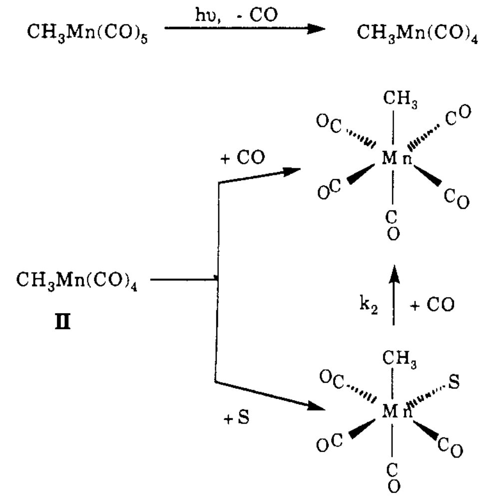
Scheme I



$C_5H_5)Rh(C_2H_4)$ following photolysis of $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$ in cyclohexane under CO.[5] The different behavior of II in THF would be consistent with the higher nucleophilicity of this solvent, giving it a greater competitive advantage vs CO.[1]

A possible explanation of the apparent selectivity of II in C_6H_{12} would be that the $CH_3Mn(CO)_4$ intermediate is formed in a triplet electronic state[6] having either a trigonal-bipyramidal C_{3v} geometry with an axial CH_3 group or a square-pyramidal geometry with a basal CH_3. Either geometric or electronic constraints might give such species sufficient lifetime to demonstrate selectivity in coordinating a sixth ligand. Formation of $Cr(CO)_5$ as a singlet state in a naked, open-faced C_{4v} geometry[7] would explain the contrasting lack of selectivity that this species shows.[8] Additional studies targeted at probing the reactions of such intermediates among acyl- and alkylmanganese carbonyls are underway.[9]

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(9) A reviewer has proposed that II might be a species such as a short-lived photogenerated acyl complex. However, in our ongoing flash photolysis studies of $CH_3C(O)Mn(CO)_5$, we find no evidence for the formation of any species that could explain the CO effects on the yields of A formed in the flash photolysis of I.

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Oxidatively Enhanced Intramolecular Carbonyl Scrambling in the Mixed-Metal Cluster $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$

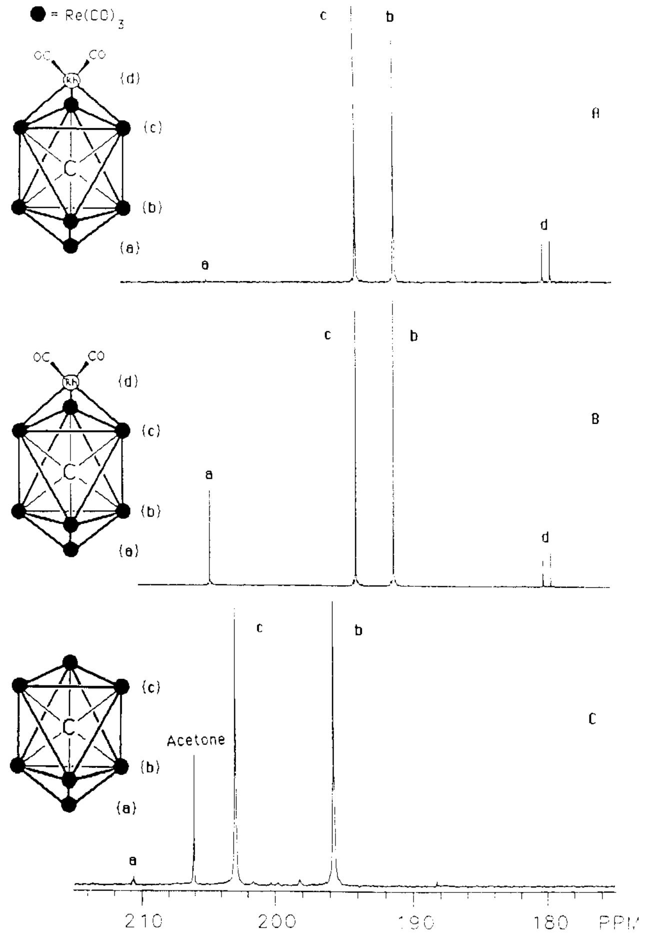

Figure 1. ^{13}C NMR Spectra of (A) $[Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$, (B) $[Re(^{13}CO)_2Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$, and (C) $[Re(CO)_3Re_6C(^{13}CO)_{18}]^{3-}$.

The effect of odd-electron configurations on the reactivity of metal carbonyl clusters has been receiving increased attention recently, as illustrated in several reviews that have been published on the electrochemistry of metal clusters.[1] The most striking result obtained involves intermolecular lability, namely the reductive, electrocatalytic (ETC) substitution of a carbonyl ligand by nucleophiles. These reactions show large rate enhancements with increased selectivity. Increases in intramolecular lability as well as the effect of oxidation have been explored to a much lesser extent.

In mononuclear systems, one-electron oxidation has been shown to promote the rate of migratory insertion reactions,[2] reductive eliminations,[3] and cis-trans isomerization.[4] Similar studies of metal clusters have been limited to a recent report by Geiger involving the oxidatively electrocatalyzed isomerization of $Cp_3Rh_3(CO)_3$ from a C_s isomer to a C_{3v} isomer.[5] We wish to report a dramatic increase in intramolecular ligand lability upon one-electron oxidation, as evidenced by unusual carbonyl scrambling behavior for the selectively ^{13}CO enriched mixed-metal cluster, $[PPN]_2[Re_7C(CO)_{21}Rh(CO)_2]$ (PPN = $N(PPh_3)_2$).

The reaction of $[Rh(CO)_2Cl]_2$ with $[Re_7C(CO)_{21}]^{3-}$ leads to the formation of the mixed-metal cluster $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$, as reported by Henly et al.[6] $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ is a 1,4-bicapped octahedron in which a $Rh(CO)_2$ moiety caps the face

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opposite the capping $Re(CO)_3$. The ^{13}C NMR spectrum of $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ shows four signals (see Figure 1B). The signal at δ 204.8 is due to the $Re(CO)_3$ (a) cap. The signals at δ 194.0 and 191.2 are due to two sets of nine carbonyls (b, c) bound to the triangular planes of the Re_6 octahedron. The doublet at δ 179.7 shows the expected coupling to a rhodium center and is assigned to the $Rh(CO)_2$ cap (d). In order to study the fluxional behavior of the carbonyls, ^{13}CO enriched samples were prepared via three synthetic routes (vide infra). While reaction 1 led to

$$[Re_7{}^{13}C(^{13}CO)_{21}]^{3-} + [Rh(CO)_2Cl]_2 \rightarrow [Re(^{13}CO)_3Re_6{}^{13}C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-} \quad (1)$$

$$[Re_7C(CO)_{21}]^{3-} + [Rh(^{13}CO)_2Cl]_2 \rightarrow [Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-} \quad (2)$$

$$[Re_7C(CO)_{21}Rh(CO)_2]^{2-} + {}^{13}CO \rightarrow [Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-} \quad (3)$$

a completely ^{13}CO enriched sample, reactions 2 and 3 resulted in the formation of the unusual, selectively ^{13}CO-enriched cluster $[Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$, in which the $Re(CO)_3$ cap shows no ^{13}CO enrichment as evidenced by a lack of signal at δ 204.8 (Figure 1A). Reaction 3 is of interest in that the treatment of $[Re_7C(CO)_{21}]^{3-}$ with ^{13}CO does not result in carbonyl enrichment, suggesting that the initial site of ^{13}CO enrichment is the rhodium cap followed by limited carbonyl scrambling.

Selective ^{13}CO enrichment of metal carbonyl clusters occurs infrequently because of two principal reasons. The similar strengths of M–CO bonds within a metal carbonyl cluster offer little site selectivity in intermolecular substitution by ^{13}CO. Furthermore, if selective ^{13}CO enrichment does occur, it is often followed by complete carbonyl scrambling. Thus, selective enrichment of $Ir_4(CO)_9[HC(PPh_2)_3]$ has been reported, but there is also slow intramolecular carbonyl exchange.[7] For $[Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$, no intramolecular carbonyl exchange has been observed for solutions allowed to stand for extended periods (greater than a week).

The cyclic voltammogram of $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ shows a reversible, one-electron oxidation at 628 mV,[6] indicating the formation of a relatively stable radical species. Chemical oxidation of $[Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$ by $[(p\text{-}BrC_6H_4)_2N][SbF_6]$ ($E° \sim 1.0$ V) for a short period of time (<5 min) followed by reduction to the starting material, resulted in total carbonyl scrambling as determined by ^{13}C NMR spectroscopy (Figure 1B). The intermediate in this reaction is believed to be the radical species $[Re_7C(CO)_{21}Rh(CO)_2]^-$, as evidenced by IR spectroscopy (2043 (s), 2019 (vs) cm^{-1} versus 2018 (s), 1998 (vs) cm^{-1} for the starting material) and a complete loss of ^{13}C NMR signal for the oxidized species.

Further studies showed that limiting the amount of oxidant to less than 1 equiv resulted in partial carbonyl scrambling onto the $Re(CO)_3$ cap; i.e., addition of 0.3 equiv of oxidant resulted in ca. 45% carbonyl enrichment. Increasing the amount of oxidant added resulted in greater carbonyl scrambling (addition of 0.4 equiv resulted in ca. 54% carbonyl enrichment). A one to one correlation between the amount of oxidant and the amount of carbonyl scrambling was not observed; however, this may be due to errors in integration because of large relaxation times of the carbonyls and/or paramagnetic impurities. More importantly, since complete scrambling does not occur with the addition of less than 1 equiv of oxidant, there must be a slow intermolecular electron exchange. An upper limit for the rate of this exchange if it does occur has been estimated at $10^{-1}\ M^{-1}\ s^{-1}$.[8] In comparison, the polynuclear species $[Mo_4S_4(edta)_2]^{m-}$ have self-exchange rate constants greater than $10^5\ M^{-1}\ s^{-1}$.[9]

We have also been able to cleave the $Rh(CO)_2{}^+$ cap to form selectively ^{13}CO-enriched $[Re(CO)_3Re_6C(^{13}CO)_{18}]^{3-}$ (Figure 1C) by the addition of large amounts of phosphines to $[Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$ in acetonitrile. This further shows that the process of cleaving Rh–Re bonds (and by reversal, the process of forming Rh–Re bonds, eqs 1 and 2) does not affect carbonyl scrambling to the $Re(CO)_3$ cap. The capping chemistry of $[Re_7C(CO)_{21}]^{3-}$ has been extensively developed,[10] and further study with the selectively enriched material will likely reveal the conditions necessary for complete carbonyl scrambling to occur. Currently, we have found that formation of $[Re_7C(CO)_{22}]^-$ following a literature route[11] involving a two-electron oxidation leads to complete carbonyl scrambling with only one ^{13}C NMR signal observed at δ 191.0 at room temperature.

These results show that, upon oxidation of the selectively enriched carbonyl clusters, there is an enhanced rate of intramolecular rearrangement of carbonyl ligands with a slow rate of intermolecular electron exchange. From reaction times the rate of carbonyl scrambling is at least 10^5 faster[12] for the radical species, similar to the rate enhancements observed for other ETC reactions.[1]

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(12) This value reflects a minimum 40-fold increase in scrambling after a 5-min period of oxidation in comparison with a solution allowed to stand for 10 days.