

Metal Cluster Complexes Containing Heteroatom-Substituted Carbene Ligands

RICHARD D. ADAMS

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received February 9, 1989 (Revised Manuscript Received May 4, 1989)

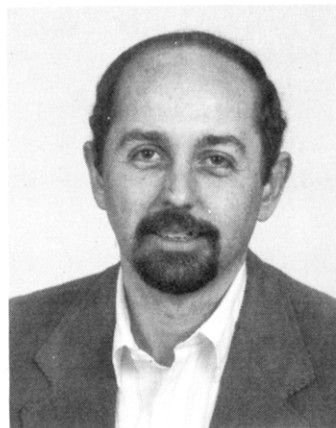
Contents

Introduction	1703
Syntheses	1704
Dinuclear Metal Complexes	1704
Trinuclear Metal Complexes	1705
Higher Nuclearity Clusters Containing Carbene Ligands	1707
Structure and Bonding	1708
NMR Spectroscopy	1709
Reactivity	1709
Metallocarbene Ligands	1711

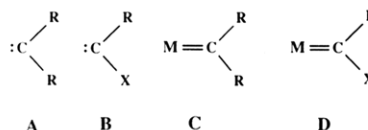
Introduction

Molecular groupings that contain carbon centers with six valence electrons are generally referred to as alkylidenes or carbenes. The former term is usually applied to those species where the substituents bonded to the carbon atom are alkyl groups, aryl groups, or a hydrogen atom (A). The latter term is usually applied to those species where one or both of the substituents X is bonded to the carbon atom by an element from one of the main groups V, VI, or VII (B).^{1,2} Carbenes can serve very effectively as ligands in metal complexes.^{1,2} Their bonding to metal atoms includes a combination of lone-pair σ -donation and synergistic π -electron acceptance. Most examples of carbene ligands contain substituents derived from the first row of the periodic table (e.g., C(R)NR₂ or C(R)OR), but carbenes containing substituents derived from the second row (e.g., C(SR)₂ or CR(PR₂)₂) have also been characterized.

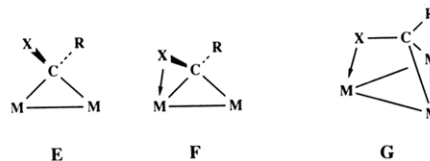
Generally 1964 is regarded as the year of the preparation of the first metal carbene complex.³ Since then, a vast number of metal carbene complexes have been prepared and studied. Recently, metal complexes containing carbene ligands have been used as reagents in a variety of novel organic syntheses.⁴ Curiously, however, there have been relatively few examples of polynuclear metal complexes (hereafter referred to as clusters) containing heteroatom-substituted carbene ligands. This review will survey the chemistry of cluster complexes containing heteroatom-substituted carbene ligands B and will focus on syntheses, structures, bonding, and reactivity. Whenever the term carbene is used in this review, it is intended to mean a heteroatom-substituted carbene of the type B. Cluster complexes will be defined as complexes that contain two or more metal atoms and at least one metal-metal bond. Excellent reviews that have focused largely on alkylidene ligands C in clusters were published recently.⁵



Richard D. Adams was born in Reading, PA, in 1947. He received a B.S. degree in 1969 from The Pennsylvania State University and a Ph.D. degree in 1973 from M.I.T. for research performed under the direction of F. A. Cotton. He was appointed Assistant Professor of Chemistry at SUNY at Buffalo in 1973 and Assistant Professor of Chemistry at Yale in 1975. He has been Professor of Chemistry at the University of South Carolina since 1984. He was the recipient of an A. P. Sloan Fellowship (1979-1981). His research interests lie in the area of the synthesis, structures, and bonding of metal carbonyl cluster compounds.



In cluster complexes, carbene ligands have been shown to exhibit the terminal coordination mode D and three bridging modes E-G. In the structural form E,

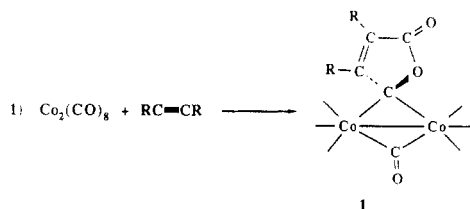


the plane of the carbene ligand is usually very close to perpendicular to the M-M vector. In structural forms F and G, the heteroatom X is coordinated to a metal atom and R = H or an aryl group. There have been very few reports of clusters containing carbene ligands with alkyl substituents attached directly to the carbene carbon atom. Studies have shown that these alkyl groups are susceptible to C-H activation processes by the neighboring metal atoms, and these lead to transformation of the carbene to other ligand species.⁶

Syntheses

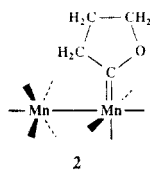
Dinuclear Metal Complexes

The first carbene-containing cluster complexes actually predated those made in 1964 by Fischer,⁴ but these were not recognized as carbene complexes at the time. The reaction of $\text{Co}_2(\text{CO})_8$ with alkynes under high pressures of CO yielded the dicobalt complexes **1** containing bridging $\text{RC}=\text{C}(\text{R})\text{COC}(\text{O})$ ligands formed by the coupling and cyclization of two CO ligands with one molecule of the alkyne (eq 1, $\text{R} = \text{H}$ or alkyl).⁷ These

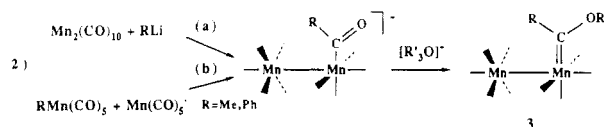


complexes were frequently referred to as "lactone" complexes because of the similarity of the heterocyclic bridging ligand to lactones, but the metal-bonded bridging carbon atom is formally divalent and could be regarded as a carbene center.⁵

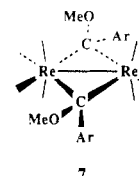
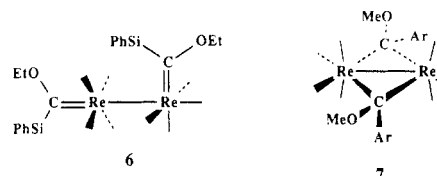
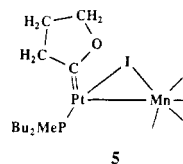
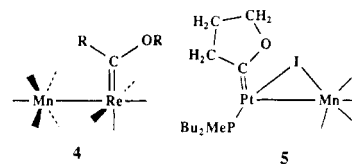
In 1963, King reported that the reaction of $[\text{Mn}(\text{C}-\text{O})_5]^-$ with $\text{Br}(\text{CH}_2)_3\text{Br}$ or $\text{Cl}(\text{CH}_2)_3\text{C}(\text{O})\text{Cl}$ yielded a compound with the empirical formula $\text{Mn}_2(\text{CO})_{10}(\text{C}-\text{H}_2)_3$.⁸ This compound was later shown to be the carbene-containing complex **2**.⁹



Subsequently, Fischer et al. prepared several dimanganese carbene complexes **3** by using the method of sequential addition of an RLi and alkylating agent to $\text{Mn}_2(\text{CO})_{10}$ (eq 2a, $\text{R} = \text{Me}$, Ph; $\text{R}' = \text{Me}$, Et).¹⁰

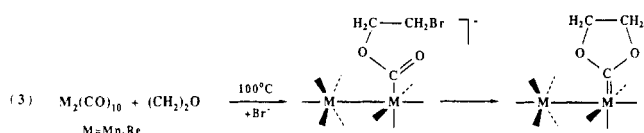


Although this method has been highly successful for the preparation of mononuclear metal carbene complexes,² its success has been relatively limited in the preparation of carbene-containing cluster complexes. The products **3** were also obtained from the reaction of $\text{MeMn}(\text{CO})_5$ with $[\text{Mn}(\text{CO})_5]^-$ and subsequent alkylation ($[\text{Me}_3\text{O}]^+$) of the acyl anion $[\text{Mn}_2(\text{CO})_9[\text{C}(\text{O})\text{R}]^-$. The formation of **2** evidently occurred by a similar process that culminated with carbene formation through an intramolecular cyclization. Surprisingly, the reaction of $\text{MeMn}(\text{CO})_5$ with $[\text{Re}(\text{CO})_5]^-$ and $[\text{Me}_3\text{O}]^+$ yielded the carbene complex **4** in which the terminal carbene ligand is located on the rhenium atom. It is believed that the carbene ligand was formed initially on the manganese atom and then migrated to the rhenium atom via a bridged intermediate.¹¹ A carbene ligand transfer was implied in the reaction of $\text{Mn}(\text{CO})_4\text{I}[\text{COCH}_2\text{CH}_2\text{CH}_2]$ with $\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PBU}^t_2\text{Me})$, which yielded the dinuclear complex $\text{PtMn}(\text{CO})_4(\text{PBU}^t_2\text{Me})\text{I}[\text{COCH}_2\text{CH}_2\text{CH}_2]$ (**5**) in which the carbene ligand is terminally coordinated



to the platinum atom.¹² Products analogous to **3** were also obtained from "R⁺/R⁻" reactions with $\text{Tc}_2(\text{CO})_{10}$ ¹⁰ and $\text{Re}_2(\text{CO})_{12}$.^{10,11} The addition of 2 equiv of Ph_3SiLi followed by 2 equiv of $[\text{Et}_3\text{O}]^+$ to $\text{Re}_2(\text{CO})_{10}$ yielded the bis[ethoxy(triphenylsilyl)carbene]dirhenium complex **6** containing an equatorially coordinated carbene ligand on one metal and an axial carbene ligand on the other;¹³ however, the addition of 2 equiv of ArLi ($\text{Ar} = \text{Ph}$ or *p*-tolyl) and 2 equiv of $[\text{Me}_3\text{O}]^+$ yielded the dirhenium complexes **7** containing two bridging carbene ligands.¹⁴

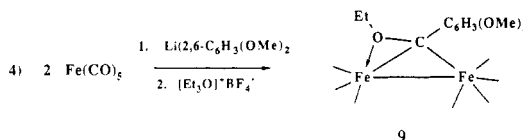
Angelici showed that oxirane, $(\text{CH}_2)_2\text{O}$, activated by bromide ion will add to a carbonyl ligand in certain metal carbonyl compounds to yield the cyclic dioxycarbene ligand $:\text{CO}(\text{CH}_2)_2\text{O}$.¹⁵ The reactions of oxirane with the dinuclear complexes $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}$, Re) yielded the monocarbene complexes **8** (eq 3). It was



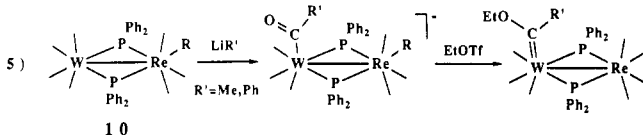
proposed that the intermediate ion, $\text{Br}(\text{CH}_2)_2\text{O}^-$, was formed by the addition of Br^- to the oxirane. The negatively charged oxygen atom of the ion was then added to the carbonyl carbon atom, and formation of the carbene ligand was completed by ring closure and displacement of bromide. With $\text{Re}_2(\text{CO})_{10}$ two oxirane additions could be achieved to yield the symmetric carbene complex $[\text{Re}(\text{CO})_4[\text{CO}(\text{CH}_2)_2\text{O}]]_2$. The reaction of oxirane with $\text{Ru}_3(\text{CO})_{12}$ yielded the bis(dioxycarbene) complex $\text{Ru}_3(\text{CO})_{10}[\text{CO}(\text{CH}_2)_2\text{O}]_2$.¹⁵ Related cyclic bis(aminocarbene) cluster complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_3-$ $[\text{CN}(\text{R})(\text{CH}_2)_2\text{NR}]$ ($\text{R} = \text{Me}$, Et) and $\text{Ru}_3(\text{CO})_{11}[\text{CN}(\text{R})(\text{CH}_2)_2\text{NR}]$ ($\text{R} = \text{Et}$) have been obtained from the

reactions of the electron-rich tetraamino olefins $\text{RN}^-(\text{CH}_2)_2(\text{R})\text{NC}=\text{CN}(\text{R})(\text{CH}_2)_2\text{NR}$ ($\text{R} = \text{Me}$, Et) with the corresponding parent carbonyl cluster.¹⁶

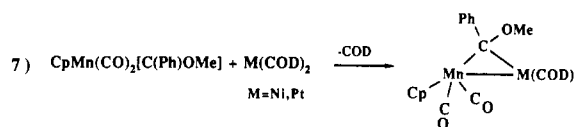
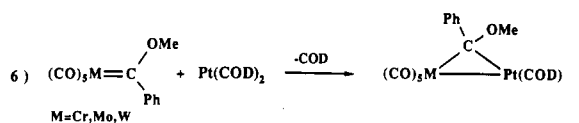
The reaction of $\text{Fe}(\text{CO})_5$ with $[2,6-\text{C}_6\text{H}_3(\text{OMe})_2]\text{Li}$ followed by $[\text{Et}_3\text{O}]\text{BF}_4$ yielded the diiron complex $\text{Fe}_2(\text{CO})_7[\mu-\eta^2-\text{C}(2,6-(\text{MeO})_2\text{C}_6\text{H}_3)\text{OEt}]$ (**9**) containing a bridging carbene of type F (eq 4).¹⁷ The mechanism of formation of **9** is not known, but it appears to be simply an $\text{Fe}(\text{CO})_3$ adduct of $\text{Fe}(\text{CO})_4[\text{C}(2,6-(\text{OMe})_2\text{C}_6\text{H}_3)\text{OEt}]$.



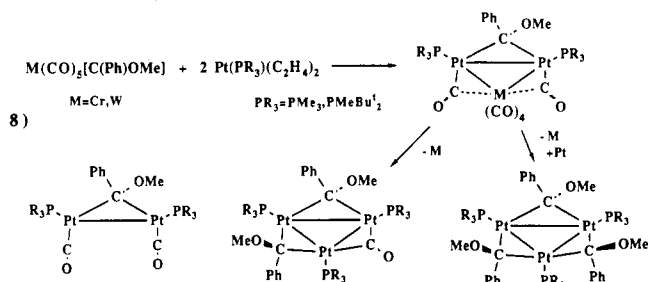
Geoffroy applied the "R⁺/R⁻" treatment to the heterodinuclear complexes WRe(CO)₇R(μ-PPh₂) (10, R = Me, Et) and obtained a terminally coordinated methylethoxycarbene ligand that was believed to be bonded to the tungsten atom (eq 5).¹⁸



Stone showed that mononuclear metal complexes containing carbene ligands could be used as reagents for cluster synthesis and prepared a number of heterodinuclear metal complexes containing bridging carbene ligands E and a metal from the nickel subgroup (eq 6¹⁹ and 7²⁰).

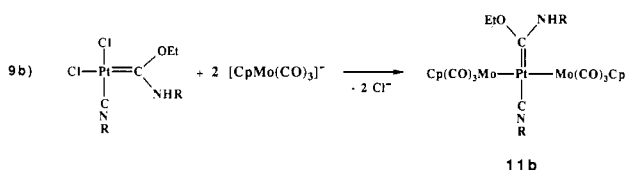
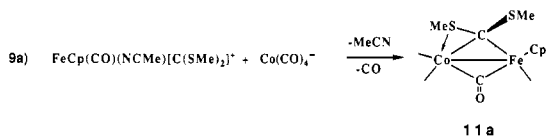


In some cases, the carbene ligand was found to migrate from the metal atom M to which it was originally attached (eq 8).²¹ Further reaction could lead to the



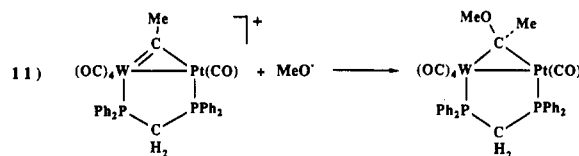
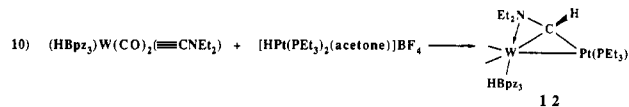
elimination of the metal atom M from the molecule with the formation of di- and triplatinum complexes containing two and three carbene ligands.²¹ The triplatinum complexes exist as mixtures of geometric isomers with bridging carbene ligands. A related trinickel tricarbene complex was also prepared.²²

Metal carbonyl anions have been used to form metal-metal bonds to complexes containing carbene ligands.²³ The reaction of the cationic iron complex FeCp(CO)(NCMe)[C(SMe)₂]⁺, which contains a bis-(thiomethoxy)carbene ligand, with Co(CO)₄⁻ led to facile replacement of the labile NCMe ligand and formation of a Co-Fe bond (eq 9a).^{23a} The product 11a contained a bridging η²-C,S-coordinated carbene ligand of type F, with a sulfur atom bonded to the cobalt atom.



The reaction of the platinum carbene complex *cis*-Pt[C(OEt)(NHR)](CNR)Cl₂ (R = *c*-C₆H₁₁) with 2 equiv of [CpMo(CO)₃]⁻ yielded the linear cluster *trans*-Pt[C(OEt)(NHR)]CNR[Mo(CO)₃Cp]₂ (11b) (eq 9b).^{23b}

The reaction of the [(diethylamino)carbyne]tungsten complex (HBpz₃)W(CO)₂(CNET₂) with the hydride-containing cationic complex [HPt(PEt₃)₂(acetone)]⁺ yielded the heteronuclear complex WPt(CO)₂(PEt₃)₂(HBpz₃)[μ-η²-C(H)NEt₂] (12) containing a bridging η²-C,N (diethylamino)carbene formed by transfer of the hydride ligand on platinum to the carbyne carbon atom on tungsten (eq 10).²⁴

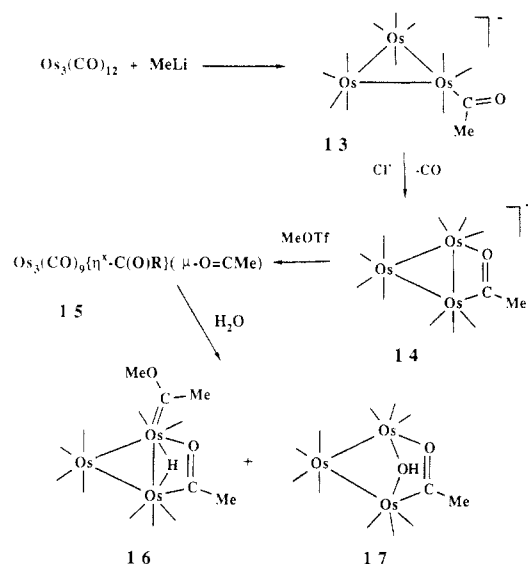


The addition of nucleophiles to bridging alkylidene ligands has yielded bridging carbene ligands with moderate success.²⁵ For example, the bridging methoxymethylcarbene ligand in the complex PtW(CO)₅(dppm)[μ-C(Me)OMe] was prepared by addition of methoxide to the ethylidene ligand in the cationic complex [WPt(CO)₅(dppm)(μ-CMe)]⁺ (eq 11).^{25a}

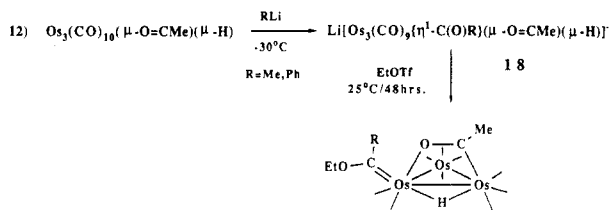
Trinuclear Metal Complexes

Kaesz et al. were the first to synthesize a carbene ligand in a preformed trinuclear metal complex.²⁶ They used the R⁻/R⁺ procedure, although the reaction did not proceed in the usual manner. The reaction of Os₃(CO)₁₂ with MeLi at -30 °C yielded the complex Li[Os₃(CO)₁₁[C(O)Me]] (13), which contained an acetyl ligand in an equatorial coordination site (see Scheme I). However, in the presence of Cl⁻, 13 was decarbonylated and transformed to [Os₃(CO)₁₀(μ-O=CMe)]⁻ (14), in which the acetyl ligand adopted a bridging position across an edge of the cluster. When treated with methyl triflate (MeOTf), 14 underwent alkylation to yield the complex Os₃(CO)₉(η²-C(O)Me)(μ-O=CMe) (15), which was formulated as a bisacetyl ligand complex and not the desired carbene complex. One of the acetyl ligands was believed to be an *edge*-bridging ligand as in 14. The character of the second acetyl ligand was not established, but it was proposed to be a η² species. A carbene complex was obtained from an unusual reaction of 15 with H₂O. In fact, two products were obtained from this reaction involving 2 mol of 15, 1 mol of H₂O, and the transfer of a methyl group from one molecule of 15 to the other to form the carbene ligand. Labeling studies showed that the transferred methyl group was not derived from the bridging acetyl ligand. The first product, Os₃(CO)₉[C(Me)OMe](μ-O=CMe)(μ-H) (16), contains a bridging acetyl ligand and a terminally coordinated methylmethoxycarbene ligand. The second product, Os₃(CO)₁₀(μ-O=CMe)(μ-OH) (17), contains a bridging acetyl ligand and a bridging hydroxyl ligand. A more direct and efficient route to carbene complexes related to 16 involves the application of the carbanion (MeLi or PhLi)/carbocation (EtOTf) treatment to Os₃(CO)₁₀(μ-O=CMe)

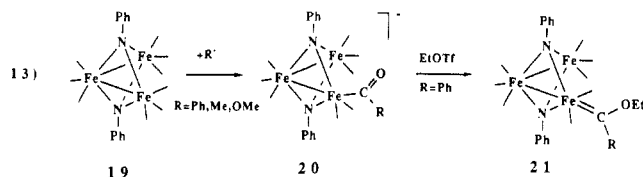
SCHEME I



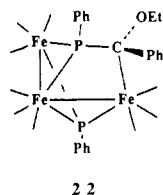
$\text{CMe}(\mu\text{-H})$ at -30°C (eq 12). Yields of up to 80% of $\text{Os}_3(\text{CO})_9[\text{C}(\text{R})\text{OEt}](\mu\text{-O}=\text{CMe})(\mu\text{-H})$ were obtained.^{6a} This reaction was proposed to proceed through the anionic bisacetyl intermediate $[\text{Os}_3(\text{CO})_9(\eta^1\text{-C}(\text{O})\text{R})](\mu\text{-O}=\text{CMe})(\mu\text{-H})^-$ (18).



Anionic nucleophiles were found to add to a carbonyl ligand in the bis(phenylnitrene)triiron cluster $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NPh})_2$ (19) to yield the anionic complexes $\text{Fe}_3(\text{CO})_8(\mu_3\text{-NPh})_2[\text{C}(\text{O})\text{R}]^-$ (20, $\text{R} = \text{Ph}, \text{Me}, \text{OMe}$) (eq 13).²⁷ The phenyl derivative was alkylated with EtOTf



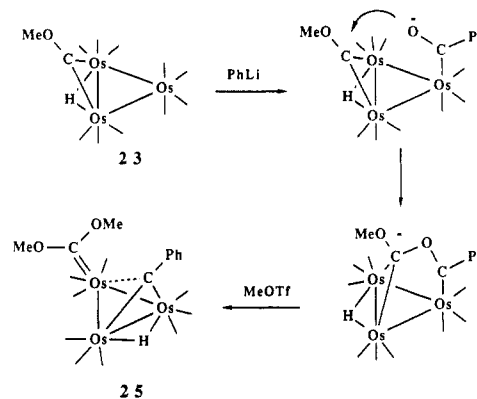
to yield the complex $\text{Fe}_3(\text{CO})_8[\text{C}(\text{Ph})\text{OEt}](\mu_3\text{-NPh})_2$ (21) containing a terminally coordinated phenylethoxy-carbene ligand. A similar series of reactions (LiPh/EtOTf) applied to $\text{Fe}_3(\text{CO})_9(\mu_3\text{-PPh})_2$ yielded the complex $\text{Fe}_3(\text{CO})_9(\mu_3\text{-PPh})_2[\mu_3\text{-P}(\text{Ph})\text{C}(\text{Ph})\text{OEt}]$ (22) in



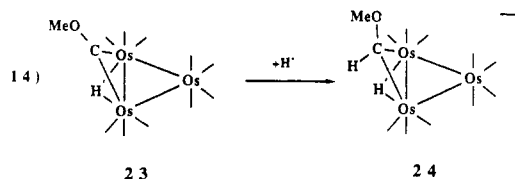
which the carbene ligand inserted into one of the iron-phosphorus bonds of one of the bridging phenylphosphinidene ligands.²⁷ This insertion is believed to be promoted by the addition of a CO ligand to the intermediate $\text{Fe}_3(\text{CO})_8(\mu_3\text{-PPh})_2[\text{C}(\text{Ph})\text{OEt}]$. This intermediate could not be isolated in a pure form.

The reaction of the methoxycarbene cluster complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-COMe})(\mu\text{-H})$ (23) with LiEt_3H yielded

SCHEME II

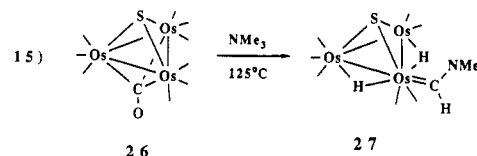


the anionic methoxycarbene cluster complex 24 by the addition of H^- to the carbyne carbon atom (eq 14).²⁸

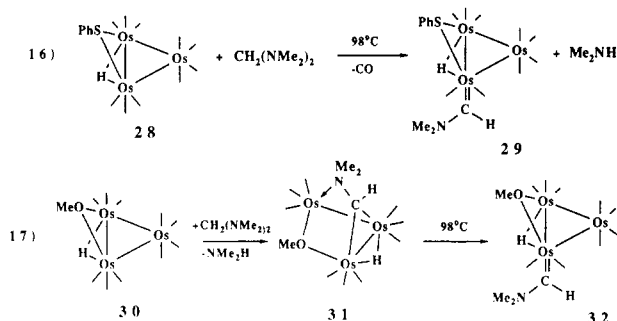


Compound 24 is believed to contain a bridging carbene ligand on the basis of a spectroscopic characterization. By contrast, the reaction of 23 with LiPh resulted in addition of Ph^- to one of the CO ligands and yielded the complex $\text{Os}_3(\text{CO})_9[\text{C}(\text{OMe})_2](\mu_3\text{-CPh})(\mu\text{-H})$ (25) after a rearrangement involving transfer of the oxygen atom of the benzoyl ligand to the carbyne carbon atom and a methylation with MeOTf ²⁹ (Scheme II). Complex 25 contains a terminally coordinated dimethoxycarbene ligand and an unusual semi-triply-bridging benzylidene ligand.

A number of cluster complexes containing amino-carbene ligands have been obtained by the activation of tertiary amines.³⁰⁻³³ The reaction of $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$ (26) with NMe_3 at 125°C yielded the complex $\text{Os}_3(\text{CO})_8[(\text{C}(\text{H})\text{NMe}_2)](\mu_3\text{-S})(\mu\text{-H})$ (27), which contains a terminally coordinated secondary (dimethylamino)carbene ligand, $\text{C}(\text{H})\text{NMe}_2$ (eq 15).³¹ The reaction involves the loss of two CO ligands from 26 and the activation of two CH bonds on one methyl group of the NMe_3 molecule. The hydrogen atoms were transferred to the cluster to become bridging hydride ligands.

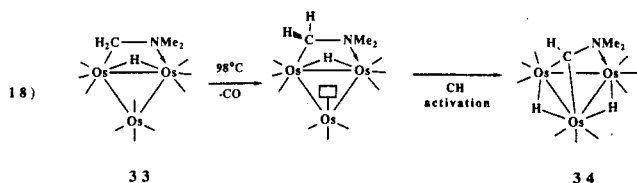


Bis(dialkylamino)methanes were found to be precursors to secondary (dialkylamino)carbene ligands. For example, the reaction of $\text{Os}_3(\text{CO})_{10}(\mu\text{-SPh})(\mu\text{-H})$ (28) with $\text{CH}_2(\text{NMe}_2)_2$ yielded the cluster complex $\text{Os}_3(\text{CO})_9[(\text{C}(\text{H})\text{NMe}_2)](\mu\text{-SPh})(\mu\text{-H})$ (29), which contains a terminally coordinated (dimethylamino)carbene ligand (eq 16).³⁶ The mechanism of the formation of the carbene ligand has not yet been established; however, a multicenter metal-based process that involves an opening of the cluster has been implicated from an investigation of the reaction of $\text{CH}_2(\text{NMe}_2)_2$ with the methoxy-bridged homologue $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})(\mu\text{-H})$



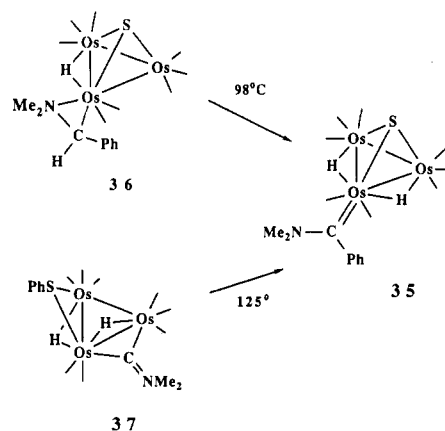
(30). The reaction of 30 with $\text{CH}_2(\text{NMe}_2)_2$ yielded two carbene-containing cluster products, $\text{Os}_3(\text{CO})_9[\mu_3\text{-C}(\text{H})\text{NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (31) and its isomer $\text{Os}_3(\text{CO})_9[\text{C}(\text{H})\text{NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (32).³² Compound 32 is structurally analogous to 29 and has a terminally coordinated carbene ligand, but 31 is very different. Compound 31 was shown by a structural characterization to consist of an "open" triangular cluster of three metal atoms with a triply-bridging η^2 secondary (dimethylamino)carbene ligand. The carbene carbon atom bridges one of the Os–Os bonds of the cluster while the nitrogen atom is coordinated to the third osmium atom. When heated, the open cluster in 31 closes and the carbene ligand is shifted to a terminal position (eq 17). This reaction establishes that 31 is a kinetic product or intermediate in the formation of 32 from 30 and $\text{CH}_2(\text{NMe}_2)_2$. It demonstrates that cluster opening and nitrogen coordination occur prior to formation of the terminal carbene ligand, but important questions concerning the cleavage of the NMe_2 group from the diaminomethane and the cleavage of one of the CH bonds of the CH_2 group were not answered by this study.

Additional information regarding these questions was provided from an investigation of the reaction of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ with $\text{CH}_2(\text{NMe}_2)_2$. One product isolated from the reaction of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ with $\text{CH}_2(\text{NMe}_2)_2$ at 25 °C is $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2\text{NMe}_2)(\mu\text{-H})$ (33).³³ Compound 33 was shown to contain an *N,N*-dimethyliminium ligand bridging an edge of the cluster. The formation of 33 involved the loss of one hydride ligand from the $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ (transferred presumably as H^+) and loss of one NMe_2 group from the $\text{CH}_2(\text{NMe}_2)_2$. Me_2NH was presumably formed, but this was not observed. This result suggests that the hydrogen ion could play an important role in the fragmentation of the diaminomethane. To date, all of the reactions that have led to the formation of aminocarbene ligands from diaminomethanes have involved clusters containing hydride ligands. It is known that the reaction of bis(dialkylamino)methanes with hydrogen ion in aqueous solutions leads to their transformation to iminium ions and secondary amines.³⁴ At 98 °C, compound 33 is spontaneously decarbonylated and transformed to the complex $\text{Os}_3(\text{CO})_9[\mu_3\text{-C}(\text{H})\text{NMe}_2](\mu\text{-H})_2$ (34), which contains a triply-bridging, η^2 -(dimethylamino)carbene ligand (eq 18). This transformation is believed to occur



by an intramolecular multicenter CH activation process

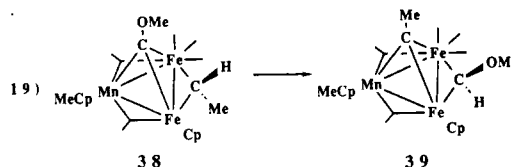
SCHEME III



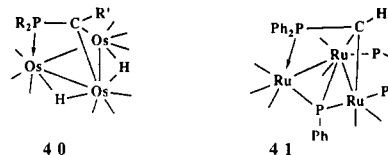
that involves a vacant site formed by the loss of a carbonyl ligand from the third metal atom.

The complex $\text{Os}_3(\text{CO})_9[\text{C}(\text{Ph})\text{NMe}_2](\mu_3\text{-S})(\mu\text{-H})_2$ (35), which contains a terminally coordinated phenyl(dimethylamino)carbene ligand, has been obtained by two routes: (1) by C–H activation of the π -bonded phenyldimethyliminium ligand in the complex $\text{Os}_3(\text{CO})_8[\eta^2\text{-Ph}(\text{H})\text{C}=\text{NMe}_2](\mu_3\text{-S})(\mu\text{-H})$ (36)³⁵ and (2) by an intramolecular shift of a phenyl group from the sulfur atom to the carbon atom of the (dimethylamino)carbyne ligand in the complex $\text{Os}_3(\text{CO})_9(\mu\text{-CNMe}_2)(\mu_3\text{-S})(\mu\text{-H})_2$ (37)³⁶ (see Scheme III).

The methoxycarbene ligand in $\text{MnFe}_2(\text{CO})_5(\text{Cp})(\text{MeCp})[\mu\text{-C}(\text{H})\text{Me}](\mu_3\text{-COMe})$ (38) was converted to a secondary methoxycarbene ligand in the complex $\text{MnFe}_2(\text{CO})_5(\text{Cp})(\text{MeCp})[\mu\text{-C}(\text{H})\text{OMe}](\mu_3\text{-CMe})$ (39) by an intramolecular shift of the hydrogen atom from the bridging alkylidene ligand (eq 19).³⁷



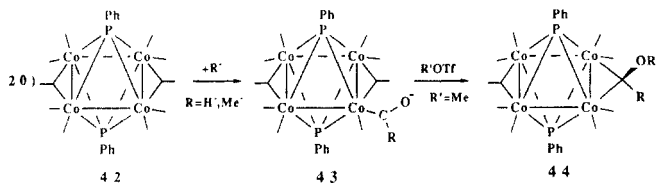
The activation of CH bonds on the α -carbon atoms of trialkylphosphine ligands in the complexes $\text{Os}_3(\text{CO})_{11}(\text{PR}_3)$ and $\text{Os}_3(\text{CO})_{10}(\text{PR}_3)_2$ ($\text{R} = \text{Me}, \text{Et}$) has led to the formation of the complexes $\text{Os}_3(\text{CO})_9(\mu_3\text{-R}_2\text{PCR}')(\mu\text{-H})_2$ (40) and $\text{Os}_3(\text{CO})_8\text{PR}_3(\mu_3\text{-R}_2\text{PCR}')(\mu\text{-H})_2$



($\text{R}' = \text{H}, \text{Me}$) containing triply-bridging $\text{R}_2\text{PCR}'$ ligands. These could be viewed as dialkylphosphino-substituted carbene ligands.³⁸ Pyrolysis of the complex $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ ($\text{dppm} = \text{CH}_2(\text{PPh}_2)_2$) yielded the complex $\text{Ru}_3(\text{CO})_7(\text{dppm})(\mu_3\text{-PPh})[\mu_3\text{-C}(\text{H})\text{PPh}_2]$ (41) containing the $\mu_3\text{-C}(\text{H})\text{PPh}_2$ ligand coordinated to an open triruthenium cluster.³⁹

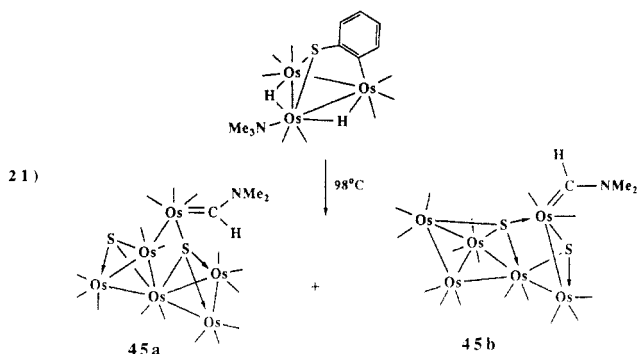
Higher Nuclearity Clusters Containing Carbene Ligands

The reaction of the tetracobalt cluster $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$ (42) with Et_3BH^- or MeLi at low temperature yielded the anions 43 containing a formyl or an acetyl ligand (eq 20).⁴⁰ Methylation of 43 with MeOTf



yielded the complexes **44** containing a bridging methoxycarbene ligand. A related product **44** ($R = H$, $R' = (CH_2)_4OMe$) was obtained when the $MeOTf$ was added in the presence of THF. The formation of the $(CH_2)_4OMe$ group is believed to have occurred by an initial methylation of THF and a subsequent ring-opening addition of the $(CH_2)_4OMe^+$ ion to **43**. Addition of trifluoroacetic anhydride to **43** yielded the (trifluoroacetyl)carbene **44** ($R = H$, $R' = C(O)CF_3$).

The hexaosmium carbonyl cluster complexes $Os_6(CO)_{16}[C(H)NMe_2](\mu_4-S)(\mu_3-S)(\mu-H)_2$ (**45a, b**) (two isomers containing a terminally coordinated secondary (dimethylamino)carbene ligand) were formed by thermolysis of the trimethylamine-containing complex $Os_3(CO)_8(NMe_3)(\mu_3-SC_6H_4)(\mu-H)_2$ (eq 21).⁴¹ The transformation involves elimination of the aryl ring (presumably as C_6H_6),⁴² the condensation of two clusters, elimination of one NMe_3 ligand, and the transformation of the second NMe_3 ligand into a carbene ligand by the activation of two CH bonds of one of the methyl groups. Compounds **45a, b** have also been made by the combination of **27** with **26**.⁴³



Structure and Bonding

The structures of terminally coordinated carbene ligands **D** in metal cluster complexes are not significantly different from those in mononuclear metal complexes. These will not be discussed further in this review. The reader is directed to earlier reviews for discussions of the structure and bonding of these ligands.^{1,2}

To a first approximation, the bonding of the bridging carbene ligand **E** should be similar to that of the bridging alkylidene ligand.^{5,44} The bonding of the latter to two metal atoms is believed to consist of a combination of a σ -donation of the lone pair of electrons on the carbon atom to an empty, symmetrically suitable orbital on the dimetal unit **I** and a π -acceptance from

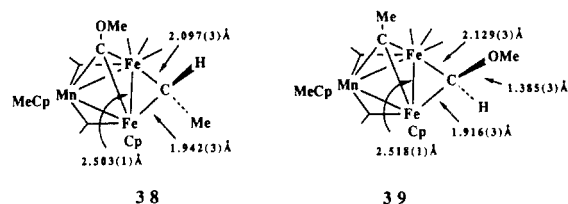
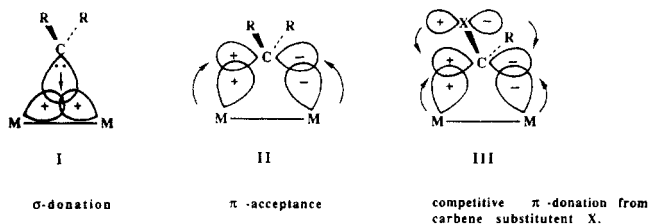
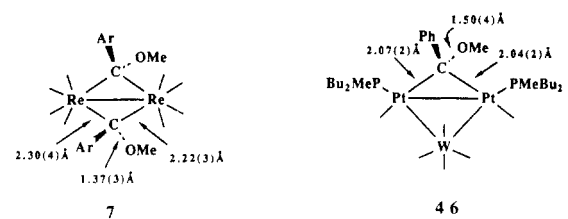


Figure 1.

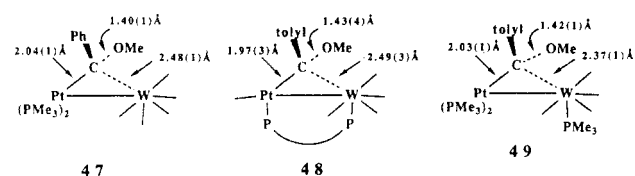
a filled, symmetrically suitable orbital on the dimetal unit to the empty p-orbital on the carbon atom, **II**. The principal effect of π -donation **III** from a heteroatom **X** on the carbene ligand should be a destabilization of the M_2C π -bonding orbital although this has not been studied quantitatively through calculations. This should weaken the metal-carbon bonding, and if sufficiently large, may ultimately cause the bridging carbene ligand to convert to a terminally coordinated structure **D** that should allow for a greater π -bonding between the heteroatom **X** and the carbene carbon atom.

There are very few examples of compounds that will permit a good comparison of the effect of the heteroatom on the bonding of bridging carbene ligands. Compounds **38** and **39** permit possibly the best comparison.³⁷ A comparison of pertinent bond distances for these two molecules is shown in Figure 1. In both molecules, the carbene ligand is bonded asymmetrically, but the asymmetry appears to be significantly greater for the carbene ligand in **39** than for the ethylidene ligand in **38**. Greater asymmetry could be interpreted as a shift toward a terminal coordination mode similar to that which occurs for bridging carbonyl ligands.⁴⁵ This would be consistent with the notion that π -donation from the heteroatom on the carbene ligand may induce the bridging ligand to shift to a terminal coordination. The current absence of cluster complexes containing aminocarbene ligands of the type **E** would also support this idea. Amino groups form stronger π -interactions to carbon than alkoxy groups do.^{2a}

Carbene ligands that bridge symmetric homodinuclear metal-metal bonds tend to be symmetrically bonded (e.g., **7**¹⁴ and $Pt_2W(CO)_6(PBu^t_2Me)_2[C(OMe)Ph]$ (**46**)²¹).



In contrast, carbene ligands that bridge heterodinuclear metal-metal bonds can be very asymmetrically bonded. This is demonstrated by the arylmethoxycarbene-bridged Pt-W complexes $PtW(CO)_5(PMe_3)_2[\mu-C(Ph)OMe]$ (**47**),¹⁹ $PtW(CO)_5(dppm)[\mu-C(tolyl)OMe]$ (**48**),⁴⁶ and $PtW(CO)_4(PMe_3)_3[\mu-C(Ph)OMe]$ (**49**).⁴⁷



Note that the asymmetry in 49, which contains three phosphorus donors, is significantly less than that in 47 and 48, which contain only two phosphorus donor ligands. The replacement of a CO ligand with a phosphorus donor should lead to an increase of electron density on the metal atoms and thus the potential for a greater π -back-bonding to the carbene ligand. An increase of metal-to-carbon π -back-bonding should cause the carbene to shift to a more symmetrical bridging position.

The C–O distances in terminally coordinated alkoxy-substituted carbene ligands lie generally in the range 1.29–1.35 Å.^{2a} The C–O distances in compounds 7, 39, 44, and 46–49 lie in the range 1.37–1.50 Å. Although the standard deviations on some of these values are fairly large, it appears to be true that the C–O distances for bridging carbene ligands are longer than those for the corresponding terminally coordinated forms. This is consistent with the notion of greater C–O π -bonding interactions for terminally coordinated carbene ligands than for bridging ligands.

Compounds 9, 11, and 12 contain carbene ligands in which the heteroatom X is also coordinated to one of the metal atoms, type F. The coordination of a pair of electrons from X to a metal atom should reduce the C–X π -bonding and result in a lengthening of the C–X bond. This appears to be the case in each of these examples (e.g., the C–O bond length in 9 is 1.431 (8) Å^{17b}). A molecular orbital description for the coordination of the carbene ligand in 11 has been reported.²³

There are two structurally characterized examples of triply-bridging (dialkylamino)carbene ligands. These were found in compounds 31 and 34, and they exhibit the coordination mode G. The C–N distances, 1.54 (2) and 1.40 (5) Å, respectively, are also significantly longer than those found in terminally coordinated carbene ligands^{2a} although the standard deviation on the value from 34 is very large.

NMR Spectroscopy

¹³C NMR spectroscopy has been fairly useful in aiding in the characterization of carbene ligands. The ¹³C resonance of the carbene carbon atom for terminally coordinated alkoxy-carbene ligands is shifted to very low field values and generally lies in the range 300–360 ppm.⁴⁸ This resonance is shifted upfield significantly when the carbene is a bridging ligand. The ¹³C resonances of bridging alkoxy-carbene ligands lie in the range 160–260 ppm. A notable exception is the anionic triosmium cluster 24 for which the carbene resonance was observed at 112.3 ppm.²⁸ The ¹³C resonances of unsubstituted bridged carbene centers generally lie at higher field values than those of alkoxy-carbene ligands.⁵ The ¹³C carbene resonance shifts for a number of compounds with bridging carbene ligands are listed in Table I.

Reactivity

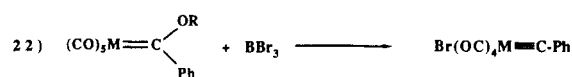
Terminally coordinated carbene ligands in cluster complexes react similarly to terminal carbene ligands in mononuclear metal complexes.² The focus of this section will be on the reactivity of carbenes that is related to processes that involve two or more metal centers.

TABLE I. Carbene ¹³C NMR Shifts for Cluster Compounds with Bridging Carbene Ligands^a

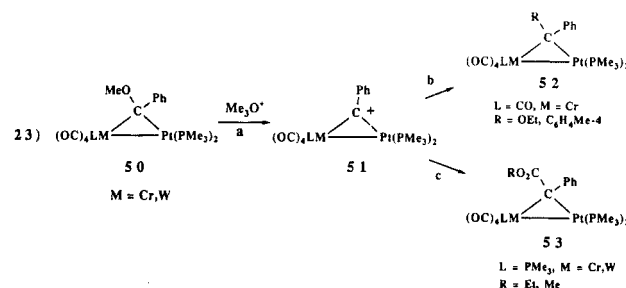
compd	¹³ C shift, ppm	ref
PtW(CO) ₅ (COD)[μ -C(Ph)OMe]	197	19
PtW(CO) ₅ (COD)[μ -C(Me)OMe]	201.6	49
PtW(CO) ₅ (dppm)[μ -C(Me)OMe]	211.9	49
PtW(CO) ₅ (μ -dppm)[μ -C(Me)OMe]	228.7	49
PtW(CO) ₄ (dppm)(μ -dppm)[μ -C(Me)OMe]	230.8	49
PtW(CO) ₅ (PMe ₃) ₂ [μ -C(Ph)OMe]	203	19
PtW(CO) ₅ (PMe ₃) ₂ [μ -C(Me)OMe]	214	19
PtCr(CO) ₅ (PMe ₃) ₂ [μ -C(C ₆ H ₄ CF ₃)OMe]	203	47
PtW(CO) ₅ (PMe ₃) ₂ [μ -C(tolyl)OMe]	204	47
PtW(CO) ₅ (PMe ₃) ₂ [μ -C(tolyl)OMe]	207	47
PtMn(CO) ₂ (COD)Cp[μ -C(Ph)OMe]	198	20
PdMn(CO) ₂ (COD)Cp[μ -C(Ph)OMe]	211	20
PtMn(CO) ₂ (PMe ₃) ₂ Cp[μ -C(tolyl)OMe]	193.6	50
PtRe(CO) ₂ (PMe ₃) ₂ Cp[μ -C(tolyl)OMe]	166.0	50
PtRe(CO) ₂ (PMe ₃) ₂ Cp[μ -C(tolyl)OMe]	165.4	50
Pt ₂ W(CO) ₆ (PBu ₂ Me) ₂ [μ -C(Ph)OMe]	237	21a
PtW(CO) ₅ (μ -dppm)[μ -C(tolyl)OMe]	226.3	46
PtW(CO) ₄ (dppm)(μ -dppm)[μ -C(tolyl)OMe]	224.7	46
PtW(CO) ₅ (COD)[μ -C(tolyl)OMe]	199.7	21b
PtW(CO) ₅ (PMe ₃) ₂ [μ -C(tolyl)OMe]	202.4	21b
PtW(CO) ₅ (dppe)[μ -C(tolyl)OMe]	218.3	21b
PtW(CO) ₅ (dpma)[μ -C(tolyl)OMe]	210.5	21b
Pt ₂ (CO) ₃ [μ -C(tolyl)OMe]	255.5	21b
Pt ₂ (CO) ₃ [μ -C(tolyl)OMe]	254.8	21b
Co ₂ (CO) ₈ (μ -PPH) ₂ [μ -C(H)OMe]	235	40
Fe ₂ Mn(CO) ₅ Cp(MeCp)(μ -CMe)[μ -C(H)OMe]	228.4	37
[Os ₃ (CO) ₁₀ (μ -H)[μ -C(H)OMe] ⁻	112.3	28
PtW(CO) ₅ (μ -dppm)[μ -C(tolyl)S(tolyl)]	209.5	46
CoFe(CO) ₄ Cp[μ - η ² -C(SMe) ₂]	176.44	23

^a dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane, COD = 1,5-cyclooctadiene.

It is known that Lewis acids promote the elimination of alkoxy groups from alkoxy-substituted carbene ligands to yield alkylidyne ligands (e.g., eq 22²).



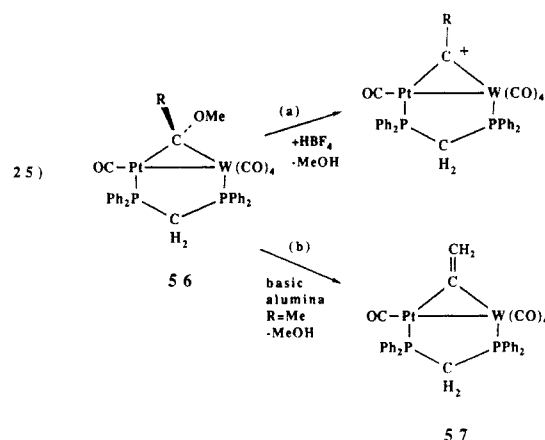
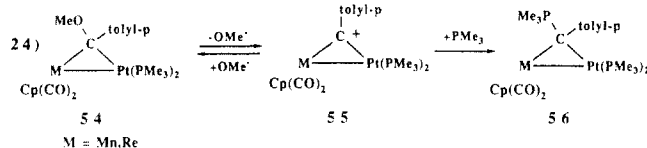
In a similar fashion, bridging phenylmethoxycarbene ligands have been transformed to bridging alkylidyne ligands. For example, the reaction of the complexes MPt(CO)₄L(PMe₃)₂[μ -C(Ph)OMe] (50, M = Cr, W; L = CO, PMe₃) with [Me₃O]⁺BF₄⁻ yields the benzylidyne complexes [MPt(CO)₄(PMe₃)₂(μ -CPh)]⁺ (51) (eq 23a).⁵⁰



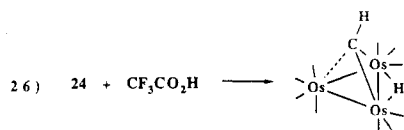
The addition of nucleophiles R = OEt and C₆H₄Me-4 to the complexes 51 leads to the formation of the carbene-containing complexes MPt(CO)₄L(PMe₃)₂[μ -C(Ph)R] (52) when L = CO, but when L = PMe₃ the carbalkoxycarbene complexes 53 (R = CO₂Me, CO₂Et) are formed. The latter reaction occurs, presumably, by addition of the nucleophile to a CO group, but the location of this CO group when the addition occurred was not established. Two possible mechanisms are (1) the nucleophilic addition occurs at a metal-coordinated CO ligand and the carbalkoxy group then migrates to the alkylidyne carbon atom or (2) a CO ligand migrates

from a metal atom to the alkylidyne carbon atom to form a bridging ketenyl ligand, $\text{RC}=\text{C}=\text{O}$, and the nucleophile is then added. Casey has demonstrated the existence of bridging ketenyl ligands and their ability to add nucleophiles.⁵¹ This argues in favor of the latter mechanism. Stoichiometrically, reaction 23b adds 1 equiv of CO. Curiously, the yields of the carbalkoxy-carbene products were not increased when the reactions were performed under a CO atmosphere.⁵⁰

The platinum-manganese/rhenium carbene complexes $\text{MPt}(\text{CO})_2(\text{PR}_3)_2\text{Cp}[\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{OMe}]$ (**54**, $\text{M} = \text{Mn, Re}$) will eliminate methoxide in a reversible reaction when treated with $[\text{Me}_3\text{O}]^+ \text{BF}_4^-$ (eq 24).⁵⁰ The alkylidyne-containing products **55** will add PMe_3 at the alkylidyne carbon atom to form the phosphonium ylide complexes **56** (eq 24).⁵² In some cases, H^+ is a suffi-

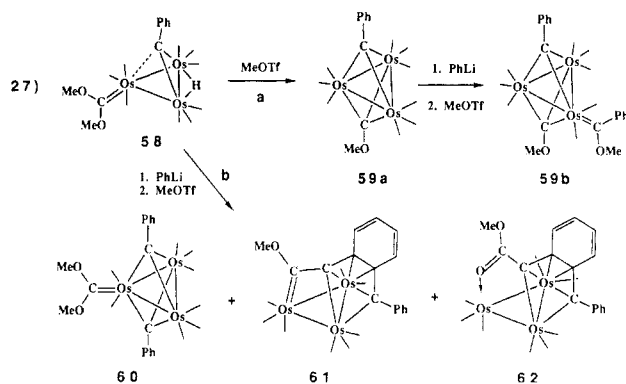


ciently strong Lewis acid to promote the elimination of OMe^- from bridging alkoxy-carbene ligands to yield complexes containing bridging alkylidyne ligands (eq 25a^{46,49} and 26).²⁸ In fact, OCH_3 elimination from **56** is so facile that simple treatment with basic alumina leads to formation of a μ -vinylidene complex **57** by elimination of MeOH (eq 25b).⁴⁹

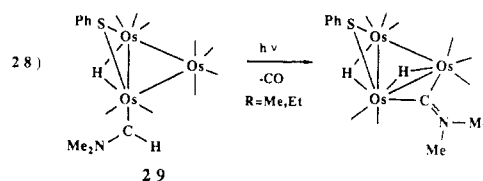


Treatment of the dimethoxycarbene complex $\text{Os}_3(\text{CO})_9[\text{C}(\text{OMe})_2](\mu\text{-CPh})(\text{H})$ (**58**) with MeOTf yields the (carbyne)(alkylidyne)triosmium cluster complex $\text{Os}_3(\text{CO})_9(\mu\text{-CPh})(\mu\text{-C}(\text{OMe}))$ (**59**) containing a triply-bridging methoxycarbyne ligand (eq 27a).^{29,53} Treatment of **58** with PhLi followed by MeOTf yields the bis(benzylidyne)(dimethoxycarbene) cluster complex $\text{Os}_3(\text{CO})_8[\text{C}(\text{OMe})_2](\mu\text{-CPh})_2$ (**60**) plus two other products, $\text{Os}_3(\text{CO})_8(\mu\text{-C}(\text{OMe}))\text{C}(1,2\text{-C}_6\text{H}_4\text{CPh})$ (**61**) and $\text{Os}_3(\text{CO})_8(\mu\text{-C}(\text{OMe}))\text{C}(1,2\text{-C}_6\text{H}_4\text{CPh})$ (**62**) (eq 27b).^{54a} The latter products were formed by undefined transformations that involved the carbene ligand. Treatment of **59a** with PhLi and MeOTf yielded the carbene-containing cluster complex **59b**.^{54b}

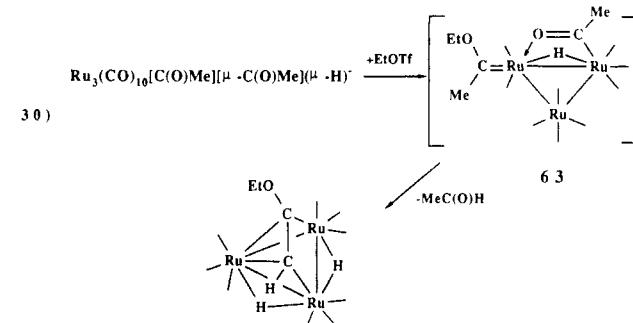
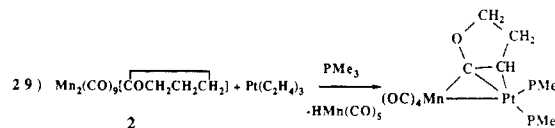
Secondary (dialkylamino)carbene ligands, HCNR_2 , are capable of undergoing an α -CH activation reaction



that appears to involve two metal atoms to convert the carbene in **29** to a bridging (dialkylamino)carbyne ligand and a bridging hydride ligand in $\text{Os}_3(\text{CO})_9(\mu\text{-CNMe}_2)(\mu\text{-SPh})(\mu\text{-H})_2$ (eq 28).²⁶



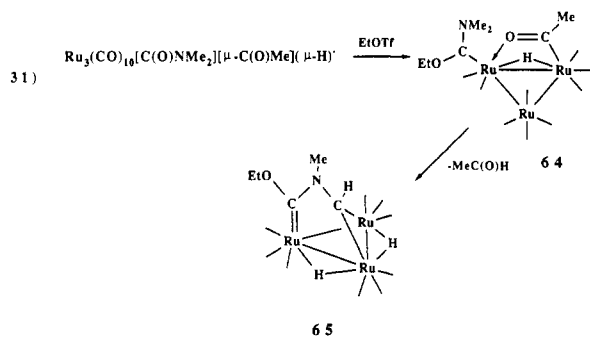
Carbenes containing an aliphatic CH grouping bonded directly to the carbene carbon atom appear to be able to undergo facile β -CH activation reactions that appear to involve two or more metal atoms (eq 29²⁰ and 30). In reaction 30 the carbene-containing intermediate



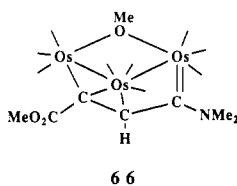
63 was not isolated but was strongly indicated by the nature of the reaction sequence.⁵⁵ Facile transformations of this type may explain the paucity of cluster complexes containing carbenes with alkyl substituents on the carbene carbon atom.

CH activation on alkyl substituents bonded to the heteroatom can occur, and multicenter processes appear to be involved. In reaction 31, the intermediate **64** containing an ethoxy(dimethylamino)carbene ligand was transformed to the product $\text{Ru}_3(\text{CO})_9[\mu\text{-C}(\text{OEt})(\text{NMe}_2)\text{CH}](\mu\text{-H})_2$ (**65**) by the activation of two CH bonds on one of the *N*-methyl groups.^{6b,55}

There have been very few reports of reactions of heteroatom-substituted carbene cluster complexes with unsaturated hydrocarbons. The reaction of **31** with $\text{HC}\equiv\text{CCO}_2\text{Me}$ yielded the product $\text{Os}_3(\text{CO})_9[\mu\text{-C}(\text{NMe}_2)\text{C}(\text{H})(\text{CO}_2\text{Me})](\mu\text{-OMe})$ (**66**) and was proposed to involve a coupling of the alkyne with some form of bridging carbene ligand since **32** (the isomer of **31** that

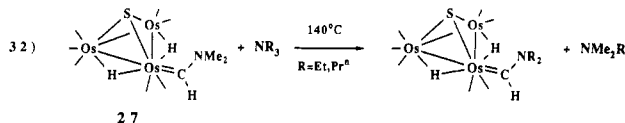


contains the terminal carbene ligand) failed to react with $\text{HC}_2\text{CO}_2\text{Me}$.^{32a} At some unknown stage, the hydrogen atom on the carbene carbon atom and the hydride ligand in 31 were eliminated from the cluster in the formation of 66.



Solutions of 21 slowly decompose to yield $\text{PhN}=\text{C}(\text{Ph})\text{OEt}$, formed by a coupling of the phenylethoxy-carbene ligand to the triply-bridging phenylnitrene ligand.²⁷

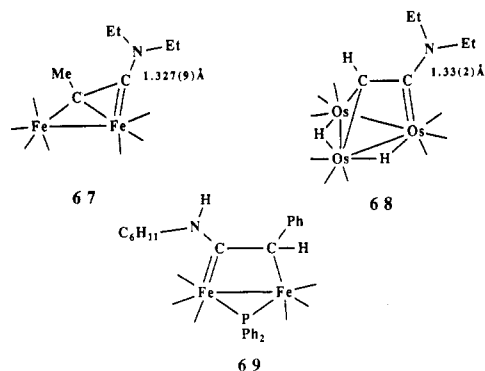
The carbene ligand in 27 was found to react with secondary amines by exchange of the amino group.³¹ Mononuclear metal carbene complexes engage in similar reactions.^{1,2} Of greater interest was the observation that 27 reacts with tertiary amines, NR_3 , to exchange the amino group of the carbene ligand and yield the new tertiary amines, NMe_2R ($\text{R} = \text{Et}, \text{Pr}$), by transfer of one alkyl group (eq 32).³¹ Although it was originally pro-



posed that the exchange occurred by a direct attack of the tertiary amine upon the carbene carbon atom, more recent studies have shown that CH activation processes occur in the alkyl group that is shifted. This implies that some form of activation at the metal centers must be involved.⁵⁶

Metallocarbene Ligands

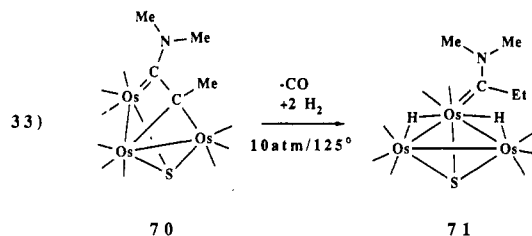
Recent structural characterizations of cluster complexes containing ynamine ligands have revealed structural features at the amine-substituted carbon atom that are indicative of carbene-like character. Two such complexes are $\text{Fe}_2(\text{CO})_7(\mu\text{-MeC}_2\text{NMe}_2)$ (67)⁵⁷ and $\text{Os}_3(\text{CO})_9[\mu_3\text{-HC}_2\text{NMe}_2](\mu\text{-H})_2$ (68).⁵⁸ In both complexes, the C-N distance is short, 1.327 (9) and 1.33 (2) Å, respectively, and indicative of C-N multiple bonding. Also, unlike normal alkyne ligands in cluster complexes, the amine-substituted carbon atom is coordinated to only one metal atom. Compound 68 was also found to possess reactivity similar to that of a carbene complex. For example, the reaction of 68 with Pr_2NH yielded the complex $\text{Os}_3(\text{CO})_9[\mu_3\text{-HC}_2\text{NPr}_2](\mu\text{-H})_2$ by an exchange of the amino group. The ynamine ligand in 68 was



described as a dimetalated methyl(diethylamino)carbene or dimetalliomethyl(diethylamino)carbene ligand. A similar description could be applied to 67, but these investigators chose to view the methyl-substituted carbon atom as a bridging alkylidene and the ynamine, overall, as mutually bonded carbene and alkylidene groups.

Similarly, the amine-substituted carbon atom of the compound $\text{Fe}_2(\text{CO})_6[\mu\text{-C}\{\text{N}(\text{H})\text{C}_6\text{H}_{11}\}\text{C}(\text{H})\text{Ph}](\mu\text{-PPh}_2)$ (69) also exhibits structural features that resemble those of a carbene ligand.⁵⁹ This ligand could be reformulated as a monometalliobenzyl(cyclohexylamino)carbene ligand.

The complex $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ has recently been found to react with $\text{MeC}\equiv\text{CNMe}_2$ to yield the open cluster complex $\text{Os}_3(\text{CO})_9(\mu_3\text{-MeC}_2\text{NMe}_2)(\mu_3\text{-S})$ (70) with a



triply-bridging ynamine ligand that was described as an α,α -dimetallioethyl(dimethylamino)carbene ligand.⁶⁰ Interestingly, this complex undergoes a novel reaction with hydrogen in which two hydrogen atoms are added to the C-methyl carbon atom of the ynamine ligand to form a terminally coordinated ethyl(dimethylamino)carbene ligand in the complex $\text{Os}_3(\text{CO})_8[\text{C}(\text{Et})\text{NMe}_2](\mu_3\text{-S})(\mu\text{-H})_2$ (71) (eq 33).⁶⁰ It is believed that the hydrogenation of ynamine ligands will prove to be a new and general route to the synthesis of aminocarbene ligands in metal complexes.

References

- (1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 119-136.
- (2) (a) Dotz, K. H.; Fischer, H.; Hoffmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Chemistry*; Verlag Chemie: Weinheim, West Germany, 1983. (b) Fischer, E. O. *Adv. Organomet. Chem.* 1976, 14, 1.
- (3) Fischer, E. O.; Maasböl, A. *Angew. Chem.* 1964, 76, 645.
- (4) (a) Dötzt, K. H. *Pure Appl. Chem.* 1983, 55, 1689. (b) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challenor, C. A.; Hyldahl, C.; Wulff, W. J. *Organomet. Chem.* 1987, 334, 9. (c) Dötzt, K. H. *Ibid.* 1987, 334, 57.
- (5) (a) Hahn, J. E. *Prog. Inorg. Chem.* 1984, 31, 205. (b) Herrmann, W. A. *Adv. Organomet. Chem.* 1982, 20, 159. (c) Knox, S. A. R. *Pure Appl. Chem.* 1984, 56, 81.
- (6) (a) Kaesz, H. D.; Jensen, C. M. *Polyhedron* 1988, 7, 1035. (b) Jensen, C. M.; Kaesz, H. D. *J. Organomet. Chem.* 1987, 330, 133.

- (7) (a) Sternberg, H.; Shukys, J. G.; Donne, C. D.; Markby, R.; Friedel, R. A.; Wender, I. *J. Am. Chem. Soc.* **1959**, *81*, 2339. (b) Mills, O. S.; Robinson, G. *Inorg. Chim. Acta* **1967**, *1*, 61. (c) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.
- (8) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1922.
- (9) Casey, C. P. *J. Chem. Soc. D* **1970**, 1220.
- (10) (a) Fischer, E. O.; Offhaus, E.; Müller, E.; Nöthe, D. *Chem. Ber.* **1972**, *105*, 3027. (b) Fischer, E. O.; Offhaus, E. *Chem. Ber.* **1969**, *102*, 2449.
- (11) Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Marten, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053.
- (12) Berry, M.; Martin-Gil, J.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1625.
- (13) (a) Fischer, E. O.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *225*, 265. (b) Schubert, U.; Ackerman, K.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *231*, 323.
- (14) Fischer, E. O.; Lindner, T. L.; Fischer, H.; Huttner, G.; Friedrich, P.; Kreissl, F. R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 648.
- (15) Singh, M. M.; Angelici, R. *Inorg. Chim. Acta* **1985**, *100*, 57.
- (16) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172.
- (17) (a) Fischer, E. O.; Winkler, E.; Huttner, G.; Regler, D. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 238. (b) Huttner, G.; Regler, D. *Chem. Ber.* **1972**, *105*, 2726.
- (18) Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1418.
- (19) Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1593.
- (20) Berry, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1601.
- (21) (a) Ashworth, T. B.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1615. (b) Jeffrey, J. C.; Moore, I.; Murray, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1741.
- (22) Fischer, E. O.; Beck, H. J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 72.
- (23) (a) Matachek, J. R.; Angelici, R. J.; Schugart, K. A.; Haller, K. J.; Fenske, R. F. *Organometallics* **1984**, *3*, 1038. (b) Braunstein, P.; Keller, E.; Vahrenkamp, H. *J. Organomet. Chem.* **1979**, *165*, 233.
- (24) Davis, J. H.; Lukehart, C. M.; Sacksteder, L. *Organometallics* **1987**, *6*, 50.
- (25) (a) Awang, M. R.; Jeffrey, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2091. (b) Mead, K. A.; Moore, I.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2083.
- (26) (a) Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926. (b) Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1982**, *104*, 4679.
- (27) Williams, G. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 3936.
- (28) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 140.
- (29) Shapley, J. R.; Yeh, W. Y.; Churchill, M. R.; Li, Y. *Organometallics* **1985**, *4*, 1898.
- (30) Adams, R. D.; Babin, J. E.; Kim, H. S. *Polyhedron* **1988**, *7*, 967.
- (31) Adams, R. D.; Wang, S.; Kim, H. S. *J. Am. Chem. Soc.* **1985**, *107*, 6107.
- (32) (a) Adams, R. D.; Babin, J. E. *Organometallics* **1988**, *7*, 2300. (b) Adams, R. D.; Babin, J. E. *Ibid.* **1987**, *6*, 1364.
- (33) Adams, R. D.; Babin, J. E. *Organometallics* **1988**, *7*, 963.
- (34) Moad, G.; Benkovic, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 5495.
- (35) (a) Adams, R. D.; Babin, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 6872. (b) Adams, R. D.; Babin, J. E. *New J. Chem.* **1988**, *12*, 641.
- (36) Adams, R. D.; Babin, J. E.; Kim, H. S. *J. Am. Chem. Soc.* **1987**, *109*, 1414.
- (37) Fong, R. H.; Hersh, W. H. *Organometallics* **1988**, *7*, 794.
- (38) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2727.
- (39) Lavigne, G.; Bonnet, J. J. *Inorg. Chem.* **1981**, *20*, 2713.
- (40) Richmond, M. G.; Kochi, J. *Organometallics* **1987**, *6*, 777.
- (41) Adams, R. D.; Babin, J. E.; Kim, H. S. *Inorg. Chem.* **1986**, *25*, 4319.
- (42) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 1301.
- (43) Kim, H. S. Ph.D. Thesis, Yale University, 1986.
- (44) (a) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554. (b) Calabro, D. C.; Lichtenberger, D. L.; Herrmann, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 6852.
- (45) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.
- (46) Mead, K. A.; Moore, I.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2083.
- (47) Howard, J. A. K.; Mead, K. A.; Moss, J. R.; Navarro, R.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 743.
- (48) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299.
- (49) Awang, M. R.; Jeffrey, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2091.
- (50) Howard, J. A. K.; Jeffrey, J. C.; Laguna, M.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 751.
- (51) Casey, C. P.; Crocker, M.; Niccolai, G. P.; Fagan, P. J.; Konings, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6070.
- (52) Jeffrey, J. C.; Navarro, R.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 2471.
- (53) Yeh, W. Y.; Shapley, J. R.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1986**, *5*, 1757.
- (54) (a) Yeh, W. Y.; Shapley, J. R.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1987**, *6*, 1. (b) Yeh, W. Y.; Wilson, S. R.; Shapley, J. R. *J. Organomet. Chem.* **1989**, *371*, 257.
- (55) Jensen, C. M.; Kaesz, H. D. *J. Organomet. Chem.* **1987**, *330*, 133.
- (56) Adams, R. D.; Babin, J. E.; Kim, H. S.; Wolfe, T. A., unpublished results.
- (57) Cabrera, E.; Daran, J. C.; Jeannin, Y.; Kristiansen, O. *J. Organomet. Chem.* **1986**, *310*, 367.
- (58) (a) Adams, R. D.; Tanner, J. T. *Organometallics* **1988**, *7*, 2241. (b) Deeming, A. J.; Kabir, S. E.; Nuel, D.; Powell, N. I. *Organometallics* **1989**, *8*, 717.
- (59) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.
- (60) Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics*, in press.