J. Am. Chem. Soc. 1982, 104, 5630–5633

that is observed at the carbide carbon in this cluster system. The positions of the HOMO and LUMO metal orbitals are somewhat artificial because of the omission of CO ligands. The significant result of these calculations is the great decrease in the gap between filled and empty carbide-containing orbitals on going from the 5- and 6-metal cluster carbides down to 3- and 4-metal carbides. In the low-coordinate carbides, the carbon p orbitals form molecular orbitals that are not as stabilized and lie near the frontier orbital interface.

Removal of one more FeH vertex from the cluster generates $(HFe)_3C$, in which a triangular array of iron atoms is capped on one face by a carbide. In this case, the large gap in energy occurs for 50 valence electrons, which superficially appears to be at variance with the 48-electron count expected for a 3-metal cluster. On closer inspection it is noted that there is a nonbonding carbide orbital of a_1 symmetry, which is 5 eu below the HOMO and is nearly pure $C(p_z)$. The $C(p_z)$ coefficient in this orbital is 0.80, and the largest bonding iron d orbital coefficient is 0.29; so the interaction is small with the framework. Therefore, this is best considered to be a carbon nonbonding lone-pair orbital, which should not be included in arriving at the cluster valence electron count. With this reassignment, the number of cluster valence electrons is the expected 48. This situation is reminiscent of the nonbonding "exodeltahedral" sulfur orbitals that Rudolph and co-workers[25] have described for sulfur-containing carboranes. Clearly, the existence of a carbon lone pair in the $(HFe)_3C$ moiety should confer reactivity at the carbon, but the substantial HOMO–LUMO gap indicates that the detection of a μ_3-carbide may not be out of the question. As with the other clusters considered above and recent calculations on $Co_3(CO)_9CX$ molecules,[24] the carbide carbon is strongly bonded to the metal triangle. The prospects seem particularly good for the isolation of Fe_3C species in which the carbide is "stabilized" by coordination to main-group or transition-metal acceptor species.

Conclusions

The simple MO results correlate well with the observed reactivity of the carbide atom in the iron carbonyl carbides. In the octahedral Fe_6C species and square-pyramidal Fe_5C, strong interaction between all of the carbon p orbitals and the metal framework results in a large separation of the highest filled and lowest empty orbitals having significant carbide contributions. This results is in harmony with the observation that neither of these cluster types displays reactivity at the carbide. For the more exposed carbide of the butterfly Fe_4C species, the gap between highest filled and lowest empty carbide orbitals is greatly reduced, in agreement with the observed carbide atom reactivity. The Fe_3C species has a somewhat smaller carbide orbital energy gap. In addition, it contains an orbital with relatively little cluster interaction, which is best described as a carbide lone pair. These features of the electronic structure parallel the lack of observation of a simple μ_3-carbide, although derivatives of the type M_3CR are well-known. Despite experimental and theoretical indications of great reactivity at the μ_3-carbide, the extended Hückel results do show a significant energy gap between empty and filled carbide-containing molecular orbitals, so the detection of a μ_3-carbide remains a distinct possibility. The MO calculations were based on idealized geometries close to those in observed known clusters. Large distortions of the M_nC array such as pulling the C atom significantly out of the basal plane in an M_4C or away from the M_4 butterfly array will significantly alter the metal–carbon interactions and should therefore affect the reactivity of the carbide.

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Proton-Induced Reduction of CO to CH_4 in Homonuclear and Heteronuclear Metal Carbonyls: A Survey of the Influence of the Metal and Nuclearity

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Abstract: The reactions of mononuclear, dinuclear, trinuclear, tetranuclear, and hexanuclear metal carbonyls with HSO_3CF_3 have been studied. Mononuclear through trinuclear metal carbonyls produce no appreciable amounts of CH_4. Trace amounts of methane, which were sometimes generated from these low-nuclearity systems, are attributed to small amounts of higher nuclearity cluster. Methane production in the case of the tetranuclear clusters increases in the order $Co_4(CO)_{12} < [FeCo_3(CO)_{12}]^- < [Ru_3Co(CO)_{13}]^- < [Fe_3Co(CO)_{13}]^- < [Ru_4(CO)_{13}]^{2-} < [Fe_4(CO)_{13}]^{2-}$. The indication from these studies is that polynuclear metal centers are required for the proton-induced reduction of CO to methane.

A distinctive feature of the conversion of CO to hydrocarbons on Fe, Ru, and Ni surfaces appears to be the scission of the CO bond and subsequent hydrogenation of the surface carbide.[2-4] By contrast, CO activation and reduction by mononuclear metal complexes are thought to be dominated by CO migratory insertion as the primary step.[5-7] It is probable that the differing patterns of reactivity arise because surface interactions with several metal atoms promote CO bond cleavage and formation of surface intermediates, whereas these multimetal interactions are not possible in homogeneous reactions at single-metal complex centers.[8]

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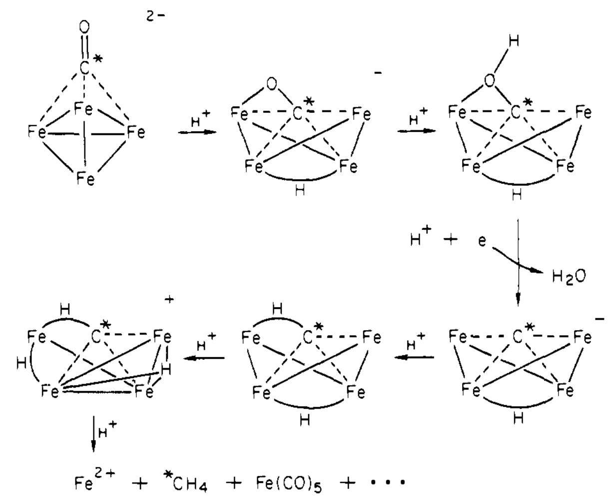
Scheme I



Fe = iron with three attached CO ligands (which are not shown)

Recently, a reaction involving homogeneous proton-induced reduction of coordinated CO to CH_4 was described (eq 1).[9]

$$[Fe_4(CO)_{13}]^{2-} \xrightarrow{H^+} CH_4 + H_3O^+ + CO + Fe^{2+} + \text{iron clusters} \quad (1)$$

Subsequently, it was shown that CO bond cleavage appears to occur as an early step in this reaction of a 4-iron cluster with acid (Scheme I).[10,11] Metal cluster carbide formation is followed by conversion of the active metal carbide to methane.[9-11] Structural data indicate that the interactions of the 4-iron cluster with an η^2-CO ligand promote CO cleavage.[10] The question arises as to the number of metal atoms required to promote CO cleavage and subsequent carbide reduction. Accordingly, we have investigated the yield of methane from a series of metal carbonyls ranging from mononuclear to hexanuclear containing several different metal atoms.

Experimental Section

General Procedures. Solvents and reagents were dried and distilled by using standard methods and stored under N_2. Infrared spectra were obtained on a Perkin-Elmer 399 spectrometer. Mass spectra were obtained on a Hewlett-Packard 5985 by using 70-eV electron impact.

Preparation of Metal Carbonyls. $Cr(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$, $Ru_3(CO)_{12}$, and $Rh_6(CO)_{16}$ (Strem Chemicals, Inc.) were used as supplied. $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ (Strem Chemicals, Inc.) were sublimed before use, and $Fe(CO)_5$ (Alfa Products) was vacuum distilled. $H_3Mn_3(CO)_{12}$,[12] $H_3Re_3(CO)_{12}$,[13] $Na_2Fe(CO)_4$·1,5-dioxane,[14] $[PPN]_2[Fe_2(CO)_8]$,[15] $[PPN][MnFe(CO)_{12}]$,[16] $Fe_3(CO)_{12}$,[17] $[PPn][Ru_3H(CO)_{11}]$,[18] $[PPn][Co(CO)_4]$,[19] $Co_4(CO)_{12}$,[20] $[PPN][FeCo_3(CO)_{12}]$,[21] $[PPN]Fe_3Co(CO)_{13}]$,[19] $[PPN]_2[Fe_4(CO)_{13}]$,[22] $[PPN][Ru_3Co(CO)_{13}]$,[19] $[PPN]_2[Ru_6(CO)_{18}]$,[23] and $[PPN]_2[Co_6(CO)_{15}]$[12] were prepared by using previously reported syntheses, PPN = bis(triphenylphosphine)nitrogen(1+) cation. $[PPN][V(CO)_6]$ was prepared by metathesis from $[Na(diglyme)_2][V(CO)_6]$ (Strem Chemicals, Inc.). Samples of $K_2Ru_4(CO)_{13}$,[24] $K_4Ru_4(CO)_{12}$,[24] and $H_2FeOs_3(CO)_{13}$[25] were prepared at The Ohio State University. All materials prepared in the course of this research were checked for purity by infrared spectrometry and elemental analysis.

Table I. Gaseous Products from the Reaction of Low-Nuclearity Carbonyls with HSO_3CF_3 Reported as Moles of Product per Mole of Carbonyl Compound[a]

metal carbonyl[b]	runs	H_{2av}	CO_{av}	CH_{4av}
$[PPN][V(CO)_6]$	3	0.59	3.88	0.00
$Cr(CO)_6$	1	0.00	0.00	0.00
$W(CO)_6$	1	0.00	0.00	0.00
$Mn_2(CO)_{10}$	2	0.88	0.00	0.00
$H_3Mn_3(CO)_{12}$	1	3.00	0.00	0.00
$Re_2(CO)_{10}$	1	1.00	0.00	0.00
$H_3Re_3(CO)_{12}$	2	2.78	0.00	0.00
$Na_2Fe(CO)_4$·1.5 dioxane	1	0.74	0.54	0.00
$Fe(CO)_5$	1	0.00	0.00	0.00
$[PPN]_2[Fe_2(CO)_8]$	2	1.22	0.94	trace
$Fe_3(CO)_{12}$	1	0.62	0.31	0.00
$[PPN][Ru_3H(CO)_{11}]$	2	1.77	0.00	trace
$Ru_3(CO)_{12}$	3	0.78	0.00	0.00
$[PPN][Co(CO)_4]$	2	1.21	3.98	0.00
$Co_2(CO)_8$	2	1.48	4.99	0.00
$[PPN][MnFe_2(CO)_{12}]$	2	0.56	0.46	trace
$Co_2(CO)_8$[c]	2	1.72	7.90	0.00

[a] Other systems that did not yield CH_4 inder similar conditions are $W(CO)_6$, $W(CO)_3(di(en))$, $W(CO)_4(diphos)$, $W(CO)_4(dppme)$, $Mo(CO)_2(PPh_3)(CH_3CN)_2$, $Mo(CO)_2(PPh_3)_2(bipy)$, $Mo(CO)_2(PPh_3)(di(en))$, and $Mo(CO)_2(PPh_2(en)$. [b] 3-day reaction time unless otherwise noted. [c] 6-day reaction.

Several of the clusters, $[Ru_4(CO)_{13}]^{2-}$, $[Ru_4(CO)_{12}]^{4-}$, and $[FeCo(CO)_{12}]^-$, were enriched with ^{13}CO by exposure of solutions of these anions (THF solution for the dinegative clusters and acetonitrile for $[Ru_4(CO)_{12}]^{4-}$) to 99% ^{13}CO gas. After removal of the solvent, a portion of the solid carbonyl salt was pyrolyzed on the vacuum line, and the degree of enrichment of the CO was determined by IR. Similarly, the abundance of $^{13}CH_4$ in the methane evolved from the proton-induced reduction was determined by IR.

Reaction of Metal Carbonyls with HSO_3CF_3. Compounds were transferred to a reaction flak in a nitrogen-filled drybox. After evacuation of the flask and freezing with liquid nitrogen, distilled HSO_3CF_3 was slowly added via a gas-tight syringe under a purge of N_2. The acid was added so as to freeze it on the sides of the reaction vessel before coming in contact with the compound. This was followed by evacuation on a vacuum line and thawing to room temperature. After 3 days of stirring at room temperature, the noncondensible gases were removed and analyzed. Low-temperature adsorption on silica gel was employed to separate CO and CH_4 from H_2. The yields of each gas were determined by using PVT measurements for H_2 and for the CO–CH_4 mixture. Methane in the latter mixture was determined by quantitative gas-phase infrared spectroscopy.

Results and Discussion

Table I lists the yields of gaseous products from the reaction of neat HSO_3CF_3 with the lower nuclearity metal carbonyl systems (mononuclear through trinuclear). In no case was a significant amount of methane produced per mole of compound.

A shown in Table II, significant quantities of methane were obtained among the gaseous products from the reaction of HSO_3CF_3 with some homonuclear and heteronuclear tetranuclear metal carbonyl clusters. This table also lists the metal-containing products that were recovered from the reaction mixture after removal of the gaseous products. These products were isolated by a series of solvent extractions and identified by IR, chemical tests, and/or mass spectroscopy. For all cases that were checked by Carbon-13 labeling, the percent ^{13}CO enrichment agreed well with the $^{13}CH_4$ content of the methane product: $[Ru_4(CO)_{13}]^{2-}$,

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Table II. Gaseous and Transition-Metal Products from the Reaction of High-Nuclearity Clusters with HSO_3CF_3

metal carbonyl[c] cluster	runs	av H_2 produced	av CO produced	av CH_4 produced	isolated reaction products
$Co_4(CO)_{12}$	3	0.24	1.42	0.08	Co^{2+}, $HCo(CO)_4$
$[PPN][FeCo_3(CO)_{12}]$	4	2.74	6.42	0.07	Co^{2+}, Fe^{2+}, $Fe(CO)_5$
$[PPN][Fe_3Co(CO)_{13}]$	3	0.55	1.39	0.32	Co^{2+}, Fe^{2+}, $Fe(CO)_5$
$[PPN]_2[Fe_4(CO)_{13}]$		0.31	2.58	0.52	see ref 9
$[PPN][Ru_3Co(CO)_{13}]$	3	1.34	0.00	0.21	Co^{2+}, $HRu_3(CO)_{12}^+$
$K_2Ru_4(CO)_{13}$	3	0.20	0.00	0.30	$HRu_3(CO)_{12}^+$, $H_4Ru_4(CO)_{12}$, and one unidentified cluster
$H_2FeOs_3(CO)_{13}$	1	0.07	0.20	0.01	
$K_4Ru_4(CO)_{12}$	3	0.33	0.00	0.16	$HRu_3(CO)_{12}^+$, $H_4Ru_4(CO)_{12}$, and one unidentified cluster
$[PPN]_2[Ru_6(CO)_{18}]$	3	0.22	0.00	0.16	$H_4Ru_4(CO)_{12}$ and one unidentified cluster
$[PPN]_2[Co_6(CO)_{15}]$	5	1.94	3.56	0.03	Co^{2+}, $HCo(CO)_4$
$Rh_6(CO)_{16}$	1	0.16	0.05[b]	0.05[b]	

[a] Quantative results are presented in moles of product per mole of metal carbonyl. [b] Pressure of CO and/or methane was too low to analyze the gas by our infrared technique.

50% ^{13}CO, 50% $^{13}CH_4$; $[Ru_4(CO)_{12}]^{4-}$, 50% ^{13}CO, 48% $^{13}CH_4$; $[FeCo_3(CO)_{12}]^-$, 40% ^{13}CO, 40% $^{13}CH_3$. Similar results have been reported previously for $[Fe_4(CO)_{13}]^{2-}$.[1]

As noted in Table II, the range of H_2 and CO yields for a given reaction deviates approximately ±10% from the average. For the CH_4 analysis, the deviation is slightly larger. Some of the variation may arise from the varying water content of the acid.

Low-Nuclearity Systems. As noted above, none of these systems produced significant quantities of CH_4. In the few cases in which trace amounts (less than 0.01 mol/mol of cluster) of CH_4 were detected, it is thought that higher nuclearity metal carbonyl clusters formed in small quantity at the onset of the reaction may be respondible for the CH_4. Convincing evidence for such a process is seen in the reaction of $[Ru_3H(CO)_{11}]^-$ with strong acid. Reaction of $[Ru_3H(CO)_{11}]^-$ with 1 equiv of HSO_3CF_3 has been shown to give as products, besides $Ru_3(CO)_{12}$, small quantities of $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$.[26] These are the same clusters that are most likely initially formed in the reactions of $[Ru_4(CO)_{12}]^{4-}$ and $[Ru_4(CO)_{13}]^{2-}$ with excess strong acid, as studied here. Therefore, the probable course of the reaction of $[Ru_3H(CO)_{11}]^-$ with excess HSO_3CF_3 is the initial production of small quantities of the tetranuclear hydrides, which, as discussed in the next section, do produce significant yields of methane.

High-Nculearity Clusters. In contrast to the reactions of lower nuclearity complexes (Table I), the tetranuclear and hexanuclear clusters did produce significant amounts of CH_4 (Table II).

As illustrated in the introduction, reaction of $[Fe_4(CO)_{13}]^{2-}$ with HSO_3CF_3 appears to proceed through many steps, which ultimately convert cluster-bound CO to CH_4.[10,11] The surprising stability of the series of 4-iron butterfly clusters in strong acid media may be responsible for the relatively high efficiency that can be obtained for the production of methane in the iron system. By contrast, cobalt carbonyl clusters interconvert very readily in a variety of polar solvents and at slightly elevated temperatures.[27] We are thus inclined to attribute the low yields of CH_4 obtained in the cobalt systems to the rapid cleavage of the cobalt cluster in the acid medium. This interpretation is supported by an IR study of a solution of $[PPN]_2[Co_6(CO)_{15}]$ in HSO_3CF_3 at room temperature. After 15 min of reaction time, approximately one-third of the total yield of gas (given off in 3 days) is produced, and an IR of the reaction mixture shows almost complete breakdown of the cluster to $HCo(CO)_4$. The same general results was obtained for $Co_4(CO)_{12}$. The yield of methane increases in the order $Co_4(CO)_{12} \sim [FeCo_3(CO)_{12}]^- < Fe_3Co(CO)_{13}]^- < [Fe_4(CO)_{13}]^{2-}$ may thus be rationalized by proposing that increasing the cobalt content in the tetrametal cluster series increases the tendency for cluster cleavage in strong acid media and decreases methane production. The same explanation may hold for the mixed cobalt–ruthenium clusters in which the methane yield increases with decreasing cobalt: $Co_4(CO)_{12} < [CoRu_3(CO)_{13}]^- < [Ru_4(CO)_{13}]^{2-}$. (Ruthenium clusters appear to be even more robust in strong acid media than iron clusters.)

In the case of ruthenium clusters, somewhat lower yields of CH_4 are obtained than those observed with the 4-iron clusters. This may result from the lower reactivity of the hydridoruthenium carbonyl clusters with acid. Indeed, a small quantity of $H_4Ru_4(CO)_{12}$, as confirmed by mass spectroscopy, is isolated at the end of the 3-day reaction of $[Ru_4(CO)_{13}]^{2-}$ and $[Ru_4(CO)_{12}]^{4-}$ with strong acid. The course of the reaction of ruthenium is less clear than that in the case of iron because we have not detected any ruthenium butterfly carbides or methynes analogous to those formed in the proton-induced reduction of $[Fe_4(CO)_{13}]^{2-}$, Scheme I.[10]

The contrast in yield between the low-nuclearity clusters and the 4-metal clusters may be related to the ease of forming carbidic or methyne carbon clusters analogous to those observed in the iron system. In this respect the proton-induced reduction of CO is quite different from that of N_2, in which treatment of phosphine-substituted molybdenum complexes with acid leads to the production of ammonium ion.[28] Some of the phosphine-substituted mononuclear molybdenum and tungsten compounds listed in Table I are similar to those in which proton-induced reduction of N_2 was observed. The relationship between cluster nuclearity and carbide reactivity are developed in an accompanying manuscript.[29]

It is interesting that the metals commonly used in Fischer–Tropsch and methanation catalysis, namely iron, cobalt, nickel, and ruthenium,[3] are the metals that were found to produce methane in the present research (with the exception of nickel, which we did not investigate). The similarity between the Fischer–Tropsch reaction and the proton-induced reduction may extend further. The Fischer–Tropsch reaction appears to occur via dissociative chemisorption of CO and conversion of surface carbide to surface CH_x groups,[2-4] ($x = 0$–3)[3] and, as shown in Scheme I, similar cluster-attached ligands appear to be generated in the proton-induced reduction of CO.

In summary, the present results demonstrate that proton-induced reduction of CO can be achieved in tetranuclear clusters of cobalt and ruthenium, as well as tetranuclear mixed-metal clusters containing cobalt and iron. The indication is that a 4-metal cluster readily accommodates the intermediate reduction steps for the CO ligand.

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Registry No. HSO_3CF_3, 1493-13-6; CO, 630-08-0; $Co_4(CO)_{12}$, 17786-31-1; $[FeCo_3(CO)_{12}]^-$, 79829-46-2; $[Ru_3Co(CO)_{13}]^-$, 72152-10-4;

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$[Fe_3Co(CO)_{13}]^-$, 72251-84-4; $[Ru_4(CO)_{13}]^{2-}$, 75215-45-1; $[Fe_4(CO)_{13}]^{2-}$, 25767-85-5; $[PPN][V(CO)_6]$, 38856-17-6; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $Mn_2(CO)_{10}$, 10170-69-1; $H_3Mn_3(CO)_{12}$, 51160-01-1; $Re_2(CO)_{10}$, 14285-68-8; $H_3Re_3(CO)_{12}$, 12146-47-3; $Na_2Fe(CO)_4$, 14878-31-0; $Fe(CO)_5$, 13463-40-6; $[PPN]_2[Fe_2(CO)_8]$, 53368-25-5; $Fe_3(CO)_{12}$, 17685-52-8; $[PPN][Ru_3H(CO)_{11}]$, 71936-70-4; $Ru_3(CO)_{12}$, 15243-33-1; $[PPN][Co(CO)_4]$, 53433-12-8; $Co_2(CO)_8$, 10210-68-1; $[PPN][MnFe_2(CO)_{12}]$, 68520-37-6; $W(CO)_3$(dien), 34630-09-6; $W(CO)_4$(diphos), 29890-05-9; $W(CO)_4$(dppme), 41830-14-2; $Mo(CO)_2(PPh_3)_2(CH_3CN)_2$, 23526-71-8; $Mo(CO)_{12}(PPh_3)_2$(bipy), 15653-24-4; $Mo(CO)_2(PPh_3)$(dien), 24859-95-8; $Mo(CO)_2(PPh_3)_2$(en), 24859-94-7; $[PPN][FeCo_3(CO)_{12}]$, 80883-51-8; $[PPN][Fe_3Co(CO)_{13}]$, 72251-83-3; $[PPN]_2[Fe_4(CO)_{13}]$, 69665-30-1; $[PPN][Ru_3Co(CO)_{13}]$, 72152-11-5; $K_2Ru_4(CO)_{13}$, 75215-44-0; $H_2FeOs_3(CO)_{13}$, 12563-74-5; $K_4Ru_4(CO)_{12}$, 75234-73-0; $[PPN]_2[Ru_6(CO)_{18}]$, 62501-17-1; $[PPN]_2[Co_6(CO)_{15}]$, 82891-34-7; $Rh_6(CO)_{16}$, 28407-51-4; methane, 74-82-8.

Paramagnetic Organometallic Molecules. 12.[1] Electrochemical Studies of Reactions with Lewis Bases following Metal–Metal Bond Cleavage in $R_2C_2Co_2(CO)_6$ Radical Anions

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Abstract: A detailed electrochemical study of the $RC_2R'Co_2(CO)_6{}^{0/-\cdot}$ redox couple is presented [R, R′ = Ph, *t*-Bu, H, CF_3, $Si(CH_3)_3$] utilizing DC polarography and cyclic voltammetry on Hg and Pt electrodes. All acetylene complexes of this type undergo an electrochemically reversible one-electron reduction to the radical anions at potentials ranging from −0.5 to −1.1 V vs. Ag/AgCl in acetone. However, with the exception of the R, R′ = CF_3 compound, the radical anions disintegrate into a variety of monocobalt species including $Co(CO)_4{}^-$ and $RC_2R'Co(CO)_3$. These radical anions also undergo a series of complicated reactions with CO, phosphines, and phosphites that can be analyzed in terms of $\vec{E}C\overleftarrow{E}$ and $\vec{E}C\overleftarrow{E}$ mechanisms. Major products include $Co(CO)_4{}^-$, $Co(CO)_3L^-$, $RC_2R'Co(CO)_2L$, and $RC_2R'Co_2(CO)_5L$ [L = PPh_3, $P(OMe)_3$]. The electrochemistry of the R,R′ = CF_3 compound is much cleaner and does not involve fragmentation to monocobalt species. The different redox properties can be correlated with the lifetimes of the radical anions calculated from the electrochemical data. Detailed studies of the redox chemistry of the Lewis base derivatives, $RC_2R'Co_2(CO)_{6-n}L_n$ [L = PPh_3 or $P(OMe)_3$, $n = 1$–4], are also presented. These derivatives also undergo one-electron reductions to radical anions, but the $n = 3, 4$ derivatives undergo reversible one-electron oxidations to radical cations as well. The redox chemistry of all compounds can be rationalized on the basis of reactions involving intermediate radical anions produced by the reversible homolytic cleavage of the metal–metal bond. The synthetic utility of enhanced receptiveness to nucleophilic attack on the metal–metal cleaved intermediate is emphasized.

A number of generalizations and insights into the electronic structure and reactivity of capped trimetal clusters have arisen from work[1,3–6] on paramagnetic species generated from them. In particular, the generality of a nondegenerate antibonding metal-centered a_2 LUMO and the lability of the metal–metal bond in the radical anions have important consequences for the synthetic and catalytic utility of these clusters. Further, it has been demonstrated that the opportunity to add an electron to a cluster may increase the nucleophilicity of the metal atoms or, alternatively, increase the electrophilicity if radical anion formation is accompanied by opening of the capped clusters,[5–7] or enable the species to act in dissociative electron attachment reactions.[8] It is not entirely clear from the work on the trinuclear clusters which factors determine the kinetic stability of radical anions, although carbon- and germanium-capped systems appear to have the longest lifetimes.[6] In order to further elucidate these factors and to widen the scope of possible reaction modes, we have investigated the closely related acetylene complexes, $RC_2R'Co_2(CO)_6$.[9] The acetylene moiety could be regarded as a cap for the Co–Co bond, and it is interesting that acidification of alkyne complexes with an α-hydrogen is a route to the tricobalt carbon clusters.[10] Molecular orbital descriptions[11] of these complexes predict that the LUMO is a nondegenerate antibonding orbital (in this case of b_2 symmetry) that is largely centered on the two cobalt atoms. A detailed picture provided by our recent analysis[12] of the frozen solution ESR spectra of the radical anions supports this description and is also in agreement with the concept[13] of a "bent" Co–Co bond. Preliminary work[14] on this system showed a very wide range of radical anion stability. Therefore it was considered that the redox chemistry of the acetylene complexes would offer a useful comparative extension to the capped cluster system and, moreover, provide a coordinated organic substrate that might show altered reactivity compared to the neutral counterpart. The only previous

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