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Transformations of Carbon Monoxide and Related Ligands on Metal Ensembles

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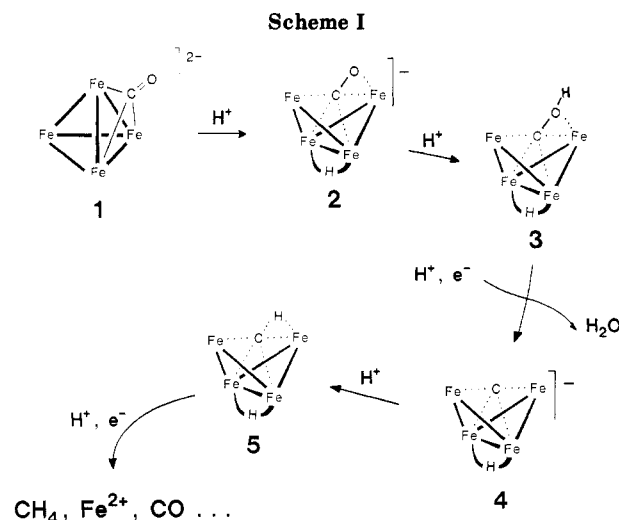
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The reactions of ligands coordinated to metal atoms have enormous importance in disciplines ranging from bioinorganic chemistry^{1,2} to organometallic chemistry³ and applications ranging from industrial homogeneous catalysis^{4,5} to inorganic and organic syntheses.^{6,7} Although the majority of these reactions occur on single metal centers, there is increasing interest in the reactivity of ligands attached to metal clusters. The presence of several metals in proximity to a ligand may result in patterns of ligand stabilization and reactivity that have not been observed for monometal complexes. In this Account, we describe the role of the metal cluster in converting carbon monoxide to C and CCO ligands and the influence of the cluster on the reactions of these ligands. This chemistry provides many examples of facile C-O, C-C, and C-H bond formation and cleavage and insight into the ways metal ensembles influence these reactions.

Aside from its tendency to coordinate metal atoms in low oxidation states and to be attacked by electrophiles, carbon monoxide is a relatively inert molecule. However, the reactions of CO are promoted by heterogeneous or homogeneous metal catalysts; examples include the oxidation of CO in automobile exhausts,^{8,9} the incorporation of CO into olefins in the hydroformylation reaction,¹⁰ the reduction of CO to methanol,^{10,11} and the conversion of CO to hydrocarbons in the Fischer-Tropsch process.¹² In each of these catalytic processes, an early step in the reaction sequence appears to be the coordination of carbon monoxide to a metal atom or metal particle. The first three processes appear to occur without CO cleavage, whereas in the Fischer-Tropsch process, CO cleavage apparently occurs to produce an intermediate surface carbide.^{13,14} In a pioneering study of the conversion of carbon monoxide to methane on copper-nickel alloys, Araki and Ponec found that an

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ensemble of several nickel atoms is required to effect the critical CO cleavage process.¹⁴ The details of this cleavage reaction on nickel are obscure because structural information on ligand-metal bonding is difficult to obtain on surfaces. By contrast, transformations in

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molecules can be elucidated by techniques such as X-ray crystallography and high-resolution NMR and infrared spectroscopy. Information of this type has produced a fascinating picture of the role of metal ensembles in the transformations of CO.

Role of Metal Ensembles in CO Cleavage

The observation of Chatt and co-workers, that certain N_2 complexes in the presence of mild acid yield NH_4^+ ,¹⁵ prompted an investigation into the possibility of a similar transformation with the isoelectronic CO ligand.¹⁶ No methane was observed with carbonyl analogues of Chatt compounds and other monometallic carbonyls, so we turned next to the possibility of proton-induced reduction of CO in $[Fe_4(CO)_{13}]^{2-}$ (1) (Scheme I). An attractive feature of this cluster was its known rearrangement in mild acid, which converts one CO from a metal-C-bonded geometry into an unusual η^2 -geometry, where the carbonyl is both C and O bonded (2).¹⁷ As judged from CO bond lengthening of ca. 0.1 Å and a decrease in CO stretching frequency of ca. 500 cm^{-1} , the C-O bond in the η^2 -CO is much weaker than in a terminally bound CO.¹⁸ In line with these inferences, the addition of strong acid to $[Fe_4(CO)_{13}]^{2-}$ leads to the cleavage of CO, as demonstrated by the evolution of about 0.5 mol of CH_4 per mol of cluster.¹⁶ In the presence of an added reducing agent, up to 1 mol of methane is produced.¹⁹

Many of the intermediates in the reaction of $[HFe_4(CO)_{13}]^-$ with acid (Scheme I) have been characterized. For example, single-crystal X-ray structural data for compounds 1, 2, 4, and 5 and a crystal structure of the methylated analogue of 3 have been obtained. Multinuclear NMR data on the reaction mixture confirm the presence of many of the intermediates shown in Scheme I.²⁰ In this proposed reaction sequence, Scheme I, the η^2 -CO ligand, 2, is first converted to COH, 3, and C-O bond scission occurs to generate a transient carbide cluster, 4, that rapidly forms a C-H-Fe three-center bond, 5. Subsequent steps leading to the evolution of CH_4 have not been elucidated, but information from Fehlner's laboratory on a boron-containing three-iron cluster suggests that stepwise formation of bridging C-H-Fe and terminal C-H bonds may lead to a coordinated CH_4 that is then rapidly released from the cluster.²¹ Recently, the tendency for an η^2 -CO to undergo cleavage was demonstrated for a gold-containing cluster $[Fe_4(CO)_{13}(AuPR_3)]^-$, which exists as two isomers similar to complexes 1 and 2 of Scheme I.²²

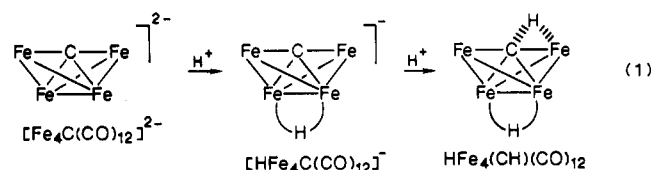
Multicenter CO interactions also are indicated by experiments in which a series of metal carbonyls were exposed to $H_2SO_3CF_3$. Insignificant yields of CH_4 were produced from carbonyl complexes containing one, two, or three metals, but larger clusters generate substantial amounts of methane.²³ Presumably, the larger metal

ensembles favor the formation of the reactive η^2 -CO ligand.

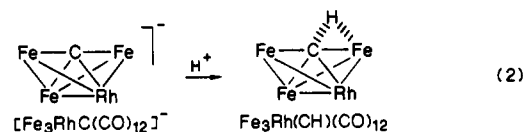
Influence of Metal Ensemble Size on Reactivity of the C Ligand

In the preceding section the existence of a transient four-iron cluster containing a reactive carbide ligand was postulated. A wide range of transition-metal carbide clusters with four or more metal atoms are known,^{24,25} and their chemistry provides striking illustrations of metal ensemble effects. In the six-metal and larger clusters the carbon atom is completely encapsulated and, short of disruption of the cluster, it lacks reactivity. The carbide atom is somewhat exposed in M_5 and M_4 clusters, and therefore reaction at the carbon atom in these clusters is a distinct possibility. Observations to date suggest that such reactivity is confined to carbide in M_4 clusters.²⁶ The first studies in this area were made in the laboratories of Bradley²⁷ and Muettterties.²⁸ For example, Bradley showed that methanol attacks the butterfly carbide compound $Fe_4C(CO)_{13}$ with formation of a carbon-carbon bond at the carbide ligand.

Reactions with proton sources provide vivid illustrations of the influence of metal ensemble size on reactivity of the carbide ligand. In the presence of 1 equiv of acid, the butterfly carbide $[Fe_4C(CO)_{12}]^{2-}$ undergoes protonation on the metal framework (eq 1). The sec-



ond equivalent of acid produces an interesting butterfly product having a C-H-Fe interaction (eq 1).²⁹ In certain heterometal butterfly clusters, the agostic C-H-Fe interaction is even more favored as indicated by the formation of an agostic C-H-Fe in the first protonation step (eq 2).³⁰ By contrast, the reaction of acids with the five-iron carbide $[Fe_5(CO)_{15}C]^{2-}$ leads to protonation on the iron framework exclusively.³¹



Another illustration of the reactivity of the exposed carbide ligand is the alkylation of the butterfly carbide

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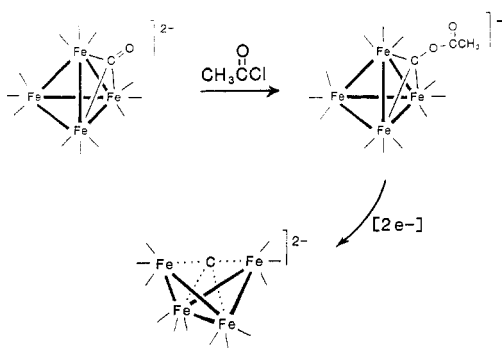
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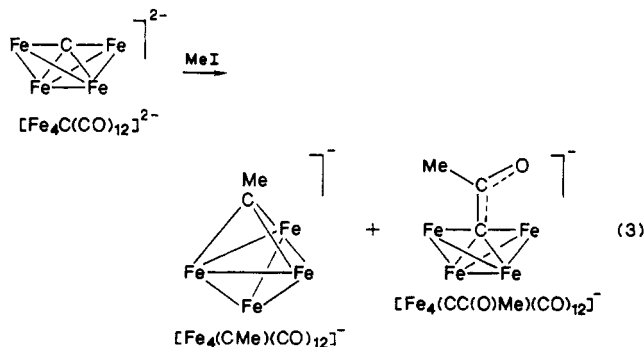
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Scheme II



$[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$, which yields a mixture of ethylidyne and acyl products (eq 3).³² Alkylation does not occur at the carbide atom in a related five-iron carbide cluster.³¹



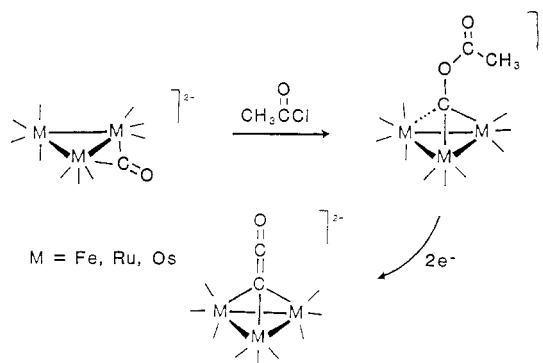
Insight into the bonding and reactivity of the four-metal cluster carbides is afforded by extended-Hückel³³ and Fenske-Hall^{34,35} molecular orbital calculations. In these calculations, the molecular orbitals with significant carbide atom character lie well below the HOMO, suggesting that the carbon atom is not the initial site of H^+ attack. To explain protonation at carbon, Harris and Bradley postulate attack of H^+ on the wingtip iron,³⁴ facilitated by the large HOMO character on this atom. The proton is then proposed to shift toward the carbon, forming a C-H-Fe bridge.

The two products that result from methylation of the iron carbide cluster, eq 3, can also be explained in terms of initial attack at a metal vertex, in this case by a CH_3^+ group. The tetrahedral ethylidyne complex could result from migration of the metal-bound methyl group to the carbide ligand directly, while the butterfly acetyl cluster could form via CO insertion into the iron-methyl bond followed by migration of the resulting metal-bound acetyl group to the carbide ligand.³²

Formation of the CCO Ligand on Three-Metal Ensembles

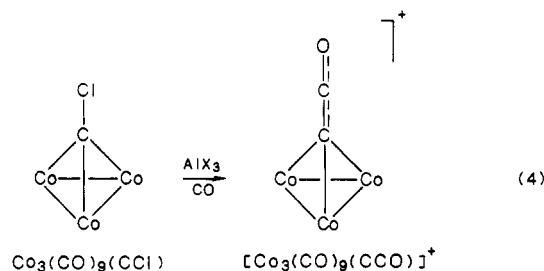
One outgrowth of the proton-induced CO reduction reaction displayed in Scheme I was the development of convenient synthetic methods for the cleavage of CO to produce metal cluster carbides (Scheme II).^{36,37} The

Scheme III



reductive cleavage reaction occurs at or below room temperature, and it is characterized by retention of the nuclearity of the starting cluster. This is a significant advance over previous methods of carbide syntheses in which changes in metal cluster size occur. For example, the reductive cleavage of CO in the four-iron cluster $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ provides the best route to the butterfly carbide $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$ discussed in the previous section. When the same CO cleavage reaction is performed with $[\text{M}_3(\text{CO})_{11}]^{2-}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) as the starting material, a three-metal carbide does not result; instead, the interesting compounds $[\text{M}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) are produced (Scheme III).^{37,38} If there is a fleeting carbide ligand in this reaction, it quickly picks up CO to produce the CCO ligand.

To date all three-metal clusters form CCO (referred to as the ketylidene ligand) rather than an exposed carbide. The first indication of the stability of CCO on a three-metal array was found in the reaction of $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCl})$ with an aluminum halide, which yields the cationic ketylidene cluster shown in eq 4.³⁹ The



Lewis acid presumably abstracts Cl^- from the chloromethylidyne ligand and CO takes its place. Other synthetic routes yield trinuclear ketylidene clusters of the manganese, iron, and cobalt families with electronic charges ranging from -2 to +1. These are produced by abstraction of X from a metal-bound CX_n group (where X = halide or H, $n = 1$ or 2) followed by C-CO coupling to produce the ketylidene ligand.³⁹⁻⁴¹ The formation of the CCO ligand in three-metal clusters and the lack of CCO in four-metal and larger complexes indicate that cluster nuclearity, rather than electron availability, determines whether the C or CCO ligand is preferred. Another example of the influence of cluster size on the preference of C versus CCO is the

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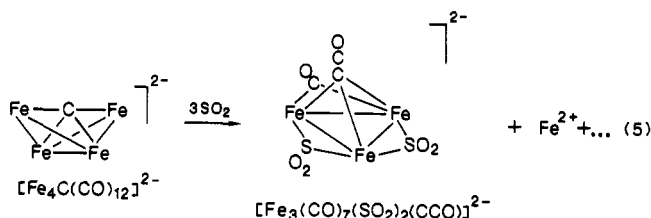
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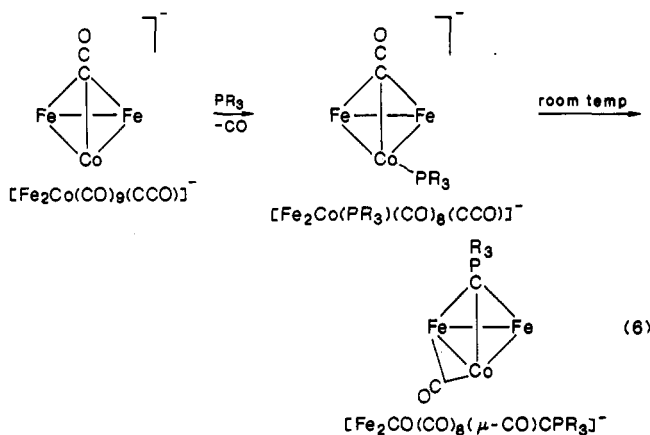
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use of SO₂ to effect oxidative cleavage of one iron vertex from the butterfly carbide [Fe₄C(CO)₁₂]²⁻ to produce a three-metal ketenylidene (eq 5).⁴² Conversely, CCO can be converted to a carbide ligand by the addition of metal vertices to the three-metal ketenylidene [Fe₃(CO)₉(μ₃-CCO)]²⁻. A variety of new four-, five-, and six-metal carbide clusters have been generated in this way.⁴³



Reactions of M₃CCO Clusters

CCO Substitution. When solutions of [Fe₃(CO)₉(μ₃-CCO)]²⁻ or [Fe₂Co(CO)₉(μ₃-CCO)]⁻ are mixed with ¹³CO, the nine metal-bound CO ligands and the CO bound to the capping carbon atom all undergo exchange. In the case of the ruthenium ketenylidene, CO exchange first occurs at the metal-bound CO ligands. Then, in a much slower process, exchange occurs at all CO sites, including the CCO.⁴⁴ There is a hint here that CO substitution on the metal centers may be followed by exchange of metal-bound CO with the carbonyl of CCO. Clear evidence for initial attack at the metal was obtained in the reactions of phosphines and phosphites with [Fe₂Co(CO)₉(μ₃-CCO)]⁻.⁴⁵ Multinuclear NMR spectroscopy at low temperatures demonstrates that phosphine substitution occurs initially at the cobalt atom (eq 6). Upon warming to room temperature and further standing, the phosphine ligand migrates to the capping carbon atom and the ketenylidene CO is displaced onto the metal framework (eq 6).⁴⁶



Kinetic measurements for the initial intermolecular substitution process reveal a second-order rate law:⁴⁶

$$\text{rate} = k[\text{PMe}_3][\text{CoFe}_2(\text{CO})_9(\mu_3\text{-CCO})^-] \quad (7)$$

This result along with the activation parameters for

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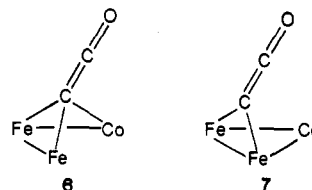
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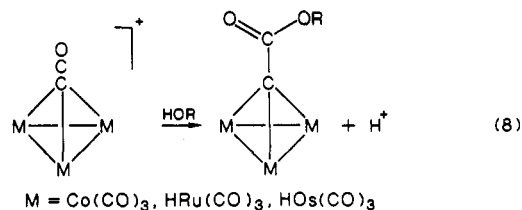
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various phosphines and phosphites, $\Delta H^\ddagger = +30$ to $+40$ kJ mol⁻¹ and $\Delta S^\ddagger = -142$ to -182 J K⁻¹ mol⁻¹, indicates that the reaction may occur by an associative process.⁴⁶ Associative ligand substitutions have been observed previously for phosphine replacement of CO in metal clusters and have been explained by invoking metal-metal bond breaking as a process prior to or simultaneous with phosphine attack.⁴⁷⁻⁵⁰ The analogue of this for our system would be 6. The ketenylidene cluster also presents the possibility of a shift of CCO from a μ₃- to a μ₂-configuration as shown in 7. Whatever the finer details, these results demonstrate that the metal ensemble mediates the reaction of the CCO ligand.



Attack of Nucleophiles on the CCO Ligand.

Although it is not necessary to invoke metal ensemble effects to explain the reactions of nucleophiles with the three-metal ketenylidenes, this chemistry will be described as a lead-in to the attack of electrophiles on coordinated CCO, where ensemble effects are important. A characteristic reaction of ketene, H₂CCO, is the attack of nucleophiles at the CO carbon. Similarly, nucleophiles are known to attack the carbon of metal-coordinated CO ligands,⁵¹⁻⁵³ and the analogous reaction at the CO carbon atom of a coordinated CCO ligand has been observed in a variety of neutral and cationic ketenylidene complexes (eq 8).^{39,54,55} Even



mononegative ketenylidene clusters undergo attack by strong electrophiles at the CO carbon of the CCO ligand.^{44,56} The electrophilicity of the carbonyl carbon in these ketenylidene compounds correlates with extended-Hückel calculations that indicate a positive charge on the carbonyl carbon of CCO and the existence of a LUMO with a large coefficient on that carbon atom.⁴⁴

Attack of Electrophiles on Metal Ketenylidene Clusters. An enormously rich chemistry is based on the reactions of anionic ketenylidene clusters, such as

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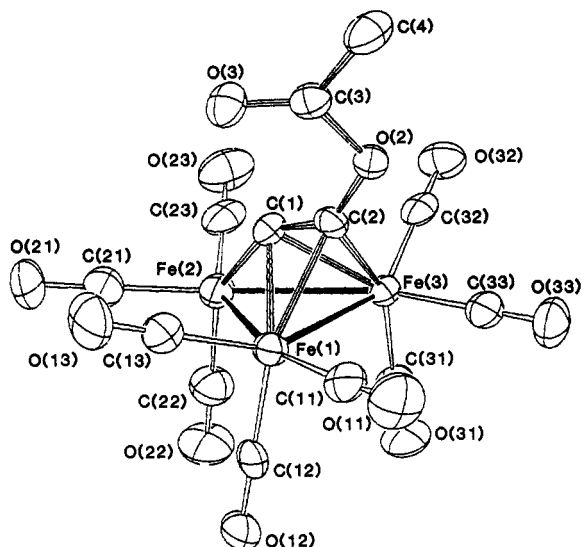
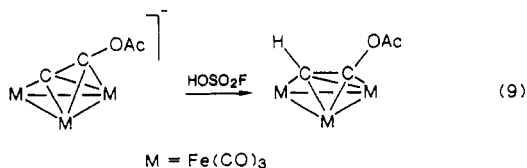


Figure 1. ORTEP diagram of the metal cluster in $[\text{PPN}][\text{Fe}_3(\text{CO})_9(\text{COC}(\text{O})\text{CH}_3)]$. Note the acetylide carbon atoms C(1) and C(2) capping the iron triangle. The atoms C(1), C(2), and O(2) originate from the CCO ligand of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$. Reprinted from ref 57; copyright 1987 American Chemical Society.

$[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$, with electrophiles. An example that has already been mentioned is the addition of transition-metal electrophiles to these ketenylidenes to produce larger clusters in which the CCO group has been transformed into a carbide ligand and a metal-coordinated CO molecule.⁴³ Another interesting and revealing set of reactions is based on the attack of the proton and simple carbocation reagents on the anionic ketenylidenes. These reactions appear to proceed by initial attack at one of these sites: the terminal carbon or oxygen of the CCO ligand, or the metal atoms of the cluster framework.

Bulky carbocation reagents, such as acetyl chloride or ethyl triflate, attack the ketenylidene oxygen atom of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$ to produce an acetylide compound. The result of acetyl chloride addition to $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$ has been characterized by an X-ray single-crystal structure determination (Figure 1).⁵⁷ The CC portion of the original ketenylidene has swung down over the metal triangle to convert the $\eta^1\text{-CCO}$ ketenylidene ligand to the $\eta^2\text{-CCOR}$ acetylide ligand. Reaction of these acetylide complexes with acid results in the formation of an acetylene complex (eq 9), which was



characterized at low temperatures by ^{13}C NMR on selectively ^{13}C -labeled samples.⁵⁷ Above ca. -70°C this compound undergoes C-C cleavage to produce a doubly capped product (eq 10). Fragmentation of cluster-bound acetylenic ligands is well documented,^{50,58-61} but

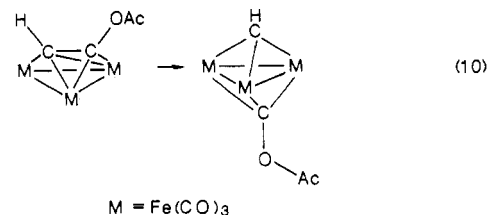
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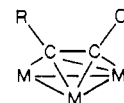
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much more forcing conditions are necessary for the reported reactions. For example, the pyrolysis of $\text{Cp}_3\text{Rh}_3(\text{CO})(\text{C}_2\text{PhTol})$ at 550°C yields $\text{Cp}_3\text{Rh}(\text{CO})(\mu_3\text{-CPh})(\mu_3\text{-CTol})$.⁵⁹ Since no crossover is observed, it was concluded that the reaction is intramolecular. The pathway that is favored for steric reasons involves reorientation of the M_3 capping alkyne and then migration of this ligand onto an M-M edge where cleavage of the alkyne occurs.⁵⁹ A similar pathway may be operative in reaction 10.



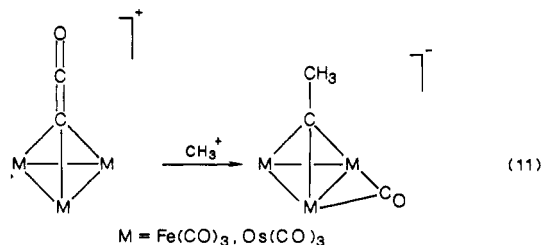
The formation of acetylenic ligands followed by cleavage also provides a basis for understanding the reactions of compact electrophiles, the proton and methyl cation, with iron and osmium ketenylidenes. However, as described below, the nature of the products is different from those observed with bulky electrophiles.

The action of proton acids with anionic ketenylidene clusters containing first transition series metals is to break up the CCO ligand into CO and methylidene (CH) ligands.^{62,63} The facile migration of the ketenyl CO onto the metal framework may occur by means of an acetylene cluster similar to those we have already discussed, 8. The accessibility of this migration path can be inferred from extended-Hückel calculations, which indicate that the potential energy surface for tilting the CCO is very shallow.



8. R = H, CH₃; M = Fe(CO)₃

The reaction of the anionic ketenylidenes $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$ and $[\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$ with the methyl source $\text{CH}_3\text{OSO}_2\text{CF}_3$ also results in the displacement of the ketene CO onto the metal cluster and forms the ethylidyne capped clusters $[\text{M}_3(\text{CO})_{10}(\mu_3\text{-CCH}_3)]^-$ (eq 11).^{63,64} As with the proton-induced CO

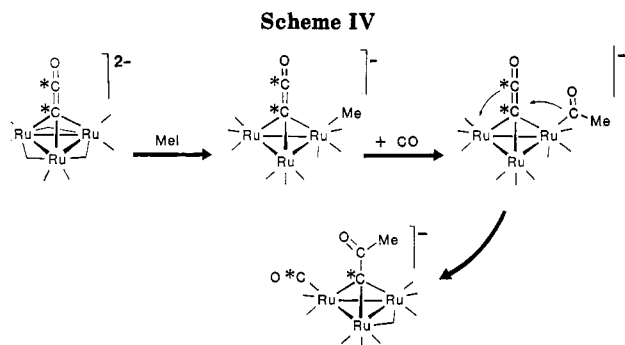


displacement, this reaction is remarkably facile. Again, the ease of C-CO cleavage may be connected with a low-energy path for the CO migration via an acetylenic cluster, 8, which then readily cleaves. Thus direct attack of electrophiles on the CCO ligand may be re-

(62) Crespi, A. M.; Shriver, D. F. *Organometallics* **1986**, *5*, 1750.

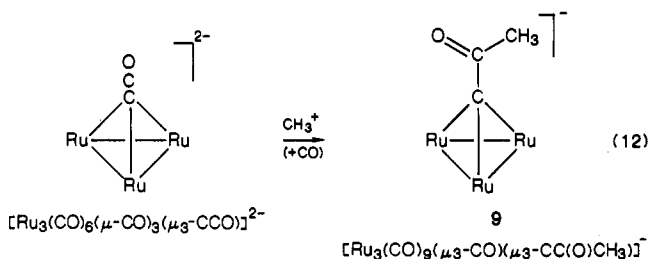
(63) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

(64) Went, M. J.; Sailor, M. J.; Bogdan, P. L.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6023.



sponsible for the formation of acetylide or acetylene ligands as well as ligands such as CH, COR, and CR that result from carbon-carbon bond scission in the acetylene complexes.

In light of the chemistry observed for the dinegative iron and osmium ketylenides, we were surprised to discover that the ruthenium ketylenide reacts with electrophiles such as CH_3I to yield a C-bound acyl instead of the expected ethynide (eq 12).⁴⁴ The product



obtained in eq 12 was puzzling because it is generated by reaction with an electrophilic reagent, but the structure is similar to that obtained when nucleophiles react with ketylenides, such as in eq 8. This result prompted the investigation of the reaction using $[\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-CCO})]^{2-}$ that had been ^{13}C labeled at various sites. As summarized in Scheme IV, the isotope tracer experiment indicates that the acyl CO in **9** is not derived from the CCO ligand but instead originates from a metal-bound CO. These results suggest a mechanism outlined in Scheme IV, with initial attack of CH_3^+ at a metal center followed by CO insertion into the Ru-CH_3 bond to produce a metal-bound acyl ligand. Such insertion reactions are well-known for mono- and bimetal carbonyls.^{3,65} Migration of the cluster-bound acyl ligand to the α -carbon of the CCO concomitant with CO migration from the CCO ligand to the metal framework completes the proposed reaction scheme.⁴⁴

Why do CH_3^+ reagents attack the iron and osmium clusters at CCO, whereas the ruthenium ketylenide is attacked at the metal? Extended-Hückel molecular orbital calculations and steric arguments, summarized in Figure 2, give a clue. As a result of its different CO ligand disposition, the Ru ketylenide has a less exposed α -carbon atom than either of the isostructural Fe or Os complexes, and a corresponding greater degree

(65) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Rose-Munch, F. J. *Am. Chem. Soc.* 1977, 99, 7381.

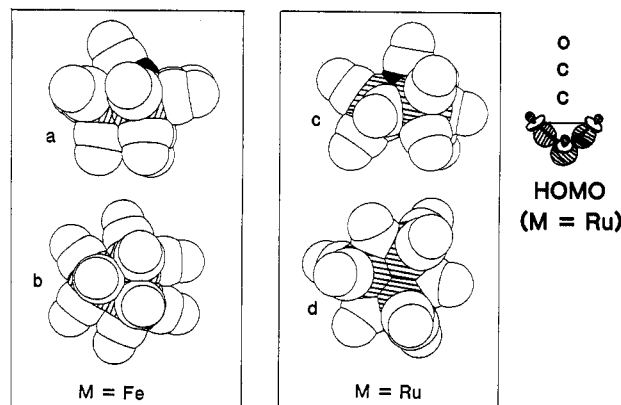


Figure 2. Space-filling models of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$ (a and b) and $[\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-CCO})]^{2-}$ (c and d). In a and c the view is toward the edge of the M_3 plane. In b and d the view is perpendicular to the plane of the metals on the side opposite from the CCO ligand. Note the exposed C_α carbon of $\text{C}_\alpha\text{C}_\beta\text{O}$ in a and the exposed metal atoms in d. A sketch of the HOMO for $[\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-CCO})]^{2-}$ is shown to the right of the box. Reprinted from ref 64; copyright 1987 American Chemical Society.

of exposure of the metal atoms. In addition, the exposed metal region of the Ru cluster is located at the highest electron population of its HOMO, as shown in the inset of Figure 2. Thus the attack of a methyl group on a Ru atom instead of at the α -carbon of CCO appears to be favored by both steric and electronic factors.⁶⁴

Conclusions

The metal ensemble strongly affects the course of some reactions of CO and CO-derived ligands:

(1) The proton-induced reduction of CO is observed for the $\eta^2\text{-CO}$ ligand in a four-metal array. Larger clusters may also effect this reaction but smaller ones, where $\eta^2\text{-CO}$ formation is less favorable, were observed to be ineffective.

(2) To date a reactive carbide has only been observed in four-metal organometallic clusters. In larger clusters the C ligand is unreactive, and in the smaller carbonyl three-metal clusters it is coordinated to CO.

(3) Even though the C-CO bond appears to be strong, the CCO ligand is readily cleaved and re-formed in three-metal clusters. Multisite interactions with the cluster are strongly implicated in these processes.

(4) As with simple single-metal organometallic molecules, the metal sites in clusters may be the site of initial attack in reactions that eventually alter the ligand. Metal clusters provide greater versatility in these metal-mediated reactions because open coordination sites can be achieved readily in clusters by either metal-metal or metal-ligand bond cleavage.

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