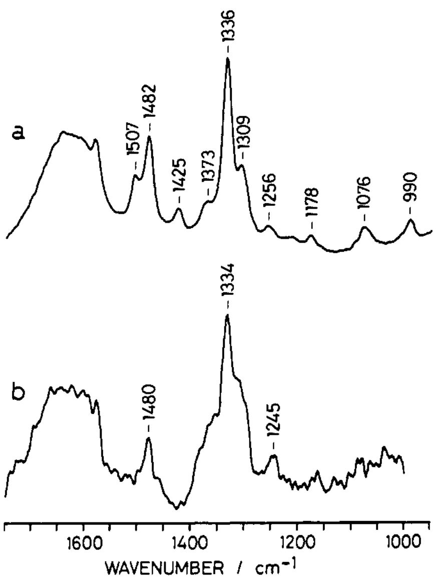

Figure 2. UVRR spectra of 55 μM cAMP (a) and a mixture of 40 μM cAMP and 65 μM CRP (b) with 266-nm excitation (1.5 mW). The binding constants[10] cited in the caption to Figure 1 predict that 70% of cAMP molecules are bound to CRP in the 1:1 complex form and 8% in CRP–cAMP$_2$, and 21% are free in spectrum b.

scattering in the amide III region clearly becomes weak and broad, indicating partial structural change in the β-sheet part of CRP–cAMP (a cAMP band around 1250 cm^{-1} is negligible in parts b and c of Figure 1). Change in the band shape of amide III on going from Figure 1b to Figure 1c is a result of increase and decrease in the content of CRP–cAMP$_2$ and free CRP, respectively, and suggests that the amide III frequency of CRP–cAMP$_2$ is also different from that of free CRP. According to the X-ray analysis of CRP–cAMP$_2$, each of the cAMP molecules is buried in the interior of the β-roll of each subunit.[12] Possibly, in solution also, the cAMP molecule is trapped in the β-roll part of CRP and distorts the β-roll structure of the subunit.

UVRR spectra of aqueous cAMP and CRP-bound cAMP excited at 266 nm are shown in parts a and b of Figure 2, respectively. Since the excitation wavelength is close to an absorption of cAMP at 260 nm, Figure 2b is dominated by the bands of the adenine ring of trapped cAMP and none of the protein bands are clearly observed. The S/N ratio of the spectrum is rather poor due to overlapping fluorescence from CRP. Certainly, however, the 1256-cm^{-1} band of free cAMP shifts to 1245 cm^{-1} upon complexation with CRP and the same shift is observed in a 253-nm-excited spectrum (not shown). This large downshift is not explained by H-bonding interaction between cAMP and CRP because the frequency is not very sensitive to the H-bonding state of the adenine ring.[16] On the other hand, UVRR bands of adenosine in the 1250–1150-cm^{-1} region show large shifts on ribosyl C(1′)–D substitution (e.g., the 1253-cm^{-1} band shifts to 1248 cm^{-1}), which suggests that adenine vibration modes in this frequency region are coupled with the ribose ring modes and their frequencies are sensitive to the adenine–ribose glycosidic-bond conformation.[17] Indeed, a downshift (−5 cm^{-1}) of the adenine Raman band at 1254 cm^{-1} has been observed[18] in conjunction with the B → Z transition of poly(dA-dT) where the glycosidic-bond conformation of adenosine changes from anti to syn.[19] Hence, the downshifted frequency in Figure 2b suggests a conformational change from anti of free cAMP to syn of CRP-bound cAMP. This result is consistent with those of ^{1}H NMR studies[20,21] in solution but inconsistent with the structure of cAMP in crystalline CRP–cAMP$_2$.[12]

Other differences between parts a and b of Figure 2 are the disappearance of the 1425-cm^{-1} band and the increase of the intensity ratio $I(1480)/I(1507)$ in part b. Thomas and Peticolas have reported that the adenyl 1424-cm^{-1} band is absent in a triple helix poly(dT)·poly(dA)·poly(dT) with Hoogsteen type base pairing, in which the adenine N(7) and C(6)–NH$_2$ are involved in H-bonding.[22] Since this band is not affected by H-bonding at NH$_2$,[16] the disappearance of the 1425-cm^{-1} band must be due to formation of an H-bond at N(7) that is stronger than that with water. On the other hand, the increase of $I(1480)/I(1507)$ indicates strong H-bonding at C(6)–NH$_2$, because the intensity ratio increases with increasing H-bonding strength at C(6)–NH$_2$ when excited at 266 nm.[16] It is concluded that the cAMP molecule in an aqueous CRP–cAMP complex is stabilized, at least partially, by H-bonds at N(7) and C(6)–NH$_2$, as is found in crystalline CRP–cAMP$_2$ by X-ray crystallography.[12]

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Registry No. cAMP, 60-92-4; Trp, 73-22-3.

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Selective Enrichment of the Metal Carbonyl Anion in Reactions between Metal Carbonyl Cations and Anions

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Reactions of cations and anions continue to occupy the attention of organic and organometallic chemists.[1-3] Electron transfer to metal carbonyl cations from anions has been shown to occur through two mechanisms: (1) a single electron transfer that leads to odd-electron complexes and ultimately to bimetallic complexes and (2) a CO^{2+} transfer that generates a new cation and a new anion.[2,3] We have previously suggested that these reactions proceed by nucleophilic attack of the anion on the carbon of a carbonyl of the cation.[3c] We now report new evidence consistent with this scheme.

The reaction of Re(CO)$_6^+$ with Mn(CO)$_5^-$ occurs by a single electron transfer and does not exhibit a CO^{2+} transfer.[4] However,

$$\mathrm{Re(CO)_6^+ + Mn(CO)_5^+ \rightarrow}$$
$$\mathrm{MnRe(CO)_{10} + Mn_2(CO)_{10} + Re_2(CO)_{10} + CO}$$

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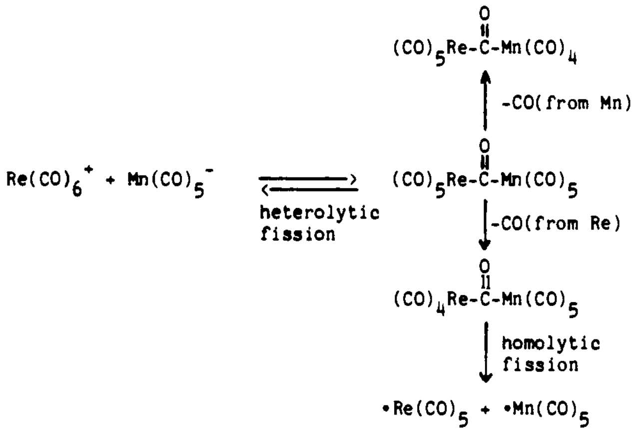

Figure 1. Scheme suggested for interaction of $Re(CO)_6^+$ with $Mn(CO)_5^-$. The path involving CO dissociation from manganese allows enrichment of $Mn(CO)_5^-$; the path involving CO dissociation from rhenium leads to electron transfer.

kinetic studies do not show the normal first-order dependence on each reactant expected for an electron-transfer process.[5] Further, a CO atmosphere inhibits the formation of bimetallic products, suggesting that CO dissociation is a component of the transition state. The reaction of $Re(CO)_6^+$ with $Mn(CO)_5^-$ under an atmosphere of ^{13}CO shows $Re(CO)_6^+$ to be a very effective catalyst for the enrichment of $Mn(CO)_5^-$. Enrichments >90% could be achieved with catalytic quantities of $Re(CO)_6^+$, the $Re(CO)_6^+$ being enriched to less than 15%.

We considered three reasonable interpretations of these results: (1) that $^{\bullet}Re(CO)_6$ is considerably more stable under CO than has previously been presumed,[6] (2) that an adduct forms that has a reasonable lifetime, or (3) that after a rapid electron transfer a selective radical reaction occurs. For a simple single electron transfer, $^{\bullet}Re(CO)_6$ and $^{\bullet}Mn(CO)_5$ would be formed. The CO dependence and selective enrichment of $Mn(CO)_5^-$ could be explained by a relatively slow rate of CO dissociation from $Re(CO)_6^{\bullet}$. To determine if $Re(CO)_6^{\bullet}$ has stability under CO, we attempted the electrochemical reduction of $Re(CO)_6^+$ under an atmosphere of CO; this reduction is not reversible, confirming the lack of stability of $Re(CO)_6^{\bullet}$.[7] $Re(CO)_5^{\bullet}$ and $Mn(CO)_5^{\bullet}$ then must result from any single electron transfer reaction. These species would very quickly incorporate ^{13}CO. If the $Mn(^*CO)_5^{\bullet}$ undergoes electron exchange with $Mn(CO)_5^-$ more rapidly than $Re(^*CO)_5^{\bullet}$ does with $Re(CO)_6^+$ and more rapidly than the combination of the 17 electron complexes, a selective enrichment of $Mn(CO)_5^-$ could be observed. Radical recombination reactions are known to occur more readily than the reaction between $Re(CO)_6^+$ and $Mn(CO)_5^-$.[8] Since all of the reactions subsequent to the initial electron transfer are known to occur rapidly, a first-order dependence on $[Re(CO)_6^+]$ and on $[Mn(CO)_5^-]$ and no dependence of [CO] would be expected. Thus, another interaction must be responsible for the kinetic and enrichment data.

Table I. Semiquantitative Rates of CO Exchange

reactions[a]	solvent	time required[b]
$PPNCpMo(CO)_3 + Re(CO)_6BF_4$	MeCN	15 min
$PPNMn(CO)_5 + Re(CO)_6BF_4$	MeCN	100 min
$PPNMn(CO)_5 + Re(CO)_6BF_4$[c]	MeCN	6 h
$PPNMn(CO)_5 + Re(CO)_5PPh_3ClO_4$	MeCN	100 min
$PPNMn(CO)_5 + Mn(CO)_6BF_4$[d]	MeCN	40 min
$PPNMn(CO)_5 + Mn(CO)_5PPh_3ClO_4$	MeCN	40 min
$PPNCo(CO)_4 + CpFe(CO)_3BF_4$	MeCN	10 min
$PPNCo(CO)_4 + Re(CO)_5PPh_3ClO_4$	MeCN	10 min
$NaMn(CO)_5$	MeCN	24 h
$NaMn(CO)_5$	THF	24 h

[a] Reactions were run in an equimolar ratio. [b] For full enrichment. [c] $[Mn(CO)_5^-] = 4[Re(CO)_6^+]$. [d] Enrichment of both cation and anion.

The scheme that we suggest is shown in Figure 1. We suggest a reversible formation of an adduct from nucleophilic attack of $Mn(CO)_5^-$ on a carbon of $Re(CO)_6^+$. This adduct has a sufficient lifetime to undergo CO dissociation from manganese, which opens a path for ^{13}CO enrichment of the $Mn(CO)_5^-$. Several studies have suggested that CO dissociation is more rapid from a manganese center than from a rhenium center.[9] The most germane involve reactions of the dionyl bridged complexes $(CO)_5MC(O)C(O)M(CO)_5$ where CO dissociation from manganese occurs at −30 °C while the rhenium center is stable at room temperature.[9c] However, since the enrichment of $Mn(CO)_5^-$ occurs without formation of bimetallic species, the CO dissociation from manganese does not lie on the reaction coordinate for the electron transfer. CO dissociation from the rhenium center of the bridged complex leading to $(CO)_4Re–C(O)–Mn(CO)_5$ is necessary for the electron transfer and homolytic fission of the carbon–manganese bond.

A few studies have demonstrated that the counter cation can affect the rate of substitution of metal carbonyl anions.[10] We have examined (semiquantitatively) the exchange of ^{13}CO with $PPNMn(CO)_5$ in CH_3CN, with $NaMn(CO)_5$ in CH_3CN, and with $NaMn(CO)_5$ in THF for comparison with the results from reaction of $Re(CO)_6^+$ with $Mn(CO)_5^-$. The PPN salt incorporated ^{13}CO to about 10% after 12 h in CH_3CN at room temperature in the dark. The exchange with the sodium salt $NaMn(CO)_5$ in CH_3CN is considerably more rapid, with 10% incorporation after 40 min and equilibrium after 24 h. The sodium salt in THF, where ion pairing is greater, shows no significant increase in exchange, reaching equilibrium in 24 h. The exchange results on $[M^+][Mn(CO)_5^-]$ indicate that ion pairing is not sufficient as an explanation for the enrichment of $Mn(CO)_5^-$ in the presence of $Re(CO)_6^+$.

Selective enrichment of the metal carbonyl anion is not unique for the $Re(CO)_6^+$,$Mn(CO)_5^+$ system, but is observed for a number of cation–anion combinations. Table I summarizes those reactions. Reaction of $Mn(CO)_6^+$, $Mn(CO)_5^-$, and ^{13}CO resulted in ^{13}CO enrichment of both cation and anion at comparable rates. In this case the CO-bridged adduct would make the manganese centers equivalent, resulting in similar rates of ^{13}CO incorporation. Previous reports have shown that nucleophilic attack on the carbon of a carbonyl labilizes a cis CO,[11] but the results reported in this paper show a labilization of CO's on the attacking nucleophile.

The results reported in this communication showing selective enrichment of metal carbonyl anions in the presence of metal carbonyl cations nicely supports the previously suggested scheme involving nucleophilic attack of the metal carbonyl anion on a

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(4) Preparation of $Re(CO)_6BF_4$ and $PPNMn(CO)_5$ has been reported previously.[3c] $Re(CO)_5PPh_3ClO_4$ and $Mn(CO)_5PPh_3ClO_4$ were prepared as previously described.[3c] **CAUTION!** Although we have experienced no difficulties with these compounds, all perchlorates should be handled carefully and should not be subjected to shock or heat. The reactions were run with (typically) equimolar solutions (3×10^{-4} M) of CH_3CN. The ^{13}CO is 99% enriched. Monitoring was accomplished by infrared spectroscopy with enrichments checked by mass spectrometry as previously described.[3c]

(5) The kinetic studies were accomplished by following the disappearance of $Re(CO)_6^+$ in the presence of an excess of $Mn(CO)_5^-$. At $[Mn(CO)_5^-] = 10[Re(CO)_6^+]$, the dependence on $[Re(CO)_6^+]$ was between 0 and first order. At $[Mn(CO)_5^-] > 30[Re(CO)_6^+]$, the dependence on $[Re(CO)_6^+]$ is 0. The dependence on $[Mn(CO)_5^-]$ is also less than first order.

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carbon of the cation. This carbonyl species has a sufficient lifetime to undergo CO dissociation before undergoing heterolytic cleavage to the most stable cation–anion combination. Eventually homolytic cleavage leads to the final bimetallic complexes.

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Olefin Polymerization by Vanadium-Containing Polyhedral Oligometallasilsesquioxanes

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Numerous catalysts have been developed, studied, and commercialized for the production of polyolefins.[1] A large fraction of these catalysts, especially the industrially relevant ones, are heterogeneous systems prepared by the deposition of soluble Ti, Zr, or Cr-containing precursors on high surface area supports, such as silica or alumina. Recently, however, silica-supported vanadium catalysts have attracted attention as olefin-polymerization catalysts because their excellent hydrogen response and high comonomer incorporation potentially allow greater control over the properties of the polymer.[2]

We recently reported[3] the synthesis and characterization of several vanadium-containing polyhedral oligometallasilsesquioxanes (POMSS) as part of our efforts to develop homogeneous models for silica-supported catalysts.[4,5] In this paper we report that the reaction of one such complex (i.e., **2**) with trialkylaluminum reagents produces a catalyst that is capable of polymerizing or copolymerizing α-olefins. Although the active catalyst in this system has yet to be identified, the similarity between **2** and surfaces sites that have purportedly been identified on monodisperse silica-supported vanadates[6] suggests that detailed studies of vanadium-containing POMSS may provide new insights into mechanisms by which silica-supported vanadium catalyzes the polymerization of olefins.

As reported previously,[3] vanadates **2** and **3**, which can be prepared from the reaction of **1** with $(n\text{-PrO})_3VO$, $(Me_3SiCH_2)_3VO$, or $VOCl_3$, are components in a monomer/dimer equilibrium ($\Delta H° = -6.02 \pm 0.27$ kcal/mol and $\Delta S° = -17.1 \pm 0.2$ eu). The dimerization of **2** is enthalphically favored, but at concentrations less than 10 mM and/or temperatures greater than 25 °C, the major (>95%) V-containing species is **2**.

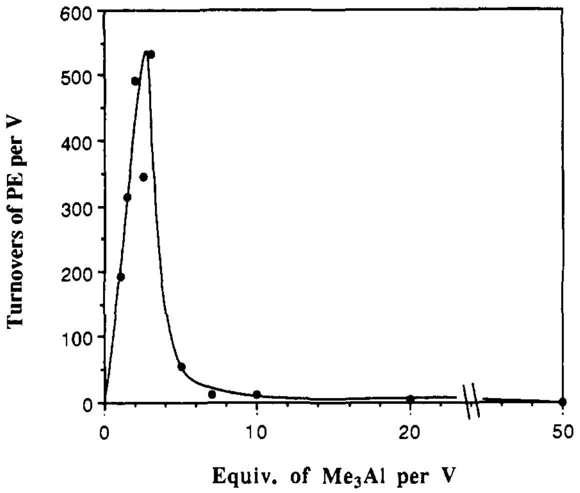
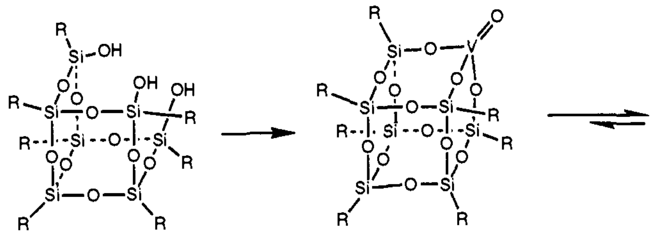
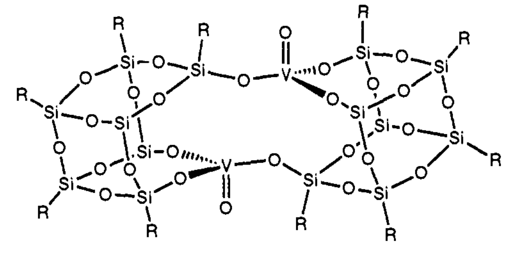


Figure 1. A plot illustrating the dependence of ethylene polymerization activity (i.e., average number of turnovers[7c] per V) on the number of equivalents of Me_3Al added to **2**. All reactions were performed under identical conditions (33.7 μmol of **2** in 10 mL of C_6H_6, 25 °C, 720 Torr of C_2H_4) and quenched with 2-propanol after 3 h.



1 R = c-C_6H_{11} 2



3

The addition of Me_3Al (1-5 equiv/V) to benzene or hexane solutions containing **2** at 25 °C produces straw-colored solutions which readily polymerize ethylene.[7] At 25 °C, ethylene pressures of 1 atm, and vanadium concentrations of 3 mM, ethylene polymerization typically proceeds for 1000–1500 turnovers[7c] before gelation of the solution prevents further uptake of ethylene and

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(7) (a) Matheson polymerization grade ethylene and propylene were purified by slow bubbling through *tri-n*-octylaluminum, followed by two freeze–pump–thaw (−196 °C/10^{-3} mTorr/25 °C) degas cycles. (b) Except were indicated, each polymerization reaction reported in this paper was performed by the addition of Me_3Al (1.03 M in toluene) to **2** (35 mg, 0.0337 mmol) in 10–50 mL of solvent. Reactions were quenched by the addition of excess 2-propanol/hexane. The crude polymers were stirred overnight in 2-propanol/hexane and then collected by filtration or decantation and dried in vacuo (~60 °C, 10^{-5} Torr, 1–2 days). Evaporation of the 2-propanol/hexane washes typically afforded silsesquioxane residues, but small amounts of oily polymers or oligomers were obtained from the reactions with propylene. (c) The "number of turnovers" was defined as (grams of PE/28)/(total moles of V present in the reaction mixture). (d) The reaction of **1** with Me_3Al affords an interesting siloxy-bridged complex[4c] which does not initiate olefin polymerization.

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