23] methyl triflate was added on the assumption that electrophilic attack at the vinylidene β-carbon would occur.[41] Instead, as shown in Scheme 4.2, loss of CH_3I occurs (as detected in the ^{1}H NMR by a resonance at δ 2.16) to generate the previously described cationic, vinylidene-bridged complexes **4** or **6**. No intermediates were detected, so whether initial CH_3^+ attack occurs at a metal or directly at an iodo ligand is not known. The same species, having the BF_4^- anion instead of $CF_3SO_3^-$, can be obtained by the addition of one equivalent of $AgBF_4$ to **8** or **9**.

Although, as noted above, electrophilic attack by CH_3^+ apparently did not occur at the vinylidene β-carbon, protonation of **8** does yield the expected ethylidyne-bridged species **10** when protonation is carried out at -40°C, as shown in Scheme 4.2. In the $^{13}C\{^1H\}$ NMR spectrum of **10** (BF_4 salt) two carbonyl resonances at δ 179.0 and 166.5 are observed and each shows coupling to a different pair of ^{31}P nuclei, indicating that these carbonyls are terminally bound to different metals. When the ethylidyne ligand is ^{13}C-enriched, the low-field ^{13}CO resonance of **10** also shows 23

Scheme 4.2



8, R=H;
9, R=Ph

4, R=H, X=SO_3CF_3 or BF_4;
6, R=Ph, X=SO_3CF_3

10, X=SO_3CF_3 or BF_4

11, X=SO_3CF_3 or BF_4

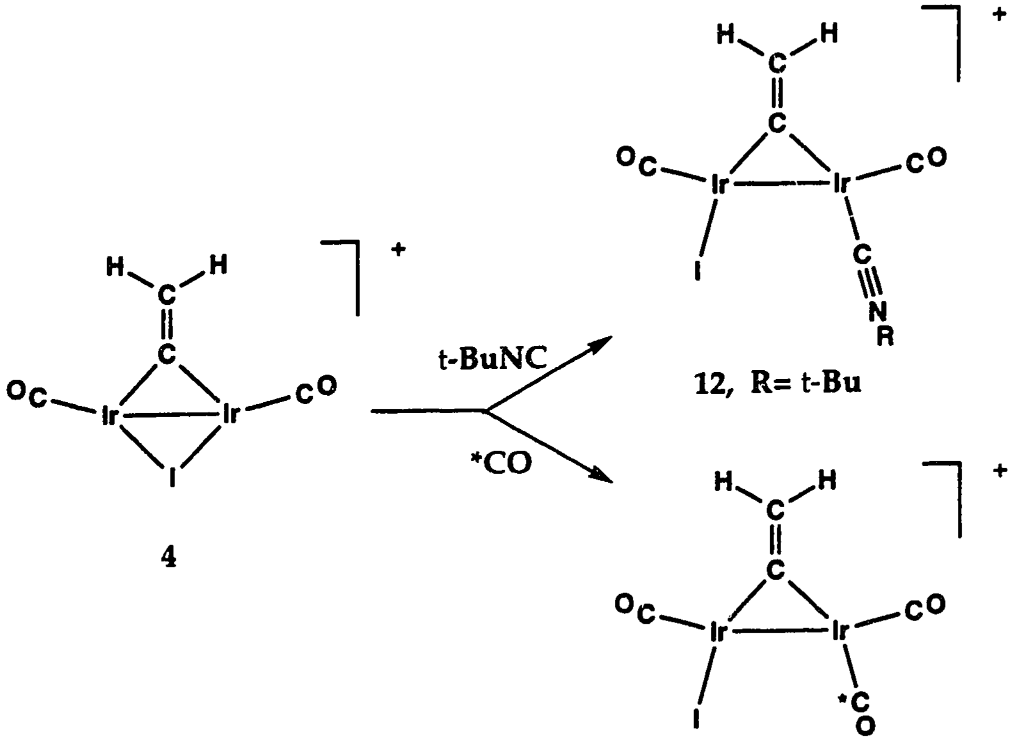
Hz coupling to the α-carbon of the ethylidyne unit. The ethylidyne carbons resonate at δ 409.1 (C_α) and 68.5 (C_β), comparing closely to the values reported (δ 405-453, C_α; δ 58, C_β) in some ethylidyne-bridged heterobinuclear complexes,[6,43] and display a mutual coupling of 23 Hz. Although we were unable to find reports of C–C coupling in bridging ethylidyne groups, presumably because these groups were not ^{13}C enriched, the value observed for **10** is comparable to the value reported for ethane (34.6 Hz), and is consistent with a C-C single bond between sp^3 carbons. In the ^1H NMR spectrum the ethylidyne methyl protons resonate as a singlet at δ 3.99 or as a doublet with 128 Hz coupling to C_β when the ethylidyne is ^{13}C enriched; again this coupling is in good agreement with that reported for ethane (124.9 Hz) consistent with sp^3 hybridization of the carbon.

Upon warming **10** to ambient temperature an immediate and surprising rearrangement occurs in which an ethylidyne proton transfers to the metals to give the hydride- and vinylidene-bridged product, $[Ir_2I_2(CO)_2(\mu\text{-}H)(\mu\text{-}CCH_2)(dppm)_2][X]$ (**11**). The $^{13}C\{^1H\}$ NMR spectrum of the BF_4^- salt shows the carbonyl ligands at δ 167.9 and δ 166.3 with the latter displaying 26 Hz coupling to the vinylidene C_α (^{13}C enriched). Resonances for the vinylidene group appear at δ 187.5 (C_α) and 132.3 (C_β) with a mutual coupling of 70 Hz; in addition the C_α resonance displays equal coupling to all four phosphorus nuclei, confirming the bridged arrangement. In the ^1H NMR spectrum only one resonance for a vinylidene hydrogen is observed at δ 8.17 with the other presumably being obscured by the phenyl protons. This resonance displays 7 Hz geminal coupling to the other vinylidene proton and 156 Hz coupling to C_β (^{13}C enriched). The hydride resonance appears as a multiplet at δ -12.48 and is shown to be bridging based on selective and broad-band ^{31}P decoupling experiments. Protonation of **8** to give **11** has resulted in a net oxidation of the metals and this is mirrored by the change in carbonyl stretches from 1960 and 1985 cm^{-1} to 2020 and 2066 cm^{-1}. The vinylidene stretch appears at 1605 cm^{-1}.

This transformation is the opposite of what one intuitively expects, with protonation generally occurring first at the metals with subsequent transfer to the hydrocarbyl ligand, and certainly the opposite has been observed in related mononuclear vinylidene complexes in which protonation at Ir with subsequent transfer to the β-carbon occurred.[41,44] Apparently in **8** the most nucleophilic site is at the β-carbon yielding **10** as the kinetic product, but with the hydride- and vinylidene-bridged species being thermodynamically favored. In spite of the favorable C-H bond enthalpy in **10**, we assume that the delocalized Ir-C$_\alpha$-Ir multiple bond is not sufficient to overcome the C=C bond and the Ir-H-Ir interaction that results in the final product **11**.

Although the cationic vinylidene-bridged complexes **4** and **6** are saturated, by virtue of the iodo ligand assuming a bridging position, they have incipient unsaturation, since movement of I$^-$ to a terminal site on one metal, can generate unsaturation at the other. Consistent with this proposal, compound **4** (as the triflate salt) reacts readily at ambient temperature with ^{t}BuNC or CO, as shown in Scheme 4.3, to give the respective compounds, $[Ir_2I(CO)_2(^tBuNC)(\mu\text{-}CCH_2)(dppm)_2]$-$[SO_3CF_3]$ (**12**) or $[Ir_2I(CO)_3(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (**13**). The $^{13}C\{^1H\}$ NMR spectrum of **12** shows the terminal carbonyls at δ 172.9 and 166.3, and selective ^{31}P decoupling shows that each CO is bound to a different metal. These carbonyls show 8 Hz mutual coupling which argues in favor of a structure in which the carbonyls are close to the trans position with respect to the Ir-Ir bond; large 3-bond coupling through a metal-metal bond has been previously noted.[45] An arrangement of ligands like that proposed for **12** has been observed in the X-ray structures of **8** and **9**.[23]

Scheme 4.3



4

12, R= t-Bu

13

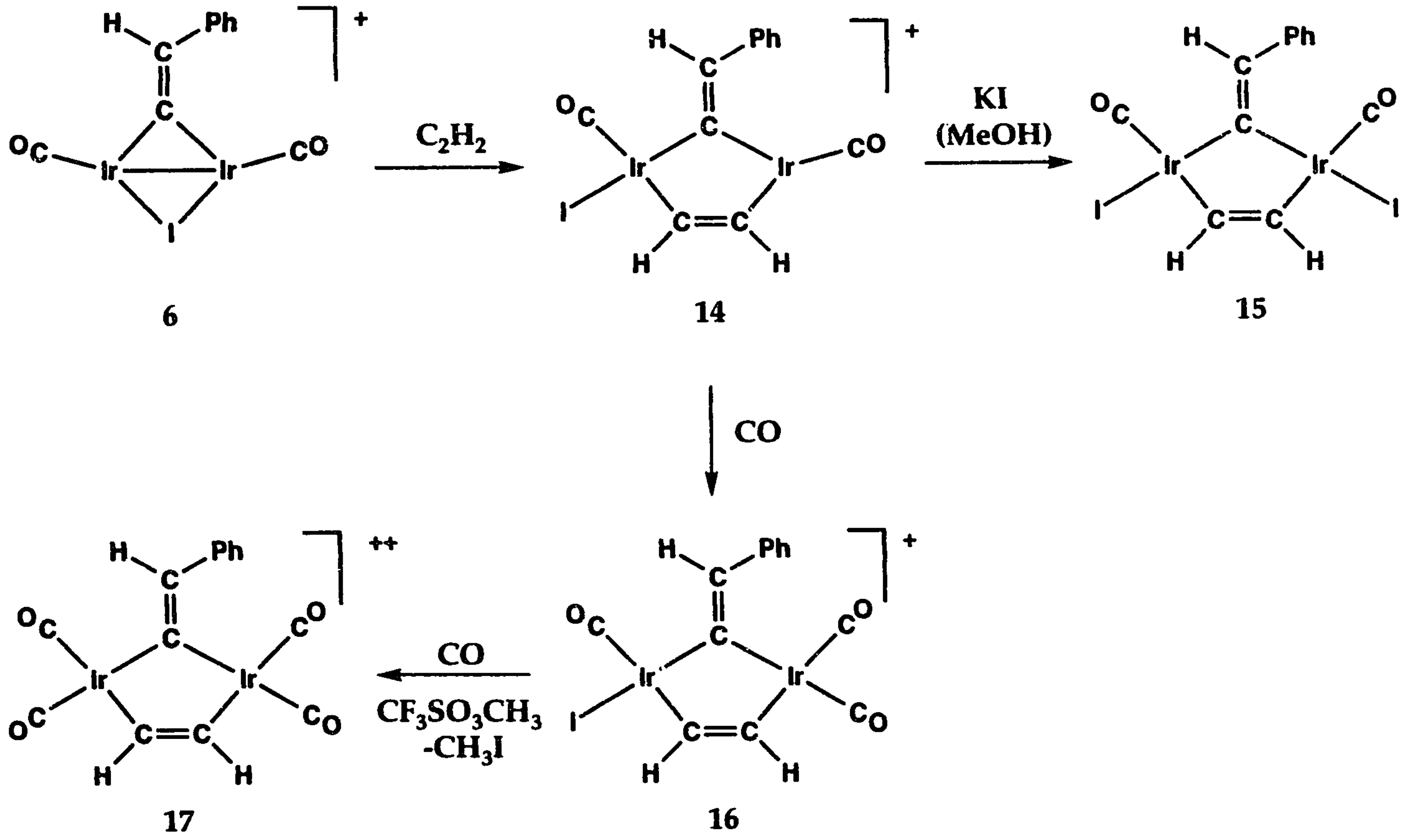
The vinylidene carbons (^{13}C enriched) are observed at δ 188.3 (C_α) and 132.0 (C_β) and display the usual C_α-C_β coupling of 67 Hz. As expected, C_α displays additional coupling to all phosphorus nuclei, confirming its bridged arrangement, whereas C_β shows no additional coupling. C_α also shows coupling to one of the carbonyls, but this is only 3 Hz, indicating that the vinylidene is cis to both carbonyls. In the ^1H NMR the vinylidene protons appear as a singlet at δ 6.75 and the ^tBuNC protons also appear as a singlet, however cooling the sample shows that the chemical shifts of the vinylidene protons are temperature dependent since the singlet resolves into an AB quartet. At ambient temperature the use of ^{13}C-enriched vinylidene splits the vinylidene proton signal into a doublet ($^1J_{CH}$ = 157 Hz). The IR spectrum supports the structural assignment showing the terminal carbonyl bands at 1990 and 1976 cm^{-1}, the C≡N stretch of the isocyanide at 2184 cm^{-1} and the vinylidene C=C stretch at 1585 cm^{-1}. The increase in the isocyanide stretch from *ca.* 2125 cm^{-1} in the free molecule indicates that this ligand functions mainly as a σ donor.[46]

For the carbonyl adduct **13** the spectroscopic data are closely comparable. In the $^{13}C\{^1H]$ NMR three carbonyl resonances are observed at δ 174.1, 170.0 and 162.4, and all are shown to correspond to terminally bound CO's, based on ^{31}P decoupling experiments. All carbonyls display weak coupling (<3 Hz) with each other, but only the low-field resonance displays substantial coupling (15 Hz) to C_α of the ^{13}C-enriched vinylidene. This coupling suggests an arrangement of this carbonyl and the vinylidene group which is close to trans. If the ^{13}CO enriched sample of **4** is reacted with ^{12}CO the $^{13}C\{^1H\}$ NMR of the product shows that the low-field carbonyl signal is substantially less intense (ca. 30 %) than the other two, supporting the structural assignment shown for **13** in which the attacking group binds at the site vacated by the bridging I^- ligand. The partial occupancy of this site by ^{13}CO in the latter experiment indicates either scrambling of the carbonyls on the metals, or some attack by CO adjacent to the vinylidene group.

(b) Mixed Vinylidene-Acetylene-Bridged Complexes. In a previous study[23] it was reported that the neutral vinylidene-bridged complex **8** reacted with acetylene to give two cationic species containing both a bridging vinylidene and a bridging acetylene group,[47] and that the same two species could be obtained in the reaction of $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ with excess acetylene. It appeared likely that a cationic monobridged vinylidene intermediate such as **4** was involved in this reaction. The previously described reactions of **4** with ^tBuNC and CO demonstrated ligand attack on the face of the complex opposite the vinylidene group. Similar reactivity of **4** with acetylene, followed by movement of acetylene to the bridging position would give products analogous to those proposed in the earlier study. In agreement with these ideas the reaction of **4** with acetylene does give one of the two previously reported complexes, containing a bridged vinylidene and a bridged acetylene ligand (based on a comparison of spectral parameters with those previously reported). However the present reaction is complex, yielding a large number of additional unidentified species. Owing to the complexity of this reaction we turned instead to the reaction of the analogous phenylvinylidene-bridged species **6** with acetylene. In this case the anticipated product, $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HC_2H)(dppm)_2][SO_3CF_3]$ [**14**], containing a bridging phenylvinylidene and bridging acetylene group was obtained cleanly, as outlined in Scheme 4.4.

Since the phenylvinylidene ligand was not ^{13}C enriched we do not have ^{13}C NMR parameters for it; however it is assumed to remain bridging based on the subsequent structure determination of a derivative (**15**) (*vide infra*) and on the spectral data. The $^{13}C\{^1H\}$ NMR spectrum of **14** ($SO_3CF_3^-$ salt), in which the carbonyl and

Scheme 4.4



acetylene ligands are ^{13}C enriched, shows two resonances for the terminal carbonyls (δ 177.3, 169.2) and two acetylenic resonances at δ 133.8 and 120.8, with the latter two showing a mutual coupling of 60 Hz. Of the two CO resonances, only one displays strong coupling (30 Hz) to one of the acetylenic carbons indicating a trans arrangement at one metal - presumably at the saturated metal for which an octahedral geometry is proposed. Although the ^{13}C NMR parameters are not enough to differentiate between an acetylene and a vinylidene group, the ^{31}P coupling pattern strongly supports the acetylene-bridged formulation since both carbons show coupling to all ^{31}P nuclei; while one carbon shows 11 Hz coupling to one pair of ^{31}P nuclei and 6 Hz to the other, the adjacent carbon shows 7.5 Hz coupling to all ^{31}P nuclei. A similar coupling pattern is observed for the structurally characterized compound **15** (*vide infra*), and this coupling pattern is in contrast to that of bridging vinylidenes for which we find that only C_α generally displays coupling to the ^{31}P nuclei. In the ^{1}H NMR spectrum of **14** one acetylenic proton is observed at δ 8.60, with coupling to an acetylenic carbon ($^1J_{CH}$ = 146 Hz), and the phenylvinylidene hydrogen is observed at δ 8.53; the second acetylenic proton resonance is presumably obscured by phenyl resonances.

Reaction of **14** with KI yields the neutral diiodo product $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCH)(dppm)_2]$ (**15**). Although the local geometries at both Ir centers in **15** are identical, the orientation of the bridging phenylvinylidene ligand renders the metals inequivalent. As a result two closely spaced ^{31}P resonances are observed. Significantly, these resonances appear close to that observed for the saturated end of complex **14**, suggesting that this metal center in **14** has a similar environment to both metals in **15**, as shown in Scheme 4.4. Most other spectroscopic parameters for **15** compare well with those of **14** apart from the strong coupling of both carbonyls to an acetylenic carbon (^{13}C enriched) in **15**, in line with the trans arrangement between these groups as shown. This geometry is consistent with I$^-$ attack at **14** being directed away from the bulky phenyl substituent on the vinylidene group, and is confirmed by the X-ray structure determination.

The geometry shown for compound **15** in Figure 4.1 has the expected octahedral coordinations at both metals. Selected bond lengths and angles are shown in Table 4.5. Around each metal the angles are close to the idealized values, with the major distortions appearing to result from the very long Ir-Ir separation of 3.6011(6)Å, which has resulted from formal insertion of acetylene into the Ir-Ir bond of the precursor. By comparison the metal-metal bonded, vinylidene-bridged species **8** and **9** have Ir-Ir separations of 2.828(1) and 2.783(1)Å, respectively.[23] All angles at the acetylene carbons and at the α-carbon (C(5)) of the phenylvinylidene group are close to the idealized sp^2 values. The slight distortion at C(6), resulting in a C(91)-C(6)-C(5) angle of 131.5(7)°, appears to be steric in origin, with the phenyl substituent being forced away from the adjacent carbonyl C(1)O(1). This also appears to cause a slight tilting of the vinylidene, resulting in the Ir(1)-C(5)-C(6) angle being slightly larger than Ir(2)-C(5)-C(6) (125.0(5)° vs. 116.9(5)°). Both C=C bonds of the acetylene (1.316(9)Å) and the phenylvinylidene (1.335(9)Å) groups are close to the value expected for a double bond, in keeping with the 1,2-dimetallated olefin formulation for the acetylene group. All other parameters are essentially as expected.

Compound **14** also reacts with CO to give the cationic tricarbonyl species $[Ir_2I(CO)_3(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCH)(dppm)_2][SO_3CF_3]$ (**16**), having a structure analogous to **15**. Again the ^{31}P nuclei bound to the metal center having the iodo and carbonyl ligand resonate in the same region as the phosphines on both similar centers

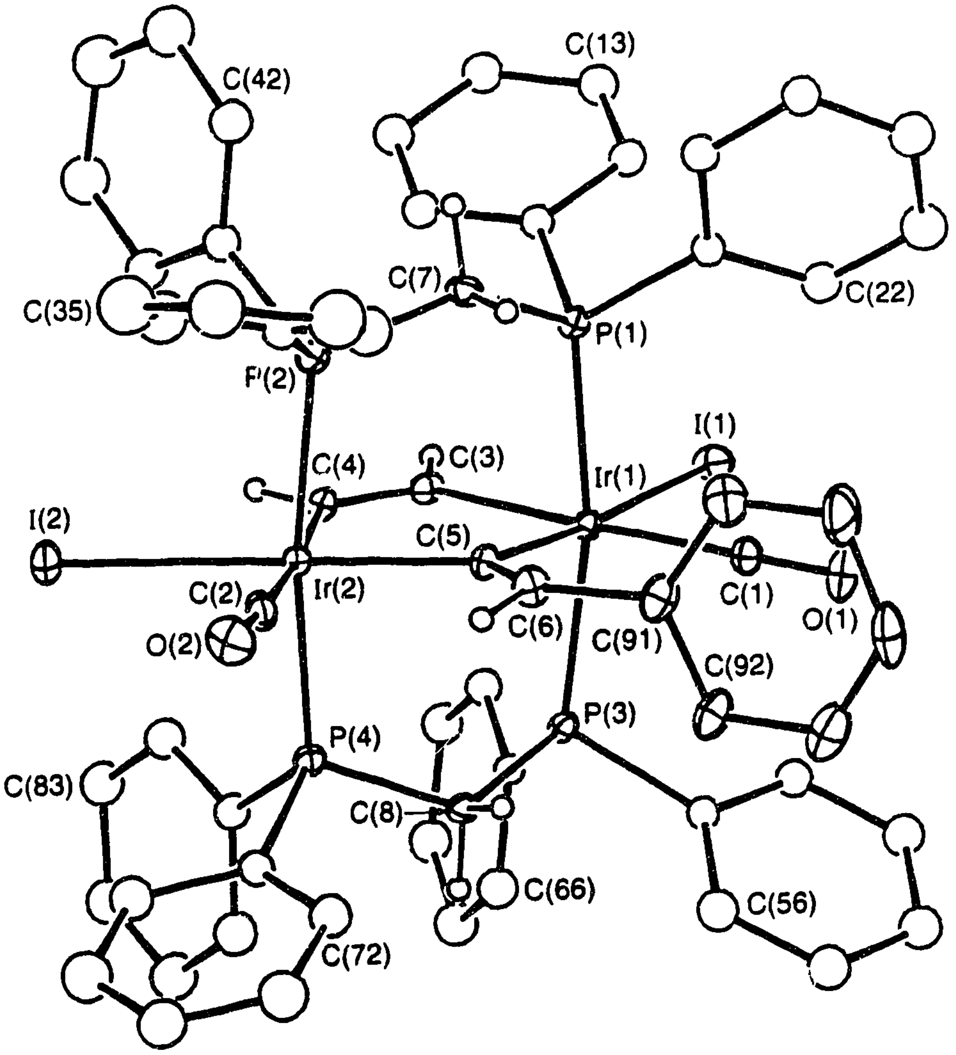


Figure 4.1. Perspective drawing of [$Ir_2I_2(CO)_2(\mu$-CC(H)Ph)(μ-HCCH)$(dppm)_2$] (**15**) showing the numbering scheme. Numbering on the phenyl carbons starts at the ipso position and proceeds sequentially around the ring. Thermal ellipsoids are shown at the 20% level except for methylene and vinylidene hydrogens which are shown arbitrarily small and phenyl hydrogens which are omitted.

Table 4.5. Selected Bond Lengths (Å) and Angles (deg) for Compound **15**.

(a) **Bond Lengths**

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ir(1)	I(1)	2.8144 (7)	Ir(2)	C(2)	1.931 (8)
Ir(1)	P(1)	2.333 (2)	Ir(2)	C(4)	2.063 (7)
Ir(1)	P(3)	2.349 (2)	Ir(2)	C(5)	2.106 (6)
Ir(1)	C(1)	1.942 (7)	O(1)	C(1)	1.120 (8)
Ir(1)	C(3)	2.078 (7)	O(2)	C(2)	1.150 (8)
Ir(1)	C(5)	2.092 (6)	C(3)	C(4)	1.316 (9)
Ir(2)	I(2)	2.8006 (8)	C(5)	C(6)	1.335 (9)
Ir(2)	P(2)	2.323 (2)	C(6)	C(91)	1.48 (1)
Ir(2)	P(4)	2.330 (2)	C(6)	H(6)	1.08 (8)

(b) **Bond Angles**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
I(1)	Ir(1)	P(1)	89.87 (5)	P(2)	Ir(2)	P(4)	171.00 (6)
I(1)	Ir(1)	P(3)	94.93 (4)	P(2)	Ir(2)	C(2)	93.2 (2)
I(1)	Ir(1)	C(1)	84.6 (2)	P(2)	Ir(2)	C(4)	85.7 (2)
I(1)	Ir(1)	C(3)	90.2 (2)	P(2)	Ir(2)	C(5)	85.3 (2)
I(1)	Ir(1)	C(5)	176.1 (2)	P(4)	Ir(2)	C(2)	92.5 (2)
P(1)	Ir(1)	P(3)	169.26 (6)	P(4)	Ir(2)	C(4)	89.0 (2)
P(1)	Ir(1)	C(1)	98.5 (2)	P(4)	Ir(2)	C(5)	87.2 (2)
P(1)	Ir(1)	C(3)	81.3 (2)	C(2)	Ir(2)	C(4)	176.2 (3)
P(1)	Ir(1)	C(5)	87.0 (2)	C(2)	Ir(2)	C(5)	95.9 (3)
P(3)	Ir(1)	C(1)	91.5 (2)	C(4)	Ir(2)	C(5)	87.5 (2)
P(3)	Ir(1)	C(3)	89.0 (2)	Ir(1)	C(1)	O(1)	170.9 (6)
P(3)	Ir(1)	C(5)	87.8 (2)	Ir(2)	C(2)	O(2)	174.8 (6)
C(1)	Ir(1)	C(3)	174.8 (3)	Ir(1)	C(3)	C(4)	123.8 (5)
C(1)	Ir(1)	C(5)	98.2 (3)	Ir(2)	C(4)	C(3)	123.1 (5)
C(3)	Ir(1)	C(5)	87.0 (3)	Ir(1)	C(5)	Ir(2)	118.1 (3)
I(2)	Ir(2)	P(2)	95.18 (5)	Ir(1)	C(5)	C(6)	125.0 (5)
I(2)	Ir(2)	P(4)	92.46 (5)	Ir(2)	C(5)	C(6)	116.9 (5)
I(2)	Ir(2)	C(2)	82.5 (2)	C(5)	C(6)	C(91)	131.5 (7)
I(2)	Ir(2)	C(4)	94.0 (2)	C(5)	C(6)	H(6)	128 (5)
I(2)	Ir(2)	C(5)	178.4 (2)	C(91)	C(6)	H(6)	100 (5)

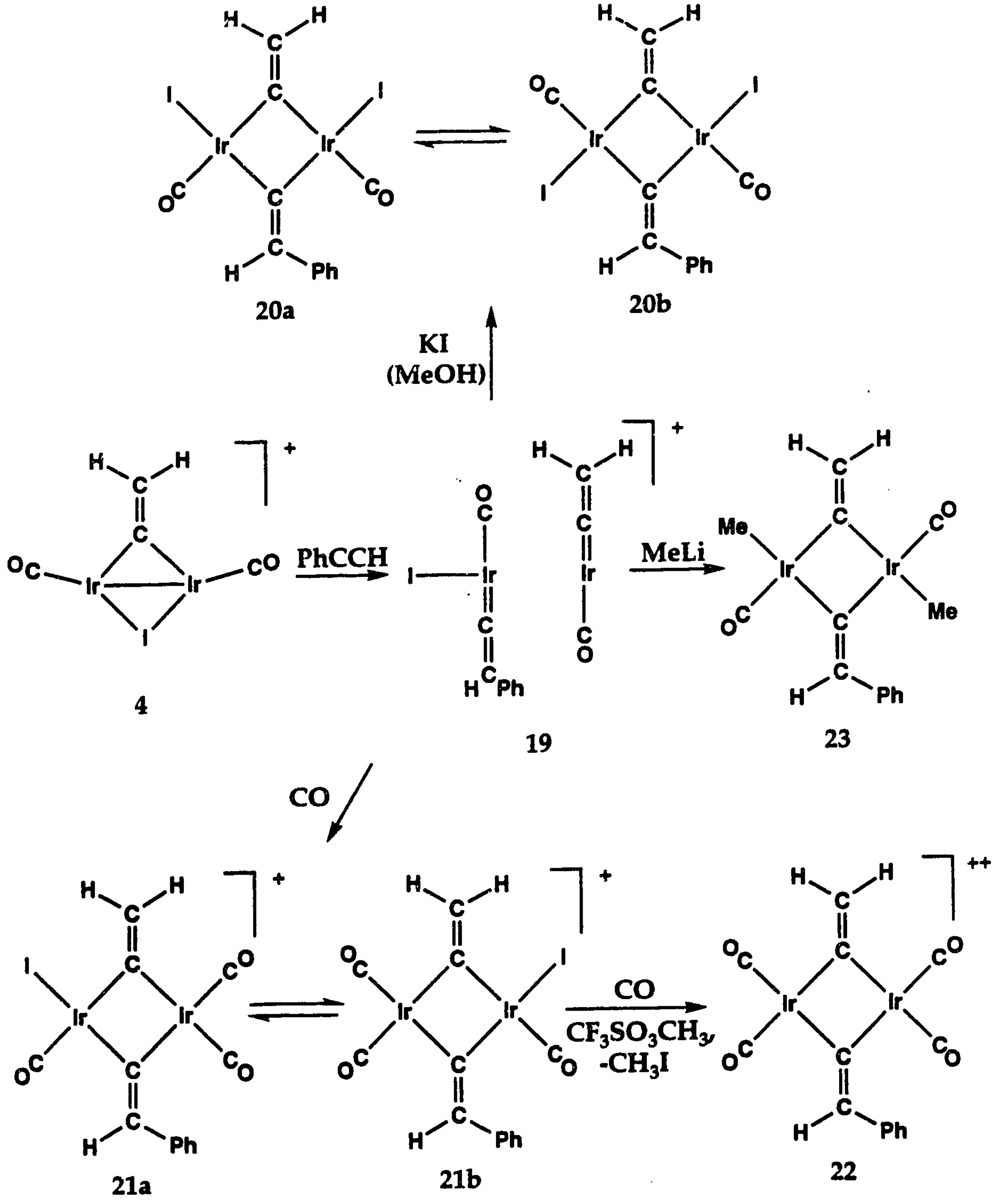
in **15** and on the related center in **14**, suggesting that the metals in all cases have similar environments. In the $^{13}C\{^1H\}$ NMR spectrum three resonances for the terminal carbonyls are observed. For this product and for **17** neither the acetylene nor the phenylvinylidene ligand were ^{13}C enriched so ^{13}C resonances for these groups were not observed. The ^1H NMR spectrum shows the protons of the coordinated alkyne as multiplets at typically low field (δ 9.91, 8.57); the phenylvinylidene proton was not observed. Consistent with two Ir^{+3} centers and an overall positive charge on the complex, the carbonyl stretches are at high frequency.

Reaction of **16** with methyl triflate under carbon monoxide results in loss of CH_3I and formation of the dicationic species $[Ir_2(CO)_4(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCH)(dppm)_2][SO_3CF_3]_2$ (**17**). Each metal center in **17** has an environment analogous to the dicarbonyl center in **16** and again the $^{31}P\{^1H\}$ resonances appear in the same region, consistent with the proposal that they have similar environments. Four resonances appear in the $^{13}C\{^1H\}$ NMR spectrum for the four terminal carbonyls and in the IR spectrum the carbonyl stretches are at even higher frequency than in **15**, consistent with the replacement of I^- by CO. In the ^1H NMR spectrum both acetylenic (δ 9.06, 8.70) and the phenylvinylidene proton (δ 8.31) appear.

Reaction of **6** with phenylacetylene also yields a mixed vinylidene-alkyne-bridged product $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCPh)(dppm)_2][SO_3CF_3]$ (**18**), analogous to **14**. Although no ^{13}C NMR parameters were obtained for the vinylidene and alkyne groups, since the phenylacetylene used was not enriched, the other spectroscopic parameters are closely comparable to those of **14**, so an analogous structure is assigned. Although we have no supporting data, we propose that the phenyl group on the bridging phenyl acetylene ligand is directed towards the unsaturated Ir in order to avoid unfavorable contacts with the iodo ligand at the opposite end.

(c) Bis-Vinylidene Complexes. As noted earlier the reaction of **4** with acetylene was complex yielding a number of unidentified species. However one product was identified as an acetylene-vinylidene-bridged species analogous to that observed in the reaction of **6** with acetylene, for which an acetylene-phenylvinylidene species, $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCH)(dppm)_2][SO_3CF_3]$ (**14**), was obtained. It was assumed that the reaction of **4**, having a bridging CCH_2 group, and phenylacetylene would yield an analogous species containing the opposite tautomer combination, i.e., vinylidene and phenylacetylene. Surprisingly this is not the case, and instead a bis-vinylidene complex, $[Ir_2I(CO)_2(CCH_2)(CC(H)Ph)(dppm)_2]$-$[SO_3CF_3]$ (**19**), results as outlined in Scheme 4.5. Compound **19** presents a rare example of a binuclear species in which the vinylidene ligands are not bridging but are terminal. Terminal vinylidene groups in binuclear complexes and clusters have been observed,[48] however in the previous cases the substituents on the β-carbon were bulky so the terminal coordination appeared to be sterically driven. In contrast, there appears to be no steric reason that demands terminal vinylidene coordination in **19**. The present compound also appears to be the only bis-vinylidene system reported on a binuclear framework. Higher clusters containing two vinylidene groups have been reported, however.[49] In a sample of **19** (triflate salt) that was ^{13}C enriched at the vinylidene ($^{13}C{=}^{13}CH_2$) and at the carbonyls, the $^{13}C\{^1H\}$ NMR spectrum shows the C_α resonance at δ 174.6 with coupling to C_β of 64 Hz, to one of the carbonyls of 35 Hz and to two phosphorus nuclei on one metal of 10 Hz. The C_β resonance is observed at δ 133.6, with coupling only to C_α. This C_α-C_β coupling is typical for vinylidenes and coupling of C_α to only two phosphorus nuclei identifies this group as terminal. The high coupling between C_α and the adjacent carbonyl (35 Hz) indicates

Scheme 4.5


20a
20b
KI
(MeOH)
4
PhCCH
19
MeLi
23
CO
21a
21b
CO
CF3SO3CH3,
-CH3I
22

that the two groups are mutually trans. Overnight data acquisition on the sample containing natural-abundance phenylvinylidene allows the C_α of this group to be identified as a broad multiplet at δ 174.3, close to that for the unsubstituted vinylidene, and C_β to be observed at δ 143.9. Appropriate decoupling experiments could not be carried out to simplify the C_α resonance. The carbonyl resonances at δ 179.9 and 163.8 each display coupling to two different sets of ^{31}P nuclei establishing that they are terminally bound to different metals, and the high-field resonance also shows the aforementioned coupling to C_α. In the ^1H NMR spectrum the phenylvinylidene proton resonates at δ 8.20 and displays weak coupling to the low-field carbonyl resonance, further supporting our proposal that these two groups are bound to one metal and in a trans orientation. The protons on the unsubstituted vinylidene group appear at δ 6.54 and 6.04, displaying a mutual coupling of 10 Hz and coupling to C_β of *ca.* 157 Hz (^{13}C enriched vinylidene). These chemical shifts for the vinylidene and phenylvinylidene protons of **19** are not abnormal for such groups of binuclear complexes in which they are usually bridging, but are far downfield of those reported for terminally bound groups as observed in mononuclear vinylidene complexes of iridium.[17,41] In particular the ^1H resonances for the closely related complexes $[IrI(CC(H)R)(PPr^i_3)_2]$ (R = H, Ph) appear at δ -5.25 and -3.58, respectively.[41] The geometry proposed, in which the iodo group is bound adjacent to the phenylvinylidene rather than the unsubstituted vinylidene group, is based on analogies with the chemistry described of **4** with CO and ^tBuNC, in which ligand attack occurred at one Ir center on the face opposite the bridging vinylidene. Assuming an analogous attack by phenylacetylene and subsequent rearrangement to a phenylvinylidene moiety, the most likely geometry which minimizes ligand rearrangements, would have the unsubstituted vinylidene moving to a terminal position on the opposite face of the metal vacated by the iodo ligand. The orientation of the phenyl substituent on the phenylvinylidene group is uncertain. Although we could not find a mononuclear analogue of the saturated Ir^{+1} site having a carbonyl and a vinylidene unit together, a very analogous species $[IrI(CCH_2)(PPr^i_3)_2]$ was reported to react with CO, but transformation to an Ir^{+3} hydride-acetylide product resulted.[41]

Although the spectroscopic data for **19** do not unequivocally rule out the presence of a phenylacetylene instead of a phenylvinylidene group, two important observations strongly support the phenylvinylidene formulation. First, in the slow transformation of **4** to **19** a hydride intermediate is observed in the ^1H NMR spectra. Such a species is consistent with the involvement of a hydride-acetylide intermediate, of the type previously shown to be involved in alkyne-to-vinylidene rearrangements in related binuclear systems.[23] Unfortunately, this species is never present in high enough concentrations to obtain additional spectroscopic data, so it could not be characterized. Furthermore, the transformation of **19** to **20**, which has been unambiguously characterized as a bis-vinylidene species (*vide infra*), is essentially instantaneous–so is clearly inconsistent with an alkyne-to-vinylidene rearrangement occurring during this step. All such rearrangements previously noted in related systems have been slow (24-72 h).[23] If **19** had been a mixed alkyne-vinylidene species like **14**, the transformation of **19** to **20** should also have been slow.

The spectroscopic parameters for the triflate and tetrafluoroborate salts of **19** are virtually identical, in spite of the differing anions, suggesting that the anions are non-coordinating. In addition, the conductivity of the BF_4^- salt in CH_3NO_2 indicates a 1:1 electrolyte (73 Ω cm^2 mol^{-1}), which also indicates that the iodo ligand remains coordinated. The IR spectrum of **19**•SO_3CF_3 shows a band at 1580 cm^{-1}, separating into two bands, at 1575 and 1525 cm^{-1} when ^{13}C-labelled vinylidene is used. It appears that in the latter spectrum the higher frequency band corresponds to phenylvinylidene whereas the lower frequency stretch is due to $^{13}C{=}^{13}CH_2$; when natural abundance vinylidene is used both bands overlap.

The addition of either an anionic (I^-) or a neutral (CO) ligand to **19** results in the unusual transformation of the terminal vinylidene ligands to bridging – a transformation that appears to be unprecedented, although it has previously been suggested.[8] In addition, the preparation of heterobimetallic, vinylidene complexes from the reaction of a mononuclear vinylidene complex with an unsaturated species is another example of terminal-to-bridging vinylidene rearrangement,[6] and the transfer of a vinylidene from one mononuclear complex to another also presumably occurs via a bridged intermediate.[40] Reaction of **19** with potassium iodide results in iodide coordination to give two isomers of $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (**20**), as shown in Scheme 4.5. Although other isomers, having an iodo ligand adjacent to the phenyl substituent of the phenylvinylidene group, are possible, they appear not to be favored owing to destabilizing steric repulsions involving these larger groups. At ambient temperature in CH_2Cl_2 only isomer **20a** is observed. Its $^{31}P\{^1H\}$ NMR spectrum shows two resonances indicating two phosphorus environments and the $^{13}C\{^1H\}$ NMR also shows two terminal-carbonyl resonances at δ 171.9 and 170.4. Each carbonyl shows coupling to two adjacent phosphorus nuclei, and in the $^{13}C{=}^{13}CH_2$ sample each shows coupling (27 Hz) to C_α of this vinylidene group, indicating that both are trans to C_α. The vinylidene carbon nuclei resonate at δ 102.2 (C_α) and 143.3 (C_β) with a mutual coupling of 61 Hz. Coupling of C_α to the ^{31}P nuclei is not resolved. The chemical shift for C_α is at exceptionally high field and can be compared with previous determinations for bridged vinylidenes which are usually downfield of δ 230;[1] the value observed for **20a** is at even higher field than those noted earlier in the paper, which are already unusual in their chemical shift (*vide supra*). In the ^{1}H NMR spectrum the vinylidene protons appear at δ 9.19 and 9.16 with coupling (for $^{13}C{=}^{13}CH_2$) of 153 Hz to C_β. No resonance for the phenylvinylidene proton is observed so it is presumed to lie under the phenyl resonances. The IR spectrum of **20a** shows a carbonyl stretch at 2027 cm^{-1}.

At -80°C in CH_2Cl_2 both isomers, **20a** and **20b** appear in the approximate molar ratio of 2:1. The $^{31}P\{^1H\}$ NMR spectrum of **20b** displays four different signals indicating a top-bottom as well as a left-right asymmetry in the complex. Although the iodo, carbonyl and vinylidene ligands all form a plane perpendicular to the plane of the phosphorus atoms, the top-bottom asymmetry can be broken by a skewing of the phenylvinylidene about the C=C bond, as is shown in the X-ray structure (vide infra). In support of the structure shown only the carbonyl resonance at δ 174.7 displays trans coupling (30 Hz) with the $^{13}C{=}^{13}CH_2$ group; the carbonyl at δ 172.7 is cis to the vinylidene ligand, displaying no coupling to it. The resonance for C_α coincidentally occurs at exactly the chemical shift as for **20a**, whereas C_β resonates at δ 133.0. In the ^{1}H NMR spectrum the vinylidene protons appear at δ 8.81 and 8.14, and again the phenylvinylidene proton is not observed. Although **20a** is the only species observed in solution at ambient temperature, crystallization at this temperature yields only **20b** as a solid, as shown by IR spectroscopy and the X-ray structure. This isomer shows only one carbonyl stretch at 2009 cm^{-1}. The facile interconversion of the two isomers presumably occurs by I^- loss and recoordination.

The structure of **20b** is shown in Figure 4.2, confirming the geometry assigned in Scheme 4.5 on the basis of the spectroscopic analysis. Selected bond lengths and angles are given in Table 4.6. Although the phenyl substituent on the

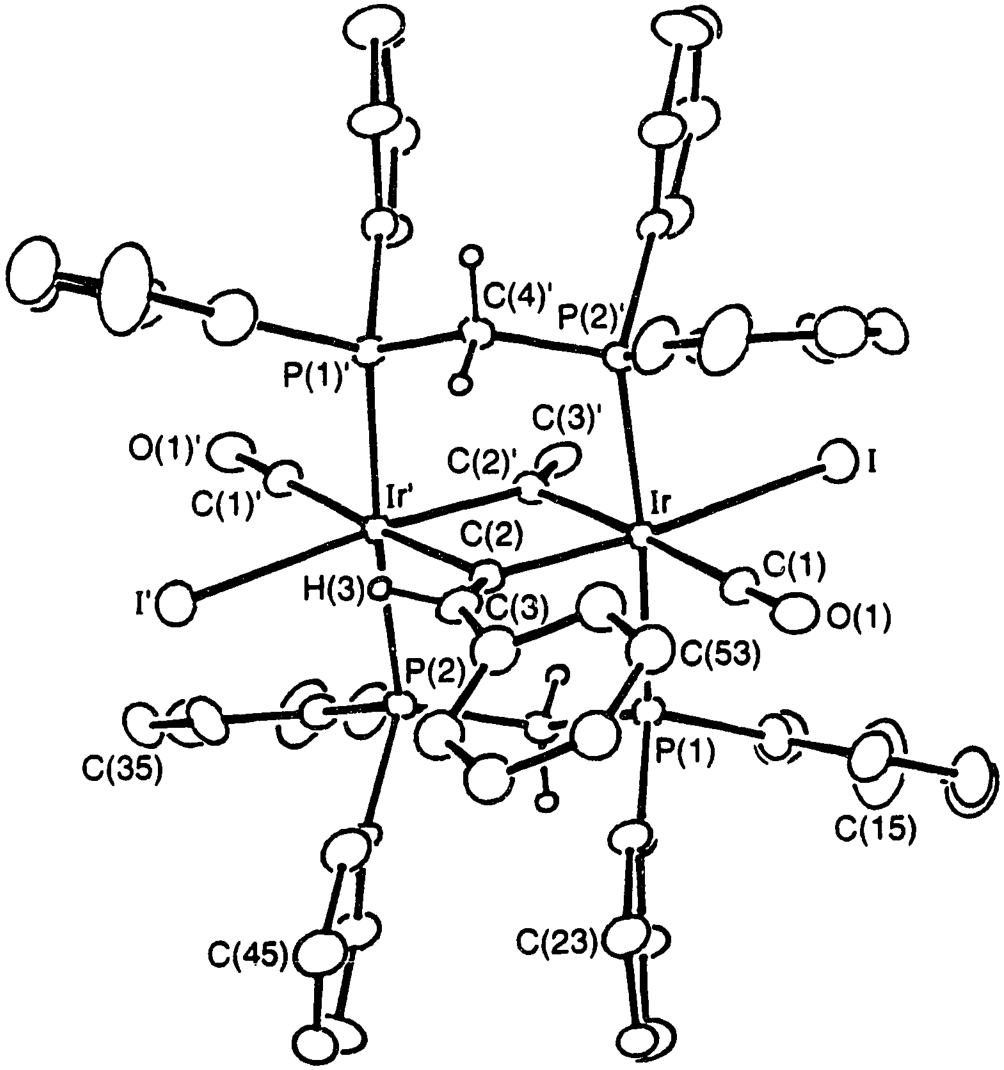


Figure 4.2. Perspective drawing of $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (**20b**). Numbering and thermal ellipsoids are as described for figure 4.1.

Table 4.6. Selected Bond Lengths (Å) and Angles (deg) for Compound **20b**.

(a) **Bond Lengths**

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ir	I	2.845(1)	Ir	P(1)	2.365(3)
Ir	P(2)	2.356(3)	Ir	C(1)	1.94(2)
Ir	C(2)	2.08(1)	Ir	C(2)	2.13(1)
O(1)	C(1)	1.07(2)	C(2)	C(3)	1.28(2)
C(3)	C(51)	1.59(2)			

(b) **Bond Angles**

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
I	Ir	P(1)	92.78(8)	I	Ir	P(2)	89.88(9)
I	Ir	C(1)	84.3(5)	I	Ir	C(2)	173.0(3)
I	Ir	C(2)	96.6(3)	P(1)	Ir	P(2)	175.4(1)
P(1)	Ir	C(1)	92.5(5)	P(1)	Ir	C(2)	90.9(3)
P(1)	Ir	C(2)	85.2(3)	P(2)	Ir	C(1)	91.5(5)
P(2)	Ir	C(2)	86.0(3)	P(2)	Ir	C(2)	90.7(3)
C(1)	Ir	C(2)	101.5(6)	C(1)	Ir	C(2)	177.6(5)
C(2)	Ir	C(2)	77.8(5)	Ir	C(1)	O(1)	177(1)
Ir	C(2)	Ir	102.2(5)	Ir	C(2)	C(3)	130.4(10)
Ir	C(2)	C(3)	127.1(10)	C(2)	C(3)	C(51)	148(1)

phenylvinylidene group is inversion disordered, having half occupancy on C(3) and half on C(3)', the rest of the molecule is well behaved and the disorder was satisfactorily resolved. In this disorder the two vinylidene carbons are directly superimposed on those of the phenylvinylidene, masking any subtle differences that there might be in their parameters. Nevertheless, the structure unambiguously establishes both the bridging nature of the two vinylidene groups and the mutually trans arrangement of the iodo ligands for this isomer. The metals in **20b** have slightly distorted octahedral geometries that are characteristic of Ir^{+3}, in which case the bridging vinylidene units are considered as dianionic ligands. Structurally this species is closely related to the monovinylidene species **8** and **9** via formal insertion of the second vinylidene (CCH_2 or CC(H)Ph) into the Ir-Ir bond of the respective monobridged species. The major structural differences in the two classes of species is therefore a much longer Ir-Ir separation in **20b** (3.275(1)Å compared to 2.828(1)Å (**8**) and 2.783(1)Å (**9**)) and a wider angle at the bridging vinylidenes (102.2(5)° vs. 84.6(7)° (**8**) and 86.0(9)° (**9**)). Even so, in **20b**, the idealized 120° angle at C(2) is not attained, presumably because this would generate too acute an angle between the vinylidenes at Ir, with the resulting poor Ir-C_α overlap; this angle is already quite acute (77.8(5)°). By comparison, the structure of **15**, having the acetylene tautomer instead of vinylidene, displays angles involving the bridging groups that are close to ideal. Since the acetylene ligand binds with one end to each metal, rather than to both metals through only one carbon atom, as for the vinylidene group, the metals are able to move apart by over 0.3Å, compared to **20b**. In this geometry the undistorted angles at the acetylenic and vinylidene carbons and at the metals give rise to optimal metal-ligand overlap. All other parameters within **20b** compare well with those of **8** and **9**, and in particular, the vinylidene C(2)-C(3) separation 1.28(2)Å is typical of a double bond.

Upon reaction of **19** with CO, transformation of the terminal vinylidene ligands to bridging again occurs yielding $[Ir_2I(CO)_3(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (**21a, 21b**) and again two isomers are observed, corresponding to two orientations of the iodo ligand with respect to the phenylvinylidene group. In both of these isomers the iodo ligand remains on the same face of the Ir_2P_4 plane opposite the CC(H)Ph moiety, presumably to minimize steric repulsions. Although it appears that the isomer having the iodo ligand adjacent to the hydrogen substituent on the phenylvinylidene ligand is equivalent to isomers **21a** and **21b**, its absence suggests that the dominant repulsions involve the dppm phenyl groups, the orientations of which will be most affected by the large iodo ligand and the vinylidene phenyl group. Both possible isomers, in which the iodo group is adjacent to CC(H)Ph can be ruled out by the $^{13}C\{^1H\}$ NMR of a sample containing ^{13}CO and $^{13}C{=}^{13}CH_2$, since both isomers observed display three carbonyl resonances of which two show strong coupling (between 21 and 32 Hz) to C_α of the unsubstituted vinylidene, indicating that both of these CO's are opposite this group. At ambient temperature only isomer **21a** is observed, whereas at -60°C the **21a**:**21b** ratio is *ca.* 1:0.75. Although the previously discussed interconversion between isomers **20a** and **20b** can occur via I^- loss and recoordination, since this occurs at the same metal center, the interconversion between **21a** and **21b** appears to be different, since the iodo ligand appears to migrate from metal to metal. If this occurs by I^- dissociation, there must also be an accompanying loss of CO with its subsequent recoordination, since with the bridging vinylidene groups there is no simple way (such as a turnstile motion) that allows ligand exchange between the two metals. Iodide dissociation from **21** also appears less likely than in **20** owing to the positive charge of the former.

Another possibility is that exchange between **21a** and **21b** can occur by rotation of the phenylvinylidene group about the C=C axis. Facile rotation of terminal vinylidenes has been previously noted,[2] and examples of rotation about the C=C bond in a bridged group are also known.[50,51] In both isomers of compound **21** the $^{13}C_{\alpha}$ resonance is again at unusually high field (δ 101.0 (**a**), 99.8 (**b**)), but all other parameters are as expected.

Under an atmosphere of CO compound **21** reacts with methyltriflate resulting in iodide abstraction (as CH_3I) and yielding $[Ir_2(CO)_4(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]_2$ (**22**), which is not stable in the absence of CO. This product shows the expected four terminal carbonyl resonances, with two of them displaying strong coupling (26 Hz) to $^{13}C_{\alpha}$ of the enriched vinylidene, which is again observed at high field. The ^1H NMR spectrum of **22** shows the phenylvinylidene proton resonance at δ 8.19, which appears as an apparent triplet due to coupling to the two ^{13}CO's opposite the phenylvinylidene group, and this signal appears as a singlet when natural abundance CO is used. The protons of the unsubstituted vinylidene appear at δ 7.94 and 7.82 with the usual parameters observed when $^{13}C^{13}CH_2$ is used.

The dialkyl derivative, $[Ir_2(CH_3)_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (**23**), can be prepared from **19** by reaction with ca. 4-fold excess of MeLi. Also obtained in this reaction is compound **20**, resulting from I^- attack on **19** by the LiI produced in the reaction. Compound **23** is unstable and transforms to unidentified products at ambient temperature, so it was characterized only by NMR. Two carbonyl resonances, at δ 177.9 and 177.5, are observed in the $^{13}C\{^1H\}$ NMR spectrum, and in the $^{13}C{=}^{13}CH_2$-containing sample the lower field carbonyl signal displays trans coupling (26 Hz) to $^{13}C_{\alpha}$. The vinylidene carbons resonate at δ 106.0 (C_{α}) and 133.4 (C_{β}), and display the normal couplings. Although signals were observed in the regions expected for vinylidene protons, we were unable to unambiguously assign them owing to many impurities in the sample. However, the two methyl resonances are obvious at δ -0.45 and -0.92, and are shown, by selective ^{31}P decoupling, to be bound to different metals, by displaying coupling to only the ^{31}P nuclei bound to the respective metal. We had prepared **23** with the intention of studying migratory insertions involving the vinylidene ligands, however the instability of the species has precluded this study. It may be, however, that this instability is induced by migratory insertion which creates unsaturation in the complex. Further studies are underway, investigating other alkyl and aryl derivatives of **23**.

Conclusions

The cationic, vinylidene-bridged complexes, $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CC(H)R)(dppm)_2][X]$ (R = H (**4**), Ph (**6**)), were studied with the idea that their incipient coordinative unsaturation, could result in the incorporation of alkynes, leading to unusual products, containing the vinylidene group together with a modified or unmodified alkyne. Verification that unsaturation in these species could result from movement of the bridging iodo ligand to a terminal site came from the products in the reactions of **4** with ^tBuNC and CO, which showed each of these ligands in the respective products occupying the site vacated by the iodo group. Reaction of **4** or **6** with alkynes appears to proceed in much the same manner yielding two unusual classes of complexes in which the added alkyne either remains unmodified or undergoes tautomerism to a second vinylidene group.

With the phenylvinylidene-bridged precursor **6**, reaction with either acetylene or phenylacetylene yielded products, $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCR)(dppm)_2][X]$ (R = H (**14**), Ph (**18**)), bridged by a phenylvinylidene group and the alkyne molecule.

In addition to the spectroscopic evidence supporting the presence of two alkyne tautomers in the same complex, an X-ray structure determination of the neutral diiodo species (**15**) confirmed the formulation.

Reaction of the vinylidene-bridged precursor **4** with acetylene gives an analogous vinylidene- and acetylene-bridged product (together with unidentified products), however the reaction of **4** with phenylacetylene yields the unusual bis-vinylidene species, $[Ir_2I(CO)_2(CCH_2)(CC(H)Ph)(dppm)_2][X]$ (**19**), which appears to have each vinylidene group terminally bound to a different metal. Reaction of this species with I^-, CH_3^- or CO yields the respective adducts in which the vinylidene groups move to the bridging sites. This formulation, in which the vinylidene and the phenylvinylidene groups are bridging, is confirmed by an X-ray determination of the diiodo species (**20b**). Compound **20b** is an isomer of **15** in which the bridging vinylidene is replaced by a bridging acetylene group. Compound **19** is an unusual example in which a vinylidene ligand is terminally bound in a binuclear system. The previous rare examples involving terminal, instead of bridging vinylidenes have large vinylidene substituents suggesting that their terminal coordination is sterically driven. This appears not to be the case with **19**, since the addition of ligands leads to a bridged arrangement. The facile reversible interconversion between the terminal and bridging modes is also unusual.

The obvious question that arises from these results relates to the generation of a mixed vinylidene-acetylene complex by one route and a divinylidene complex by another. Why does the unsubstituted vinylidene-bridged compound **4** yield a bis-vinylidene compound when reacted with phenylacetylene while the other reactions attempted yield the mixed vinylidene-alkyne products? It is noteworthy that only **4** yields the bis-vinylidene species, and this occurs only with phenylacetylene. We assume that the tendency to yield the bis-vinylidene species results from the tendency to undergo initial oxidative addition to yield the hydride-acetylide intermediate. Phenylacetylene has a stronger tendency to undergo alkyne C-H bond cleavage than acetylene[23] so should be more prone to vinylidene formation. Why this occurs only with the unsubstituted vinylidene precursor **4** and not with the phenylvinylidene-bridged analogue **6** may result from the stronger π acidity of the latter group. This would leave the metals less electron rich and less prone to oxidative addition. These ideas remain to be tested through the use of different substituents on the vinylidene precursor.

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Chapter 5

Conclusions

One of the goals of this research was to determine how adjacent metals in binuclear complexes could act in a cooperative manner leading to unusual chemistry. Although a large number of possible metal combinations could be investigated, this thesis concentrated on two systems. In the first, the two metals involved are Rh and Mn, whereas in the second, both metals are iridium. The RhMn system was studied to address a number of points relating to the difference in the two metals. Whereas Rh has a strong tendency to be coordinatively unsaturated, Mn usually has a saturated 18-electron configuration. In addition, most previous studies within our group had utilized second- and third-row elements; with the introduction of a first-row element such as Mn, it was reasoned that important differences would result when compared to the heavier metals. In this regard some of the preliminary RhMn chemistry was carried out in order to make comparisons with the analogous RhRe chemistry which had been previously studied.[1-2] The diiridium system was investigated with intentions of extending a previous study on vinylidene-bridged complexes[3] in order to gain information on the transformations of 1-alkynes to vinylidene groups in the presence of adjacent metals and to investigate the reactivity of bridging vinylidene groups related to that of terminally bound vinylidenes.

From the first study on the RhMn complex, [RhMn$(CO)_4$$(dppm)_2$] (A), and from the previous studies on the closely related complex [RhRe$(CO)_4$$(dppm)_2$] (B)[1-2] the strong tendencies of both Mn and Re to adopt octahedral 18-electron configurations and the tendency of the adjacent Rh center to maintain a coordinatively unsaturated, 16-electron square planar geometry, has been reaffirmed. The coordinatively unsaturated Rh center in complex A and its derivatives plays an important role in accepting substrates, which can be either nucleophiles (such as thiols and alkynes) or electrophiles (such as H^+ and CH_3^+), and in inducing chemistry at the adjacent metal center. As was proposed for complex **B**, the initial site of attack for nucleophiles appears to be the Rh center of complex A, as indicated by the formation of the pentacarbonyl species [RhM$(CO)_5$$(dppm)_2$] (M=Re or Mn) in both cases, which were shown to have an additional carbonyl on Rh. In addition, low temperature NMR studies on these complexes allowed the detection of a number of adduct intermediates confirming the substrate binding at Rh. The ability of the Rh center in A or **B** to undergo attack by nucleophiles results from the coordinative unsaturation at this metal, in which it can attain an 18-electron configuration by coordination of the nucleophile. Even though this metal is unsaturated, it is nevertheless electron rich, being a d^8 metal in a low oxidation state and can function as a base toward electrophiles, by utilizing its doubly occupied d_{z^2} orbital which lies above and below the square plane of the metal.

The first difference noted in the reactions of the RhMn species A with H_2S and thiols, compared to the same reactions involving the analogous RhRe species **B**, is the stronger tendency of the latter to retain all carbonyls. All intermediates observed in the RhRe reactions were tetracarbonyl species which apparently only lost CO in the final transformation from a terminal to a bridging thiolato group.[1] This shows an interesting effect of the first-row metal; either the carbonyl group is lost from this metal, which would be in keeping with the known greater lability of Mn systems compared to Re,[4] or, possibly more interesting, the Mn might be exerting a labilizing influence on Rh. Previous studies within the group had shown that CO loss in related compounds seemed to occur from Rh,[5] owing to its tendency to adopt a 16-electron, coordinatively unsaturated Rh(+1) configuration upon CO loss. Unfortunately the two possibilities could not be distinguished in the present study.

It is also of interest that a series of stable RhMn complexes containing terminal SR ligands, [RhMn(SR)$(CO)_3$(μ-H)$(dppm)_2$] (R=H, Et and Ph), have been obtained at ambient temperature. By comparison, the RhRe complexes with terminal SR (R=H, Et and Ph) were only observed at low temperature; upon warming to ambient temperature either the sulfido-bridged complex (R=H) or thiolato-bridged complexes were obtained.[1] Although the sulfido-bridged complex [RhMn$(CO)_3$(μ-S)(μ-CO)$(dppm)_2$] is also obtained as the final product from the H_2S reaction with complex **A**, no thiolato-bridged RhMn analogues are formed in its reaction with thiols.

Another significant difference between the RhMn and RhRe systems was found in the studies of alkyne-addition reactions. The reaction of complexes **A** or **B** with internal alkynes such as DMAD and HFB generate the parallel, alkyne-bridged complexes [RhM$(CO)_3$(μ-RCCR)(μ-CO)$(dppm)_2$] (M=Mn or Re; R=CF_3 or COOMe), and both systems undergo facile CO loss.[2] This CO loss is accompanied by the formation of a Rh→Mn or Rh→Re dative bond, demonstrating one way in which the adjacent metal (Rh) can assist in the labilization of a ligand from the normally inert, 18-electron center (Mn or Re). For the RhRe system, the bridging alkyne remains parallel to the metal-metal vector in the product. However, for the

RhMn system, both parallel and perpendicular alkyne-bridged complexes are simultaneously obtained; the transformation to a perpendicular alkyne bridging mode is a second way of maintaining a saturated configuration at Mn, with transformation of a 2-electron-donor alkyne to a 4-electron donor upon rotation. The facile, reversible interconversion between the two alkyne bridging modes occurs with unprecedented ease in this system, and clearly demonstrates the cooperative effects of the two adjacent metals in accommodating the facile rotation of the alkynes by the change of the metal-metal bond polarity.

It is an interesting contrast that the perpendicular alkyne binding mode is observed for the RhMn system but not for the RhRe analogues. We propose that the stronger Rh→Re dative bond, compared to the Rh→Mn (presumably because of better overlap involving the heavier metals) favours retention of this interaction in the RhRe compounds. It should be recalled that for RhMn the unsaturation upon CO loss is relieved in two ways: either by Rh→Mn dative bond formation or rotation of the alkyne from a 2e to a 4e donor. This would suggest that both bonding modes are comparable for the RhMn system, whereas the Rh→Re formulation is more favorable for the heavy metal.

Protonation of the alkyne-bridged products at ambient temperature yields a series of Rh-bound vinyl complexes while at low temperature observation of metal-hydride intermediates by NMR techniques is possible. In the alkyne-bridged complexes without a Rh-Mn bond, protonation appears to occur at the Rh center while in the Rh-Mn bonded complexes the metal-metal bond appears to be protonated. Although in the latter case the hydride and alkyne ligands are on opposite faces of the dimer, appearing not to be well placed for subsequent migratory insertion, movement of the hydride between two metals to the opposite face has been shown to be facile,[6] so the observed structure presents no appreciable barrier to vinyl formation.

The Rh-bound vinyl complexes can also be obtained from an alternate ro[illegible] the insertion of alkynes or allene into the metal-hydride bond in [RhMn(CO)$_4$(μ-H)(dppm)$_2$]$^+$. However, in the reaction with allene, both the Rh-bound vinyl and η^1-allyl isomers were observed, resulting from a hydride transfer to a terminal carbon or the central carbon of allene, respectively. The vinyl species is thermodynamically favored, presumably due to the stronger Rh-C σ-bond involving an sp^2 carbon rather than an sp^3 carbon of an η^1-allyl group. This observation of both tautomers resulting from the reaction of allene with a hydride is unusual and presents strong support for the involvement of an allene-hydride intermediate in the interconversion between allyl and vinyl complexes.[7-8]

Another goal of this thesis was to prepare vinylidene RhMn complexes and to study the reactivities of these vinylidene groups with electrophiles such as H$^+$ and CH$_3$$^+$. Unlike [Ir$_2I_2$(CO)(μ-CO)(dppm)$_2$],[3] which readily reacts with acetylene or phenylacetylene to yield the alkyne-bridged species followed by tautomerization to form vinylidene-bridged complexes, the RhMn complex A does not react with these alkynes. However, with an alkyne having an electron-withdrawing substituent, (HC≡CC(O)CH$_3$), a facile reaction occurs to generate the expected alkyne-bridged species [RhMn(CO)$_4$(μ-HC≡CC(O)Me)(dppm)$_2$] at low temperature; upon warming to ambient temperature the desired vinylidene complex [RhMn(CO)$_4$(μ-C=C(H)-C(O)Me)(dppm)$_2$] (C) is formed through a 1,2-hydrogen shift. Complex C is observed as two isomers which are related by the apparent rotation about the C=C bond of the bridging vinylidene ligand. In contrast to the facile rotation about the C=C bond in terminal vinylidenes,[9] a similar rotation in vinylidene-bridged species appears to be less common, but has been observed.[10] It has been shown that the C=C rotation in vinylidene-bridged complexes is favored by electron-withdrawing substituents at β-carbon, as was observed in the diiron complexes [$Cp_2Fe_2L_2$(μ-CO)(μ-C=C(H)C(CN)=$C(CN)_2$)] (L_2 = 2CO, dppm, dppe).[10a] Due to the presence of acyl substituent at the β-carbon of the vinylidene ligand in complex **C**, the C=C bond rotation occurs, giving the two isomers of **C**.

Loss of one carbonyl from the Mn center in one of the rotation isomers of **C** is facile, assisted by the formation of a donor bond from the ketone oxygen of the vinylidene group to yield [RhMn$(CO)_3$(μ-η^1:η^2-CC(H)C(O)Me)$(dppm)_2$] (**D**), which has been structurally characterized by X-ray techniques. The facile and reversible substitution of the Mn-bound carbonyl by the ketone oxygen, as indicated by the spin-saturation-transfer experiment, possibly stems from oxophilicity of Mn, which makes the formation of Mn-O bond favorable.

Although protonation of a vinylidene ligand generally occurs at the β-carbon,[11] the electron-withdrawing acyl substituent on the β-carbon appears to lower its nucleophilicity, so that bridging alkylidyne species were not observed. Protonation or alkylation of the tricarbonyl complex **D** seems to occur initially at Rh, with subsequent formation of a chelating vinyl group on Mn, bound through the α-carbon and ketone oxygen. In the case of alkylation, the unusual intermediate containing Rh-bound methyl and bridging vinylidene groups, [RhMn$(CH_3)(CO)_3$(μ-η^1:η^2-CC(H)C(O)Me)$(dppm)_2]^+$, was observed at low temperature. This intermediate undergoes migratory insertion of the methyl and vinylidene ligands to form a Rh-bound vinyl complex in the presence of CO or a Mn-bound, chelating vinyl complex in the absence of CO. These appear to be the only clearly defined examples involving the migratory insertion of a bridging vinylidene ligand, although such uncommon processes have been observed in mononuclear complexes.[7]

Different from the tricarbonyl vinylidene complex **D**, which yields Mn-bound vinyl complexes upon protonation or alkylation (in the absence of CO), the tetracarbonyl vinylidene species **C** generates Rh-bound vinyl complexes. Significantly, the attack by the electrophiles H^+ or CH_3^+ on an equilibrium mixture of both isomers of **C** yields only one product in each case, and even more significantly, these products differ only in their geometries about the vinyl C=C bond. These observations can be rationalized by the intervention of a rhodium-hydride or a rhodium-alkyl intermediate with subsequent migratory insertion involving the bridging vinylidene groups. Protonation appears to occur initially at the ketonic oxygen to yield an enol product for which only one isomer can give facile proton transfer to the Rh, giving the vinyl product observed. Alkylation of the isomeric mixture of **C** apparently occurs directly at the Rh, with attack being favored only in one isomer (the vinylidene acyl substituent trans to Rh), in which there is better access to the Rh. Again, subsequent migratory insertion of this product yields the Rh-bound vinyl complex.

The migratory insertion involving bridging vinylidene and alkyl or hydride, yielding vinyl complexes, has relevance to Fisher-Tropsch reaction–a heterogenuous process by which carbon monoxide and hydrogen are converted to water and a mixture of hydrocarbons, alkenes and alcohols, in the presence of a metal catalyst.[12] It was proposed that vinylidene[13] and vinyl groups[14] are possible Fisher-Tropsch reaction intermediates. This study shows that these two groups are not unrelated since the facile transfer of hydride and alkyl groups to bridging vinylidene ligands generates vinyl species. Although vinylidene ligands were proposed to explain the branched products[13] it may be that their involvement is limited to vinyl formation, which have been shown by Maitlis to be important species.[14]

The last objective of this thesis was to study some transformations involving alkynes on homobimetallic diiridium complexes. In contrast to rhodium, which has a strong tendency to maintain a 16-electron configuration, iridium has a greater tendency to adopt an 18-electron configuration as shown by previous studies.[6b,15] In this respect, if the starting complexes are coordinatively saturated, coordinative unsaturation will need to be generated in order to develop further chemistry of these species.

As mentioned in the Chapter 1, mixed alkyne- and vinylidene-bridged complexes can be obtained from the reaction of the coordinatively saturated vinylidene-bridged complex $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2]$ (**E**) with acetylene.[3] It was rationalized that I^- loss was occurring at same stage to generate the required coordinative unsaturation, therefore it was reasoned that removal of an iodo anion to give a cationic vinylidene-bridged species would yield unsaturation at one of the Ir centers and provide a more facile route into subsequent chemistry with alkynes.

Two routes were explored into the desired cationic, vinylidene-bridged species: either reaction of the cationic precursor $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2]^+$ with 1-alkynes, or iodide removal from the neutral vinylidene-bridged complex **E**. In the first study, the progress of the reaction of the iodo-bridged A-frame $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2]^+$ with acetylene, phenylacetylene and allene was monitored at low temperature and showed the formation of a series of terminal alkyne or allene complexes $[Ir_2(CO)(L)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (L=acetylene, phenylacetylene or allene), suggesting that the alkynes or allene attack at the less sterically hindered coordination site on the outside of the A-frame. The observation of the terminal alkyne complexes in this study supports the involvement of the intermediates containing terminal alkyne ligands in the reactions of alkynes with the A-frame complex as previously proposed.[16] The alkyne adducts generated the desired vinylidene-bridged species, $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CC(H)R)(dppm)_2][X]$ (R=H, (**F**) or Ph, (**G**)) at ambient temperature. Iodide removal from the neutral vinylidene-bridged complex, $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ (R=H or Ph) also proceeded readily to obtain the same products **F** or **G**.

Although complexes **F** and **G** are still coordinatively saturated due to the bridging iodo ligand, they have incipient unsaturation since movement of the iodo ligand from a bridging to a terminal position generates unsaturation at one center. Therefore complexes **F** and **G** can function as coordinatively unsaturated complexes. Verification of this incipient unsaturation came from the reactions of **F** with ^tBuNC and CO, which showed each of these ligands in the respective products occupying the site vacated by the iodo group.

The idea that the incipient coordinative unsaturation could result in the incorporation of alkynes, leading to the unusual products, containing the vinylidene group together with an alkyne ligand or another vinylidene group, also met with success, proceeding in much the same manner as those of ^tBuNC and CO, yielding two unusual classes of complexes, in which the added alkynes either remain unmodified or undergo a 1, 2-hydrogen shift to yield a second vinylidene group.

Reaction of the phenylvinylidene-bridged complex **G** with either acetylene or phenylacetylene yielded the complexes $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCR)(dppm)_2][X]$ (R=H or Ph) bridged by a phenylvinylidene group and an alkyne ligand. In addition to the spectroscopic data showing the presence of two alkyne tautomers in the same complex, an X-ray structure determination of $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCH)(dppm)_2]$ unequivocally confirmed the formulation.

Although an analogous alkyne- and vinylidene-bridged complex (together with unidentified products) was obtained from the reaction of the vinylidene-bridged complex **F** with acetylene, the unusual divinylidene species $[Ir_2I(CO)_2(CCH_2)(CC(H)Ph)(dppm)_2][X]$ (**H**), containing two terminal vinylidene groups on each metal, was generated with phenylacetylene. These two terminal vinylidene groups adopt bridging positions upon the coordination of nucleophiles such as I^-, CH_3^- and CO. The formulation of the bis(vinylidene)-bridged complex, $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$, was confirmed by X-ray studies. The facile interconversion between the terminal and bridging modes, with the addition or removal of nucleophiles, appears to be unusual. Complex **H** is also an unusual example showing terminal vinylidene groups in a binuclear system. The previous rare examples involving terminal, rather than bridging vinylidene ligands, have bulky vinylidene substituents, suggesting that the terminal mode was favored over bridging owing to steric factors.[17] This seems not to be the case with complex **H**, since the addition of ligands causes transformation of terminal to bridging coordination of these groups in spite of the greater crowding that results.

The interesting results, relating to the formation of a mixed vinylidene-acetylene complex from one route and a divinylidene complex from another, were rationalized by the tendencies for alkynes to undergo oxidative addition on metal centers. We assumed that the tendency to yield divinylidene species results from the tendency for alkynes to undergo initial oxidative addition to yield the hydride-acetylide intermediate, which is presumed to precede vinylidene formation. The stronger π-acidity of the phenylvinylidene group should leave the metals less electron rich and less prone to oxidative addition of alkynes, which explains the formation of a divinylidene complex from the vinylidene-bridged **F**, but not from the phenylvinylidene-bridged **G**. On the other hand, if the tendencies of alkynes to undergo oxidative addition of the alkyne-H bond are parallel to the acidities of the alkynes,[18] we might expect phenylacetylene to oxidatively add more readily than acetylene. Therefore the divinylidene complex **H** is only observed in the reaction of complex **F** with phenylacetylene; apparently, the acetylene has too low a tendency to undergo C-H activation in these cationic vinylidene-bridged species.

The diverse chemistry involving dinuclear complexes observed in this study can be attributed to metal-metal cooperativity by virtue of the close proximity of the two metal centers. The changes in the nature of the metal-metal bonds in these compounds, from no bond, to a single bond, to a dative bond, in one direction or another, aids in the transfer of ligands from one metal to the other, as the addition or removal of electron density as ligands moved from one metal to the other could be compensated for by changing metal-metal bond polarity. The bridging modes of ligands, as a result of metal-metal cooperativity, also plays an important role in this chemistry, such as migratory insertion involving bridging alkyne or vinylidene groups. Also reaffirmed in this study is the importance of coordinative unsaturation in dinuclear complexes, which leads to high reactivity of these complexes towards substrates. The readiness of these dinuclear complexes to undergo nucleophilic reactions stems from the coordinative unsaturation at the Rh center in complex **A** and the incipient unsaturation in complexes **F** and **G**.

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Appendix

Solvents and Drying Agents

Benzene	Sodium metal
Dichloromethane	Phosphorus pentoxide
Diethyl ether	Sodium benzophenone ketyl
Hexanes	Sodium-potassium alloy
Methanol	Sodium metal
Nitromethane	4A Molecular sieves
Tetrahydrofuran	Sodium benzophenone ketyl
Toluene	Sodium metal