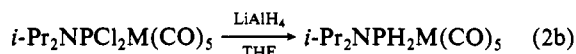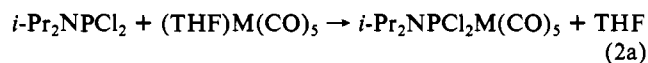cm^{-1} suggest an impurity, possibly some Fe(CO)$_5$ produced as a byproduct in its preparation from Fe$_2$(CO)$_9$ and Cx$_2$NPH$_2$.

The diisopropylamino derivative *i*-Pr$_2$NPH$_2$ appeared to be too unstable to use directly for the preparation of metal carbonyl complexes. However, its metal carbonyl complexes *i*-Pr$_2$NPH$_2$M(CO)$_5$ (M = Cr, W) can be obtained from *i*-Pr$_2$NPCl$_2$ by the reaction sequence

$$i\text{-Pr}_2\text{NPCl}_2 + (\text{THF})\text{M(CO)}_5 \rightarrow i\text{-Pr}_2\text{NPCl}_2\text{M(CO)}_5 + \text{THF} \quad (2a)$$

$$i\text{-Pr}_2\text{NPCl}_2\text{M(CO)}_5 \xrightarrow[\text{THF}]{\text{LiAlH}_4} i\text{-Pr}_2\text{NPH}_2\text{M(CO)}_5 \quad (2b)$$

A similar method has been used by Mercier and Mathey[10] to prepare Et$_2$NPH$_2$W(CO)$_5$. The complexes *i*-Pr$_2$NPH$_2$M(CO)$_5$ (M = Cr, W) are yellow, relatively air-stable solids that can be

sublimed under vacuum without significant decomposition. Their spectroscopic properties are similar to those of the other R$_2$NPH$_2$M(CO)$_5$ derivatives. The $|^1J(^{31}\text{P}-^{183}\text{W})|$ coupling constant of 371 Hz in *i*-Pr$_2$NPCl$_2$W(CO)$_5$ falls to 244 Hz upon reduction to *i*-Pr$_2$NPH$_2$W(CO)$_5$ in accord with the expected greater π-acceptor strength of *i*-Pr$_2$NPCl$_2$ relative to *i*-Pr$_2$NPH$_2$; the relationship of $|^1J(^{31}\text{P}-^{183}\text{W})|$ to ligand π-acceptor strength has been known for some time.[17-19]

Registry No. Cx$_2$NPH$_2$, 93583-23-4; (CH$_2$)$_3$(CMe)$_2$NPH$_2$, 93583-24-5; *i*-Pr$_2$NPH$_2$, 93583-25-6; Cx$_2$NPH$_2$Cr(CO)$_5$, 93492-97-8; Cx$_2$NPH$_2$W(CO)$_5$, 93492-98-9; Cx$_2$NPH$_2$Fe(CO)$_4$, 94152-55-3; (CH$_2$)$_3$(CMe$_2$)$_2$NPH$_2$Cr(CO)$_5$, 97704-71-7; (CH$_2$)$_3$(CMe$_2$)$_2$NPH$_2$W(CO)$_5$, 97704-72-8; *i*-Pr$_2$NPH$_2$Cr(CO)$_5$, 97704-73-9; *i*-Pr$_2$NPH$_2$W(CO)$_5$, 97704-74-0; *i*-Pr$_2$NPCl$_2$Cr(CO)$_5$, 97704-75-1; *i*-Pr$_2$NPCl$_2$W(CO)$_5$, 97704-76-2; Cx$_2$NPCl$_2$, 93583-22-3; (CH$_2$)$_3$(CMe$_2$)$_2$NPCl$_2$, 64945-24-0; *i*-Pr$_2$NPCl$_2$, 921-26-6; (THF)Cr(CO)$_5$, 15038-41-2; (THF)W(CO)$_5$, 36477-75-5.

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Relationship between Structure and Reactivity for Metal Clusters Formed in Ion–Molecule Reactions in Decacarbonyldimanganese and Pentacarbonyl(pentacarbonylmanganio)rhenium

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Relative rate constants for ion–molecule reactions in Mn$_2$(CO)$_{10}$ and ReMn(CO)$_{10}$ are reported. Electron-impact-produced fragment ions react with the parent to form cluster ions containing three and four metal atoms. Subsequent sequential reactions lead to cluster ions containing as many as eight metal atoms. Most of the clusters formed in ReMn(CO)$_{10}$ contain equal numbers of Re and Mn atoms. A rough correlation is found between the average electron deficiency per metal atom and the rate constant. Electron deficiencies are assigned with use of the effective atomic number rule and on the assumption of closed-polyhedral structures for most of the ions. The rate constants tend to increase with electron deficiency until the deficiency reaches two per metal atom. Exceptions to this behavior are rationalized in terms of ligand crowding and electronic effects such as multiple bonding and ligand-induced restructuring analogous to that observed in coordinatively unsaturated metal surfaces. Several cases are identified where substituting Mn for Re in a metal cluster changes its behavior substantially.

Introduction

We have recently reported relative rate constants for gas-phase cationic clustering reactions in Re$_2$(CO)$_{10}$[2] and for gas-phase anionic clustering reactions in Fe(CO)$_5$.[3] A direct correlation was found to exist between the relative rate constants of the reactant species and their electron deficiencies. Species that are nearly coordinatively saturated and have low electron deficiencies react slowly, if at all. On the other hand, species with large electron deficiencies react rapidly.

Electron deficiencies were calculated for the anionic species[3] by utilizing the 18-electron rule. The difference between 18 and the average number of valence electrons available to each metal atom is the electron deficiency. For the cationic species[2] electron deficiencies were calculated by using a modified 18-electron rule that allows for the effects of delocalized bonding based on Teo's topological electron-counting theory.[4] Relative rate constants for the clustering reactions observed in both Re$_2$(CO)$_{10}$ and Fe-(CO)$_5$ showed a similar relationship to electron deficiency.

Re$_n$(CO)$_m^+$ and Fe$_n$(CO)$_m^-$ ions with large electron deficiencies react rapidly with the neutral parents, Re$_2$(CO)$_{10}$ and Fe(CO)$_5$, respectively, to form larger clusters. In fact, for species with electron deficiencies greater than 2 the rates of reaction are relatively constant and approximately equal to the collision rate. For species with electron deficiencies less than 2 the rate constants drop smoothly and dramatically with decreasing electron deficiency until the clusters become nearly coordinatively saturated. This is consistent with the general behavior of coordination compounds, since a cluster with an electron deficiency of 2 has on the average a vacancy for a two-electron donor such as CO at each metal center and therefore should be quite reactive. As the vacancies fill and the electron deficiency drops, the species should become less and less reactive.

In order to assign electron deficiencies to the anions in Fe(CO)$_5$ and the cations in Re$_2$(CO)$_{10}$, it was necessary to estimate the number of metal–metal bonds in the clusters. This was done by analogy with known condensed-phase structures or by assumption of closed-polyhedral structures. The correlation of rate constant with electron deficiencies suggested that these structural assignments were correct. In a few cases the correlation was actually used to assign structures if other considerations led to an ambiguous assignment.[2,3]

Our present study reports some relative rate constants for gas-phase positive ion clustering reactions in Mn$_2$(CO)$_{10}$ and ReMn(CO)$_{10}$. These compounds were chosen because they are periodic congeners of Re$_2$(CO)$_{10}$. They provide an opportunity

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(2) Meckstroth, W. K.; Ridge, D. P.; Reents, W. D., Jr. *J. Phys. Chem.* **1985**, *89*, 612–617.
(3) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67–71.
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Table I. Relative Intensities of Positive Ions in the Mass Spectra of $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$ Obtained by 70-eV Electron Impact

| | $Mn_2(CO)_{10}$ | | $ReMn(CO)_{10}$ | |
| | nominal | rel | nominal | rel intens of largest isotope |
stoichiometry	mass, m/z	intens, %	mass, m/z	peak,[a] %
M^+	55	97.9	55	52.1
			187	23.1
MC^+	67	...[b]	67	...
			199	4.8
$M(CO)^+$	83	10.6	83	7.1
			215	5.4
$M(CO)_2^+$	111	4.7	111	...
			243	7.2
$M(CO)_3^+$	139	4.0	139	...
			271	8.7
$M(CO)_4^+$	167	...	167	...
			299	6.1
$M(CO)_5^+$	195	15.0	195	...
			327	10.0
$M(CO)_6^+$	223	2.9	223	...
			355	48.9
M_2^+	110	100.0	242	43.2
M_2C^+	122	...	254	6.7
$M_2(CO)^+$	138	6.3	270	41.7
$M_2(CO)_2^+$	166	21.2	298	56.7
$M_2(CO)_3^+$	194	22.1	326	51.9
$M_2(CO)_4^+$	222	95.0	354	100.0
$M_2(CO)_5^+$	250	63.9	382	87.1
$M_2(CO)_{10}^+$	390	34.3	522	34.9

[a] For fragments with one metal atom M = Mn for the first value listed and M = Re for the second value. For species with two metal atoms, M_2 = ReMn. [b] Intensities of peaks indicated with dotted lines are not observed or are less than 2%.

to probe the effect of substituting a first-row transition metal, Mn, for a third-row metal, Re, on cluster ion formation. They also provide an opportunity to probe the generality of the relationship between reactivity and electron deficiency for ionic transition-metal carbonyl clusters.

Experimental Section

The preliminary studies and the double-resonance experiments were done at the University of Delaware with an ion cyclotron resonance spectrometer that is described elsewhere.[5] A Nicolet FT/MS-1000 Fourier transform mass spectrometer at AT&T Bell Laboratories was used to obtain the high-resolution spectra. This instrument has also been previously described.[6] A 2-in. cubic cell was used to obtain the electron impact spectra, and a 1 in. × 1 in. × 3 in. rectangular cell was utilized to obtain the kinetic data. Typical operating parameters were as follows: magnetic field strength, 2.95 T; trapping voltage, 1 V; pressure, 1 × 10⁻⁷ torr; trapping time, 1 ms to 3 s.

$Mn_2(CO)_{10}$ was purchased from Ventron, Alfa Division, and could be used as received. $ReMn(CO)_{10}$ was prepared by published procedures[7] and purified by sublimation. The compounds were introduced into the spectrometers through leak valves, and pressures as high as (2–4) × 10⁻⁶ torr could readily be obtained. The mass spectra of these compounds showed no detectable impurities except for a small amount of water. Careful drying of the sample minimized the effects of the water impurity on the observed chemistry. The pressures were measured with a standard ionization gauge.

Mass Spectra

The observed mass spectra at short observation time (no ion–molecule reactions) are tabulated in Table I. In most respects the mass spectra in Table I are in essential agreement with spectra in the literature.[8-10] An early spectrum of $ReMn(CO)_{10}$ published

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(8) Johnson, B. F. G.; Lewis, J.; Williams, I. G.; Wilson, J. M. *J. Chem. Soc. A* **1967**, 341–344.
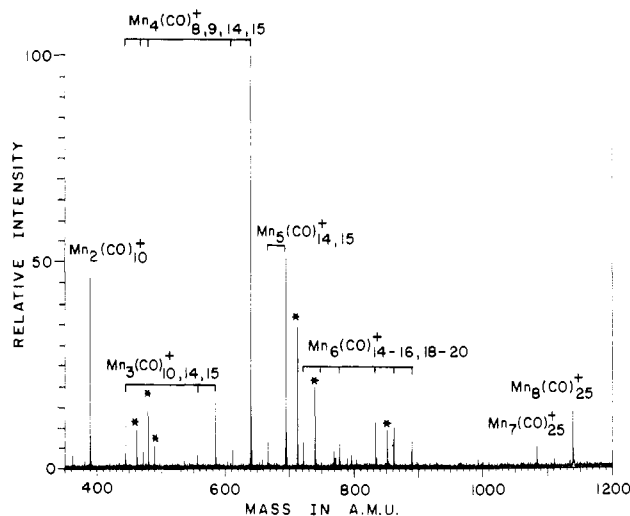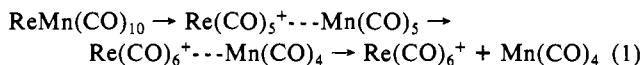(9) Junk, G. A.; Svec, H. J. *J. Chem. Soc. A* **1970**, 2101–2105.

Figure 1. Positive ion mass spectrum of ion–molecule reaction products of reactions between $Mn_2(CO)_{10}$ and its electron-impact-produced fragment ions (trapping time 1 s, pressure 1.0×10^{-7} torr). Asterisks denote species that contain H_2O and are listed in Table II (m/z = 462, 480, 490, 713, 740, and 852).

in tabular form did not include the $Re(CO)_6^+$ fragment.[8] The peak may have been observed and dismissed as an impurity or misassigned. In any case it is included in the other published spectrum.[9] The $Re(CO)_6^+$ fragment is presumably the result of a ligand-transfer reaction between the electron-impact-produced fragments of $ReMn(CO)_{10}$ as shown in eq 1. The fragments,

$$ReMn(CO)_{10} \rightarrow Re(CO)_5^+\cdots Mn(CO)_5 \rightarrow$$
$$Re(CO)_6^+\cdots Mn(CO)_4 \rightarrow Re(CO)_6^+ + Mn(CO)_4 \quad (1)$$

held together by the electrostatic interaction, react before they separate. This process accounts for 43% of all the ionization involving cleavage of the Re–Mn bond. This suggests that D-$(Mn(CO)_4–CO) < D(Re(CO)_5^+–CO)$. The $Re(CO)_6^+$ ion is isoelectronic with $W(CO)_6$ and might be expected to be quite stable. One published tabulated spectrum of $ReMn(CO)_{10}$ includes a small $Mn(CO)_5^+$ fragment peak,[8] which we do not observe. The authors of the earlier work suggest that their sample had an $Mn_2(CO)_{10}$ impurity.[8] This could account for the small $Mn(CO)_5^+$ peak in their spectrum. The observation that $Re(CO)_5^+$ forms on electron impact on $ReMn(CO)_{10}$ but $Mn(CO)_5^+$ does not suggest that $IP(Re(CO)_5) < IP(Mn(CO)_5)$. The literature values of these ionization potentials, $IP(Re(CO)_5)$ = 8.40 eV[9] and $IP(Mn(CO)_5)$ = 8.32 eV,[9] suggest otherwise, but the uncertainties in the ionization potentials ($\sim\pm0.2$ eV) exceed their difference, so it is possible that $Re(CO)_5$ has the lower ionization potential.

Ion–Molecule Reaction Products

Figure 1 shows the mass spectrum of $Mn_2(CO)_{10}$ at 1-s trapping time, 1.0×10^{-7} torr, and 70 eV ionizing energy. The stoichiometries and relative abundances of the product species seen in the spectrum are listed in Table II. Figure 2 shows the mass spectrum of $ReMn(CO)_{10}$ at 500 ms trapping time, 1.1×10^{-7} torr, and 70 eV ionizing energy. Table III gives the stoichiometries and relative abundances of the product species seen in this spectrum. Measured and precise masses for representative ions from both of these spectra are given in Table IV. The mass calibration table was constructed by extrapolating from known masses (initially the electron impact fragment ions) to heavier ions as they were formed. Each additional heavier ion that was added to the calibration table allowed further extrapolation ($\sim20\%$ greater than the largest mass in the calibration table). A mass was added to the calibration table if a calculated mass from a reasonable stoichiometry was within 100 ppm of the measured

(10) Lewis, J.; Manning, A. R.; Miller, J. R.; Wilson, J. M. *J. Chem. Soc. A* **1966**, 1663–1670.

Table II. Relative Intensities of Positive Ions Formed by Ion–Molecule Reactions in Mn$_2$(CO)$_{10}$[a]

stoichiometry	nominal mass, m/z	rel intens, %
Mn$_2$(CO)$_{10}^+$	390	48.4
Mn$_4$(CO)$_8^+$	444	3.7
Mn$_3$(CO)$_{10}^+$	445	11.0
Mn$_4$(CO)$_8$(H$_2$O)$^+$	462	9.6
Mn$_4$(CO)$_9^+$	472	4.5
Mn$_4$(CO)$_8$(H$_2$O)$_2^+$	480	16.5
Mn$_4$(CO)$_9$(H$_2$O)$^+$	490	5.6
Mn$_3$(CO)$_{14}^+$	557	3.8
Mn$_3$(CO)$_{15}^+$	585	16.2
Mn$_4$(CO)$_{14}^+$	612	4.2
Mn$_4$(CO)$_{15}^+$	640	100.0
Mn$_5$(CO)$_{14}^+$	667	5.8
Mn$_5$(CO)$_{15}^+$	695	51.8
Mn$_5$(CO)$_{15}$(H$_2$O)$^+$	713	33.9
Mn$_6$(CO)$_{14}^+$	722	6.6
Mn$_6$(CO)$_{14}$(H$_2$O)$^+$	740	19.1
Mn$_6$(CO)$_{15}^+$	750	1.0
Mn$_6$(CO)$_{16}^+$	778	5.8
Mn$_6$(CO)$_{18}^+$	834	10.2
Mn$_6$(CO)$_{18}$(H$_2$O)$^+$	852	9.4
Mn$_6$(CO)$_{19}^+$	862	9.7
Mn$_6$(CO)$_{20}^+$	890	6.6
Mn$_7$(CO)$_{25}^+$	1084	5.1
Mn$_8$(CO)$_{25}^+$	1139	12.5

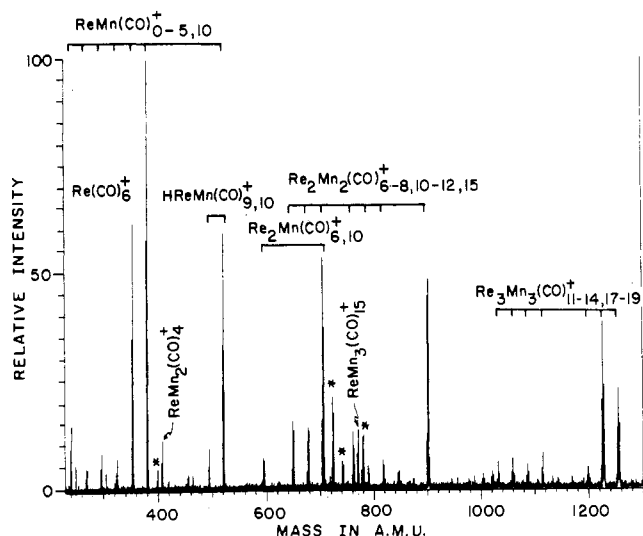[a] Conditions: trapping time, 1 s; pressure, 1.0 × 10^{-7} torr.

Figure 2. Positive ion mass spectrum of ion–molecule reaction products of reactions between ReMn(CO)$_{10}$ and its electron-impact-produced fragment ions (trapping time 500 ms, pressure 1.1 × 10^{-7} torr). Asterisks denote species that contain H$_2$O and are listed in Table III (m/z = 400, 724, 742, and 780).

mass. The ions used in the calibration tables are noted in Table IV. This calibration "hopping" technique works well for inorganic systems when only a small set of elements are present. Some higher mass ions were observed at longer trapping times in both Mn$_2$(CO)$_{10}$ and ReMn(CO)$_{10}$. Those of these higher mass ions that gave sufficiently strong signals so that the change in their relative abundances with time could be followed are identified in the tables of kinetic data discussed below.

Clustering Reactions

The clustering reactions of the primary ions in Mn$_2$(CO)$_{10}$ could be identified by double resonance. These are summarized in Table V. Double resonance beyond m/z 650 was prevented by resolution limitations at high mass in this system. In general the ion and neutral molecule combine and two or three carbonyls are lost. Only in the case of Mn$^+$ was cleavage of the Mn–Mn bond observed, but Mn$^+$ does react to form a series of Mn$_2$(CO)$_m^+$ ions. Particularly interesting is the observation of what appear to be direct association reactions 2 and 3. Ions formed by direct

Table III. Relative Intensities of Positive Ions Formed by Ion–Molecule Reactions in ReMn(CO)$_{10}$[b]

stoichiometry	nominal mass,[a] m/z	rel intens of largest isotope peak, %
ReMn$^+$	242	13.2
ReMn(CO)$^+$	270	6.0
ReMn(CO)$_2^+$	298	8.4
ReMn(CO)$_3^+$	326	7.8
ReMn(CO)$_4^+$	354	16.5
Re(CO)$_6^+$	355	57.3
ReMn(CO)$_5^+$	382	100.0
ReMn(CO)$_5$(H$_2$O)$^+$	400	5.0
ReMn$_2$(CO)$_4^+$	409	11.1
HReMn(CO)$_9^+$	495	9.9
ReMn(CO)$_{10}^+$	522	57.1
HReMn(CO)$_{10}^+$	523	24.1
Re$_2$Mn(CO)$_6^+$	595	7.0
Re$_2$Mn$_2$(CO)$_6^+$	650	14.0
Re$_2$Mn$_2$(CO)$_7^+$	678	12.5
Re$_2$Mn$_2$(CO)$_8^+$	706	43.3
Re$_2$Mn(CO)$_{10}^+$	707	5.8
Re$_2$Mn$_2$(CO)$_8$(H$_2$O)$^+$	724	19.9
Re$_2$Mn$_2$(CO)$_8$(H$_2$O)$_2^+$	742	6.0
Re$_2$Mn$_2$(CO)$_{10}^+$	762	12.3
ReMn$_3$(CO)$_{15}^+$	772	14.7
Re$_2$Mn$_2$(CO)$_{10}$(H$_2$O)$^+$	780	12.5
Re$_2$Mn$_2$(CO)$_{11}^+$	790	5.9
Re$_2$Mn$_2$(CO)$_{12}^+$	818	6.9
Re$_2$Mn$_2$(CO)$_{15}^+$	902	43.3
Re$_3$Mn$_3$(CO)$_{11}^+$	1032	5.8
Re$_3$Mn$_3$(CO)$_{12}^+$	1060	6.2
Re$_3$Mn$_3$(CO)$_{13}^+$	1088	5.5
Re$_3$Mn$_3$(CO)$_{14}^+$	1116	8.0
Re$_3$Mn$_3$(CO)$_{17}^+$	1200	4.7
Re$_3$Mn$_3$(CO)$_{18}^+$	1228	32.8
Re$_3$Mn$_3$(CO)$_{19}^+$	1256	21.1

[a] Calculated for Re = ^{187}Re, Re$_2$ = ^{185}Re^{187}Re, and Re$_3$ = ^{185}Re^{187}Re$_2$. [b] Conditions: trapping time, 500 ms; pressure, 1.1 × 10^{-7} torr.

Table IV. Precise Mass of Representative Ions

stoichiometry	precise mass, m/z calcd	precise mass, m/z measd[a]	error, ppm
Mn$_3$(CO)$_{15}^+$	584.7374	584.7350	−4.1
Mn$_7$(CO)$_{25}^+$	1084.4389	1084.4128	−24.1
Mn$_8$(CO)$_{25}^+$	1139.3770	1139.3770	0.0
^{187}ReMn(CO)$_4^+$	353.8732	353.8737[b]	+1.4
^{187}ReMn(CO)$_{10}^+$	521.8426	521.8369[b]	−11.0
^{185}Re^{187}ReMn(CO)$_{10}^+$	706.7956	706.7682[b]	−39.0
^{187}ReMn$_3$(CO)$_{15}^+$	771.6934	771.6803[b]	−17.0
^{185}Re^{187}ReMn$_2$(CO)$_{15}^+$	901.7083	901.6953[b]	−14.0
^{185}Re^{187}Re$_2$Mn$_3$(CO)$_{19}^+$	1255.5820	1255.5680[b]	−11.0

[a] Ions used in the calibration were, unless otherwise noted, Mn$_2$-(CO)$_{10}^+$ (m/z = 389.8253), Mn$_3$(CO)$_{10}^+$ (m/z = 444.7634), Mn$_4$-(CO)$_{15}^+$ (m/z = 639.6755), Mn$_5$(CO)$_{15}^+$ (m/z = 694.6136), and Mn$_6$(CO)$_{20}^+$ (m/z = 889.5262). [b] Ions used in the calibration curve were ^{187}Re(CO)$_6^+$ (m/z = 354.9249), ^{185}ReMn(CO)$_5^+$ (m/z = 379.8656), and ^{185}ReMn(CO)$_{10}^+$ (m/z = 519.8402).

Table V. Branching Ratios for Clustering Reactions in Mn$_2$(CO)$_{10}$

n, m for Mn$_n$(CO)$_m^+$ reactant ion	n, m for Mn$_n$(CO)m^+ product ions (branching ratio)
1, 0	2, 5 (0.78); 2, 7 (0.09); 2, 8 (0.05); 2, 9 (0.08)
1, 1	3, 8 (0.27); 3, 9 (0.28); 3, 10 (0.45)
1, 2	3, 10 (0.44); 3, 11 (0.56)
1, 3	3, 10 (0.63); 3, 11 (0.37)
1, 4	3, 11 (0.73); 3, 12 (0.27)
1, 5	3, 12 (0.65); 3, 15 (0.35)
2, 0	4, 8 (0.62); 4, 9 (0.38)
2, 1	4, 8 (0.63); 4, 9 (0.37)
2, 2	4, 9 (1.00)
2, 3	4, 10 (1.00)
2, 4	4, 10 (0.34); 4, 11 (0.26); 4, 12 (0.40)
2, 5	4, 10 (0.25); 4, 12 (0.15); 4, 15 (0.60)

$$Mn(CO)_5^+ + Mn_2(CO)_{10} \rightarrow Mn_3(CO)_{15}^+ \qquad (2)$$

$$Mn_2(CO)_5^+ + Mn_2(CO)_{10} \rightarrow Mn_4(CO)_{15}^+ \qquad (3)$$
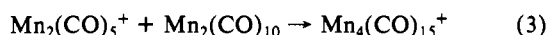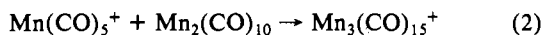
association have sufficient energy to dissociate and will do so in a characteristic lifetime unless they lose some energy first. Collisional stabilization, where a third body collides and removes a portion of the excess energy, can occur if the lifetime of the complex is long compared to the mean free time between collisions. At the operating pressure of $\sim 1 \times 10^{-7}$ torr in the Fourier transform mass spectrometer the mean free time between ion–neutral molecule collisions is ~ 100 ms. This is much longer than lifetimes characteristic of complexes formed by thermal ion–neutral molecule collisions. It is more probable that the complexes are stabilized by losing energy radiatively. It has been observed that Mn^+ attaches to $Mn_2(CO)_{10}$, forming a metastable complex that lives long enough to be observed in a time of flight mass spectrometer.[11] Although an $Mn_3(CO)_{10}^+$ product is observed in these studies, double resonance suggests that $Mn(CO)^+$, $Mn(CO)_2^+$, and $Mn(CO)_3^+$ are the precursors. This suggests that the $Mn_3(CO)_{10}^+$ species formed by association of Mn^+ with $Mn_2(CO)_{10}$ has a lifetime on the order of a few milliseconds or less. It may be that the $Mn_3(CO)_{15}^+$ and $Mn_4(CO)_{15}^+$ species have longer decomposition lifetimes or shorter radiative stabilization lifetimes or both and thus survive longer than the smaller association complex. A treatment similar to Dunbar's[12] suggests that radiative lifetimes for these species may be as small as 0.5 ms. Simple RRK calculations suggest that decomposition lifetimes for species of this complexity might easily exceed 0.5 ms if the excitation energy is small. Thus radiative stabilization seems a possibility. Radiative energy loss has been suggested as the mechanism of bimolecular Li^+ attachment to organic molecules.[13]

One of two clear double resonances observed in $ReMn(CO)_{10}$, identified in reaction 4, corresponds to a direct association analogous to eq 3. This supports the possibility of the formation

$$ReMn(CO)_5^+ + ReMn(CO)_{10} \rightarrow Re_2Mn_2(CO)_{15}^+ \qquad (4)$$
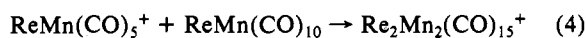
of long-lived species by direct association in these large metal carbonyl clusters. The other reaction identified by double resonance in $ReMn(CO)_{10}$ is given in eq 5. This might be viewed

$$Re_2Mn_2(CO)_{15}^+ + ReMn(CO)_{10} \rightarrow$$
$$ReMn_3(CO)_{15}^+ + Re_2(CO)_{10} \qquad (5)$$
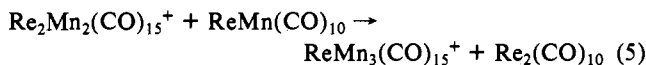
as an exchange of $Mn(CO)_5$ for an $Re(CO)_5$ by the neutral reactant.

The cluster ions in Table III generally have equal numbers of Re and Mn atoms. Reaction 5 is evidently more the exception than the rule. The general type of reaction is probably that most commonly identified by double resonance in $Mn_2(CO)_{10}$: the ion and the neutral molecule combine and eliminate two or three CO molecules. The stoichiometries of nearly all of the observed ions in both $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$ are consistent with closed-polyhedral structures. The stoichiometries of the largest observed cluster for each number of metal atoms are plotted in Figure 3. The top line represents the stoichiometries for coordinatively saturated species with open-chain structures, and the bottom line represents the stoichiometries of coordinatively saturated species with closed-polyhedral structures. Only the point for $Mn_3(CO)_{15}^+$ lies above the bottom line. That means that all the observed stoichiometries except $Mn_3(CO)_{15}^+$ in both $Mn_2-(CO)_{10}$ and $ReMn(CO)_{10}$ are consistent with closed-polyhedral structures. $Mn_3(CO)_{15}^+$ has too many carbonyl ligands to be a closed-triangular structure with three Mn–Mn bonds. It must be open to some extent. An open chain with two metal–metal bonds is possible. If each Mn has five carbonyl ligands, the species might be written $(Mn(CO)_5)_3^+$ and is analogous in an isolobal sense[14] to $(CH_3)_3^+$, which corresponds to one structure for pro-

tonated propane. The $Mn_3(CO)_{15}^+$ ion is therefore an inorganic member of the family of ions including CH_5^+ and the other protonated alkanes. An analogous compound, $HMnRe_2(CO)_{14}$, does exist in a "bent" configuration rather than with a triangular metal core.[15]

The ions formed by clustering reactions in $Re_2(CO)_{10}$ are also consistent with closed-polyhedral structures except for an $Re_3-(CO)_{15}^+$ ion.[2] The $ReMn(CO)_{10}$ system has no $M_3(CO)_{15}^+$ ion, but analogues to the precursors of $M_3(CO)_{15}^+$ in the other two systems $(Re_2(CO)_7^+$ and $Mn(CO)_5^+)$ are absent or weak in the $ReMn(CO)_{10}$ mass spectrum.

A unique feature of the $Mn_2(CO)_{10}$ system is the occurrence of an $Mn_7(CO)_{25}^+$ ion. In $Re_2(CO)_{10}$ ions with six and eight Re atoms are observed but not seven.[2] No seven-metal-atom clusters were identified in $ReMn(CO)_{10}$. The $Mn_7(CO)_{25}^+$ ion probably comes from reaction of Mn_5 ions which in turn come from Mn_3 ions. The Mn_3 ions come from Mn ions as indicated by the double-resonance results in Table V. The relatively low abundance of ions containing only one metal atom in the mass spectra of $Re_2(CO)_{10}$ and $ReMn(CO)_{10}$ probably explains the absence of M_7 clusters as products of reactions of those species.

In the $Re_2(CO)_{10}$ case the relative rate constants for reactions of the various cluster ions with the neutral carbonyl to form larger clusters were determined.[2] These rate constants were found to vary regularly with the electron deficiency of the cluster ion. The electron deficiencies were determined by using the effective atomic number rule (EAN) with modifications suggested by Teo.[4] The electron deficiency, D, of the cluster $M_n(CO)_m^+$ with b metal–metal bonds is given by eq 6. The value X varies from 0 to 3

$$D = \frac{18n - (7n + 2m + 2b - 1)}{n} + \frac{2X}{n} \qquad (6)$$
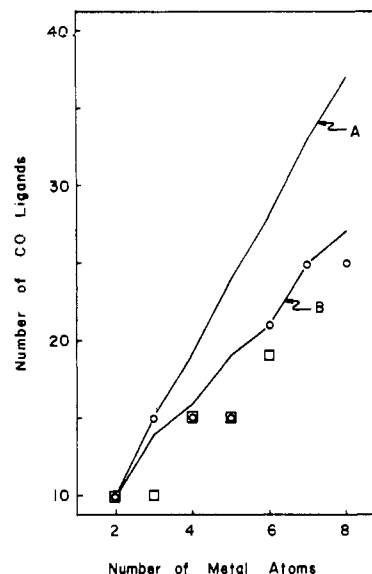

Figure 3. Number of CO ligands vs. number of metal atoms in clusters. Curve A represents the number of ligands in saturated linear clusters. Curve B represents the number of ligands in saturated closed-polyhedral structures. The circles and squares represent the largest number of CO ligands observed for clusters formed in $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$, respectively.

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Table VI. Electron Deficiencies and Relative Rate Constants for Reactions of $M_n(CO)_m{}^+$ ($M = Mn$) Ions with $Mn_2(CO)_{10}$
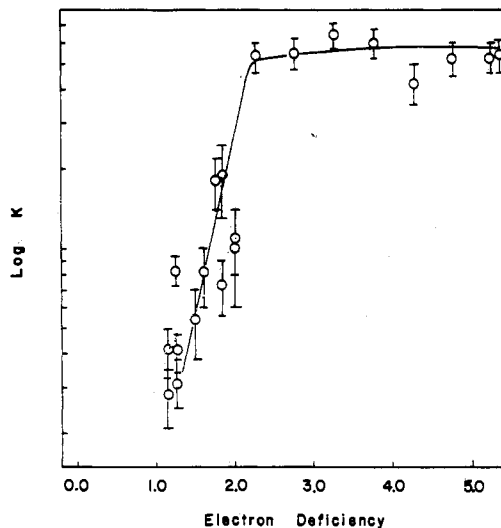
stoichiometry	rel rate const[a]	structure[f]	metal–metal bonds[b]	X[c]	electron deficiency
$Mn_2(CO)_{10}{}^+$	<0.15	L	1	0	$^1/_2$
$Mn_3(CO)_{10}{}^+$	1.4 ± 0.5	T	4[d]	0	2
$Mn_3(CO)_{14}{}^+$	<0.20	B	2	0	$^2/_3$
$Mn_3(CO)_{15}{}^+$	<0.20	B	2	0	0
$Mn_4(CO)_8{}^+$	6.9 ± 1.5	Tet	6	0	$4^1/_4$
$Mn_4(CO)_9{}^+$	6.1 ± 1.5	Tet	6	0	$3^3/_4$
$Mn_4(CO)_{10}{}^+$	10.0 ± 3.0	Tet	6	0	$3^1/_4$
$Mn_4(CO)_{11}{}^+$	9.9 ± 3.0	Tet	6	0	$2^3/_4$
$Mn_4(CO)_{12}{}^+$	7.3 ± 1.5	Tet	6	0	$2^1/_4$
$Mn_4(CO)_{14}{}^+$	0.28 ± 0.07	Tet	6	0	$1^1/_4$
$Mn_4(CO)_{15}{}^+$	0.32 ± 0.08	R	5[e]	0	$1^1/_4$
$Mn_5(CO)_{14}{}^+$	0.99 ± 0.30	TBP	9	0	2
$Mn_5(CO)_{15}{}^+$	0.85 ± 0.30	TBP	9	0	$1^3/_5$
$Mn_6(CO)_{14}{}^+$	0.59 ± 0.20	CTBP	14[d]	0	$1^5/_6$
$Mn_6(CO)_{15}{}^+$	5.6 ± 1.2	CTBP	12	0	$2^1/_6$
$Mn_6(CO)_{16}{}^+$	4.9 ± 0.9	CTBP	12	0	$1^5/_6$
$Mn_6(CO)_{18}{}^+$	0.52 ± 0.18	CTBP	12	0	$1^1/_6$
$Mn_6(CO)_{19}{}^+$	<0.28	CTBP	12	0	$^5/_6$
$Mn_6(CO)_{20}{}^+$	3.9 ± 1.5	TrBP	12	3[e]	$1^1/_2$
$Mn_6(CO)_{21}{}^+$	<0.15	TrBP	12	3[e]	$1^1/_6$
$Mn_7(CO)_{25}{}^+$	<0.28	COc	15	1	0
$Mn_8(CO)_{24}{}^+$	<0.28	BOc	18	1	$^7/_8$
$Mn_8(CO)_{25}{}^+$	<0.28	BOc	18	1	$^5/_8$

[a] In arbitrary units. [b] Except as noted, the number of metal–metal bonds in the indicated closed polyhedron of metal atoms with the bonds along the edges. [c] Except as noted, the minimum value of X consistent with the indicated structure and the modified effective atomic number rule.[4] [d] Assuming multiple metal–metal bonds as discussed in the text. [e] Assuming distorted structures because of ligand crowding as discussed in the text. [f] Abbreviations: L, linear; T, triangle; B, bent; Tet, tetrahedron; R, Rhombus; TBP, trigonal bipyramid; CTBP, capped trigonal bipyramid; TrBP, tetragonal bipyramid; COc, capped octahedron; BOc, bicapped octahedron.
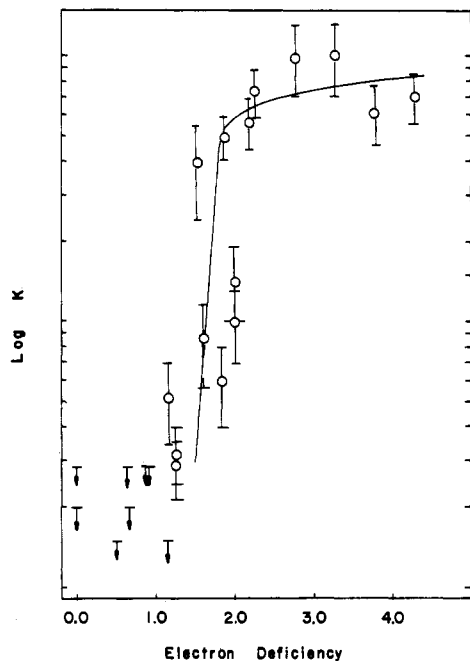
Figure 4. Relative rate constants for reaction of $M_n(CO)_m{}^+$ ($M = Mn$) ions with $Mn_2(CO)_{10}$ vs. electron deficiency.

Figure 5. Relative rate constants for reaction of $M_n(CO)_m{}^+$ ($M = Re$, Mn) ions with $ReMn(CO)_{10}$ vs. electron deficiency.

and is determined by rules outlined by Teo.[4] The X variable is introduced to account for the possibility of delocalized bonding in the larger clusters.

The relative rate constants for reaction of the cluster ions in $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$ are listed in Tables VI and VII, respectively. As with $Re_2(CO)_{10}{}^2$ the rate constants were determined from spectra taken at varying trapping times. From this data plots of ion abundance as a function of time were prepared. Rate constants for the disappearance of the clusters were determined from the portions of the time vs. abundance plots where there was exponential decay. The exponential decay was taken as evidence that the cluster in question was no longer being formed but was only reacting. An ion that is both being formed and reacting should vary nonexponentially with time. Also listed in

these tables are electron deficiencies determined from eq 6. Generally, closed-polyhedral structures were assumed so that the electron deficiencies listed are the smallest values consistent with the observed stoichiometries and the modified effective atomic number rule. Exceptions to this are discussed below.

The expected behavior is that the relative rate constants should increase with electron deficiency until $D \approx 2$. At that point the cluster has on the average a vacancy for one two-electron donor at each metal atom. Such a cluster should react efficiently, and the relative rate constant should remain approximately at the collision rate as D increases beyond 2. This behavior was observed for the cluster ions in $Re_2(CO)_{10}$. Figures 4 and 5 show that in a general way this behavior is also observed for the cluster ions in $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$ provided certain structural assumptions are made. In general, the assumptions made were the same as those for analogous clusters in $Re_2(CO)_{10}$. There are four exceptions: $Mn_3(CO)_{10}{}^+$, $Mn_4(CO)_{15}{}^+$, $Mn_6(CO)_{14}{}^+$, and $Mn_6(CO)_{19}{}^+$. Before discussing these cases, we consider briefly some effects important in determining metal cluster structures.

Table VII. Electron Deficiencies and Relative Rate Constants for Reactions of $M_n(CO)_m^+$ (M = Re, Mn) Ions with $ReMn(CO)_{10}$

stoichiometry	rel rate constant[a]	structure[f]	metal–metal bonds[b]	X^c	electron deficiency
$Re_2Mn(CO)_6^+$	5.4 ± 0.7	T	3	0	$5^1/_3$
$Re_2Mn(CO)_{10}^+$	1.0 ± 0.4	T	4^d	0	2
$Re_2Mn_2(CO)_6^+$	5.3 ± 0.7	Tet	6	0	$5^1/_4$
$Re_2Mn_2(CO)_7^+$	5.2 ± 0.7	Tet	6	0	$4^3/_4$
$Re_2Mn_2(CO)_8^+$	4.2 ± 0.7	Tet	6	0	$4^1/_4$
$Re_2Mn_2(CO)_9^+$	6.0 ± 0.7	Tet	6	0	$3^3/_4$
$Re_2Mn_2(CO)_{10}^+$	6.4 ± 0.7	Tet	6	0	$3^1/_4$
$Re_2Mn_2(CO)_{11}^+$	5.5 ± 0.7	Tet	6	0	$2^3/_4$
$Re_2Mn_2(CO)_{12}^+$	5.3 ± 0.7	Tet	6	0	$2^1/_4$
$Re_2Mn_2(CO)_{13}^+$	1.8 ± 0.4	Tet	6	0	$1^3/_4$
$Re_2Mn_2(CO)_{14}^+$	0.41 ± 0.06	Tet	6	0	$1^1/_4$
$Re_2Mn_2(CO)_{15}^+$	0.82 ± 0.10	R	5^e	0	$1^1/_4$
$ReMn_3(CO)_{15}^+$	0.31 ± 0.07	R	5^e	0	$1^1/_4$
$Re_3Mn_2(CO)_{14}^+$	1.1 ± 0.3	TBP	9	0	2
$Re_3Mn_2(CO)_{15}^+$	0.81 ± 0.20	TBP	9	0	$1^3/_5$
$Re_3Mn_3(CO)_{14}^+$	0.73 ± 0.17	CTBP	14^d	0	$1^5/_6$
$Re_3Mn_3(CO)_{17}^+$	0.54 ± 0.16	CTBP	12	0	$1^1/_2$
$Re_3Mn_3(CO)_{18}^+$	0.41 ± 0.09	CTBP	12	0	$1^1/_6$
$Re_4Mn_2(CO)_{18}^+$	0.28 ± 0.08	CTBP	12	0	$1^1/_6$
$Re_3Mn_3(CO)_{19}^+$	1.9 ± 0.6	TrBP	12	3^e	$1^5/_6$

[a] In arbitrary units. [b] Except as noted, the number of metal–metal bonds in the indicated closed polyhedron of metal atoms with the bonds along the edges. [c] Except as noted, the minimum value of X consistent with the indicated structure and the modified effective atomic number rule.[4] [d] Assuming multiple metal–metal bonds as discussed in the text. [e] Assuming distorted structures because of ligand crowding as discussed in the text. [f] For definitions of abbreviations, see footnote f of Table VI.

Delocalized bonding can make it possible for a metal cluster to accommodate more electrons in bonding orbitals than would be expected on the basis of the simple effective number rule. Teo's modified effective atomic number rule,[4] mentioned above, accounts for that effect in a semiempirical way by introducing a parameter X into the basic electron-counting equation. The quantity X is the excess number of electron pairs that the cluster can accept in bonding orbitals because of delocalized bonding. In the $Re_2(CO)_{10}$ case the behavior of several of the clusters was consistent with $X \neq 0$ as expected from Teo's rules.[4]

Multiple bonds, especially in highly unsaturated metal clusters, can be important. Lauher points out that multiply bonded clusters might be expected in the Cr, Mn, and Fe triads.[16] The $Re_4(CO)_{12}H_4$ molecule has two double bonds,[17] for example. A double bond in a metal cluster would reduce the number of ligands required for coordinative saturation. It was not necessary to postulate that any of the clusters formed in $Re_2(CO)_{10}$ have multiple bonds to explain their kinetic behavior. Nevertheless, some of the highly unsaturated clusters could have multiple bonds.

The packing of carbonyl ligands around the metal cluster can have an important effect on the bonding in the cluster. Benfield and Johnson point out many metal carbonyl structures that can be rationalized by considering arrangements of CO ligands which minimize the steric crowding around the metal core.[18] The cluster can be pictured as concentric polyhedra. The outer polyhedron is formed by carbonyl ligands, and the inner polyhedron is formed from the metal atoms. The two polyhedra arrange themselves to provide the lowest energy compromise of metal–metal and metal–ligand bonding. For a metal polyhedron geometry which has the steric limit of carbonyl ligands around it, this effect could cause addition of a carbonyl ligand to actually increase coordinative unsaturation and electron deficiency. The enlargement of the polyhedron of carbonyls could result in a rearrangement of the inner polyhedron of metal atoms. Metal–metal bonding might decrease in favor of stronger metal–ligand bonding. In fact, addition of a CO ligand might result in breaking one or more metal–metal bonds and opening up the cluster, making it more susceptible to reactions. This might be expected to occur only for certain stoichiometries where there is just the right balance between the size of the metal core and the size of the polyhedron of carbonyl ligands.

The effects of delocalized bonding, multiple bonding, and ligand crowding are seen in the structures of stable metal clusters in the condensed phase. Many of the clusters formed in the gas-phase processes described here are much more highly unsaturated than any stable clusters that can be prepared in the condensed phase. It might be expected that the highly unsaturated gas-phase clusters might exhibit properties not evident in condensed-phase stable clusters. Another regime in which highly unsaturated metal centers may be examined is that of clean metal surfaces. Various properties of the surface may be examined as a function of the fraction of ligand sites occupied. This is similar to the present results, where reaction rate constants for $M_6(CO)_n^+$ clusters, for example, are examined as a function of n, the number of ligands attached to the metal cluster. Thus, metal surfaces might be better models for gas-phase metal clusters than the stable condensed-phase clusters. There are, of course, important features unique to metal surfaces, most notably a highly delocalized electronic structure. Nonetheless, it is instructive to note some features of the behavior of metal surfaces that change with fraction of sites occupied, Θ. Most importantly, properties of the surface do not change in a simple linear fashion with Θ.[19] At small values of Θ adsorbed molecules dissociate extensively. At large values of Θ there are a number of changes as a result of ligand crowding. It has recently been discovered that as Θ increases from zero but is well below $\Theta = 1$ for H_2 and CO on tungsten and molybdenum surfaces there is a change in the geometry of the surface layer of metal atoms.[19,20] There are attendant sharp changes in properties like the work function and the heat of adsorption.[19-21] This appears to be a local phenomenon similar to a Jahn–Teller distortion. Other surfaces exhibit dramatic changes in ligand mobility as Θ increases.[19] These surface behaviors suggest that properties of highly coordinatively unsaturated clusters might change discontinuously with increasing saturation as a result of electronic effects or changes in bonding mode. As the clusters approach saturation, we might expect to see ligand-crowding effects.

These structural effects are not all independent, and other effects might be discussed. The effects are also difficult to treat quantitatively. The fact of the matter is that no simple scheme accounts comprehensively for the great variety of metal cluster structures observed. The effects specified above are, nonetheless, useful in discussing the cluster ions that exhibit exceptional kinetic behavior.

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The ions that behave in an exceptional manner fall into two categories. $M_3(CO)_{10}^+$ and $M_6(CO)_{14}^+$ have electron deficiencies of $2^2/_3$ and $2^1/_2$, assuming closed-polyhedral structures and no double bonds. These ions react more slowly than expected for highly unsaturated ions. $M_4(CO)_{15}^+$ and $M_6(CO)_{19}^+$ have electron deficiencies of $^3/_4$ and $^5/_6$, assuming closed-polyhedral structures and no delocalized bonding ($X = 0$). These ions react more rapidly than expected for ions near coordinative saturation. We suggest below possible structural reasons for these behaviors.

$M_3(CO)_{10}^+$. Two ions with $M_3(CO)_{10}^+$ stoichiometry were observed: $Mn_3(CO)_{10}^+$ in $Mn_2(CO)_{10}$ and $Re_2Mn(CO)_{10}^+$ in $ReMn(CO)_{10}$. No $Re_3(CO)_{10}^+$ was observed in $Re_2(CO)_{10}$. The observed ions react more slowly by a factor of 5 or more than other ions with electron deficiencies as large as $2^2/_3$. If it is assumed that there are four metal–metal bonds in $M_3(CO)_{10}^+$ rather than three, the electron deficiency becomes 2, which is more nearly consistent with the kinetic behavior of these ions. The points for the $M_3(CO)_{10}^+$ ions in Figures 4 and 5 were plotted for electron deficiencies of 2. There is precedent for a double metal–metal bond in an M_3 cluster,[16] but other effects might be at work here. There is the possibility of CO dissociation as observed on metal surfaces or one or more η^4-CO ligands bound between two metal atoms. This would perhaps decrease the steric accessibility of the metals, but it might change the reactivity in other ways. There is no chemical evidence of CO dissociation. There is no evidence for loss of an O atom or CO_2 in any of the observed reactions, for example. Another possibility is that 10 CO ligands electronically stabilize an M_3 cluster in a way that is roughly akin to the stabilization of certain structures of Mo and W surfaces by partial saturation of the surface with adsorbate.[19] We make no attempt here to be specific or quantitative about this speculation but think it useful to point out the possibility of an analogy. The exceptional behavior of $M_3(CO)_{10}^+$ is quite probably of structural origin, whatever the specific cause. Particularly significant in this respect is that two ions with different group 7[22] metal atoms show the behavior.

$M_6(CO)_{14}^+$. Three ions of this stoichiometry were observed: $Mn_6(CO)_{14}^+$ in $Mn_2(CO)_{10}$, $Re_3Mn_3(CO)_{14}^+$ in $ReMn(CO)_{10}$, and $Re_6(CO)_{14}^+$ in $Re_2(CO)_{10}$.[2] The two Mn-containing ions react more slowly by a factor of 8 or more than would be expected for ions with an electron deficiency as large as $2^1/_2$. The rate constants are more consistent with electron deficiencies of 2. If the metal clusters were capped trigonal bipyramids with 12 metal–metal single bonds and two additional bonds because of multiple metal–metal bonding, they would have an electron deficiency of 2. As in the case of $M_3(CO)_{10}^+$ other effects might be at work here as well. Dissociation of CO or η^4 bonding of CO might occur and might then stabilize the clusters. There is no direct evidence for this, however. Subtle electronic effects could be involved such as those that produce adsorbate-sensitive structural changes in metal surfaces. Particularly interesting is the fact that $Re_6(CO)_{14}^{+2}$ and $Mn_6(CO)_{15}^+$ react rapidly, as expected for highly unsaturated species. This suggests that if it is a structural feature that decreases the reactivity of the $M_6(CO)_{14}^+$ species, it must be a subtle structural feature. Actually a subtle feature could well be sufficient since a change in activation energy of 6 kJ mol^{-1} is all that is required for an order of magnitude change in the rate constant. We note that adsorbate-induced structural changes in metal surfaces are quite sensitive to adsorbate coverage and temperature. For example, changing the H atom coverage of a W(100) surface from $\Theta = 0.4$ to $\Theta = 0.5$ (where saturation is $\Theta = 2$) changes the hydrogen desorption energy by ~20 kcal mol^{-1}.[19] While acknowledging the weaknesses in the analogy between this surface and the present clusters, we point to this as an example where the behavior of highly unsaturated metal surfaces is very sensitive to the extent of saturation. We note that the change in the desorption energy is accompanied by a change in the structure of the surface layer of metal atoms. Again, we do not attempt to extract anything specific or quantitative from the surface analogy but point to it as a possibly useful example. It seems quite probable that the exceptional behavior of the $M_6(CO)_{14}^+$ ions is structurally inherent. This is supported by the fact that two different $M_6(CO)_{14}^+$ species exhibit the exceptional behavior.

$M_4(CO)_{15}^+$. Four ions of this stoichiometry were observed: $Mn_4(CO)_{15}^+$ in $Mn_2(CO)_{10}$, $ReMn_3(CO)_{15}^+$ and $Re_2Mn_2(CO)_{15}^+$ in $ReMn(CO)_{10}$, and $Re_4(CO)_{15}^+$ in $Re_2(CO)_{10}$.[2] The three Mn-containing clusters are slightly more reactive relative to $M_4(CO)_{15}^+$ clusters than would be expected for a cluster with an electron deficiency of $^3/_4$ (that corresponding to a $M_4(CO)_{15}^+$ cluster with a tetrahedral structure and six M–M bonds). A plausible explanation for this is that CO crowding enlarges the ligand shell to the point that metal–ligand interactions with a tetrahedral metal core are weakened. The metal core therefore opens to a rhomboidal structure sacrificing perhaps one metal–metal bond to better metal–ligand interactions. The more open structure might be somewhat more susceptible to reaction. There are other possibilities, but this one is relatively simple and consistent with ligand-crowding effects observed in condensed-phase clusters.[18] The fact that the effect is seen in three different $M_4(CO)_{14}^+$ ions tends to support a common structural cause. Only upper limits were obtained on the rate constants for $Re_4(CO)_{14}^+$ and $Re_4(CO)_{15}^+$,[2] so we cannot tell if their behavior parallels that of the Mn-containing $M_4(CO)_{14}^+$ and $M_4(CO)_{15}^+$ clusters.

$M_6(CO)_{19}^+$. Three ions of this stoichiometry were observed: $Mn_6(CO)_{19}^+$ in $Mn_2(CO)_{10}$, $Re_3Mn_3(CO)_{19}^+$ in $ReMn(CO)_{10}$, and $Re_6(CO)_{19}^+$ in $Re_2(CO)_{10}$.[2] The Re-containing ions are more reactive than expected for a cluster with an electron deficiency of $^5/_6$. $Mn_6(CO)_{19}^+$ does not show anomalous reactivity, but $Mn_6(CO)_{20}^+$ does. Again, ligand crowding is a simple, plausible explanation. The metal may open up to interact more strongly with the ligand shell whose size is determined by ligand–ligand repulsions. The resulting structure could be more susceptible to reaction. It is possible that, rather than reducing the number of metal–metal bonds, the distortion produces an increase in delocalized bonding corresponding to a change in X. An X value of 3 is a possibility for a distorted tetragonal bipyramid.[4] A distortion of this kind could also increase reactivity. A structural origin for the anomalous reactivity is suggested by the fact that it is exhibited by three different ions: $Re_6(CO)_{19}^+$, $Re_3Mn_3(CO)_{19}^+$, and $Mn_6(CO)_{20}^+$. It is interesting that the reactive $Mn_6(CO)_{20}^+$ cluster has one more ligand than the other two reactive clusters. This could result from a difference in the size of the metal cores of the clusters or perhaps a difference in the balance between M–M bond strengths and M–CO bond strengths.

Summary and Conclusions

The ions formed by electron impact on $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$ react with their neutral parents to form metal carbonyl cluster ions. Sequential reactions produce clusters containing as many as eight metal atoms. Generally clusters containing the same number of Re and Mn atoms were formed in $ReMn(CO)_{10}$. The relative rate constants for the clustering reactions tend to decrease with coordinative saturation. Clusters with more ligands tend to react more slowly than clusters with fewer ligands. In fact, there is a correlation between the rate constants and the electron deficiencies of the clusters. Clusters with electron deficiencies of 2 or more per metal atom tend to react rapidly while the rate constants drop off for clusters with electron deficiencies less than 2. The electron deficiencies were calculated by assuming closed-polyhedral structures for the metal atoms in the clusters with metal–metal bonds along the edges and the modified effective atomic number rules.[4] Generally this suggests the clustering reactions require vacant sites in the coordination shells of the metal atoms in the reactant ion and produce closed-polyhedral metal structures.

There are several interesting exceptions to the overall pattern. Four clusters with high electron deficiencies are much less reactive

(22) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

than expected. All four ions contain Mn and on the basis of closed-polyhedral structures without double bonds have electron deficiencies of $2^1/_2$ or $2^2/_3$. In fact, all clusters which satisfy that description are relatively unreactive. We speculate that these ions are stabilized by electronic effects perhaps related to those associated with adsorbate-induced structural changes observed on metal surfaces. Six clusters with low electron deficiencies were more reactive than expected. With one exception, these reactive clusters have on the basis of closed-polyhedral structures and no delocalized bonding ($X = 0$) electron deficiencies of $^3/_4$ or $^5/_6$. The interesting exception is $Mn_6(CO)_{20}{}^+$ in $Mn_2(CO)_{10}$ with an $X = 0$ electron deficiency of $^1/_2$. In $ReMn(CO)_{10}$ and $Re_2(CO)_{10}$ it is the $M_6(CO)_{19}{}^+$ ions that are anomalously reactive. We speculate that these reactive ions have open or distorted structures

forced upon them by ligand crowding around the central metal core. The open structures are then more susceptible to reaction. We note that these exceptional cases are the only ones of the 76 clusters observed in this and the previous study[2] of clustering reactions in the group 7 metal carbonyls.

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One- and Two-Electron Chemistry in the Reaction of Nitrogen Dioxide and Nitrosyl Halides with Binuclear Pyrophosphito Complexes of Platinum(II) and Platinum(III)

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Nitrogen dioxide adds to the bridged binuclear Pt(II)–Pt(II) complex $Pt_2(P_2O_5H_2)_4{}^{4-}$ to give the Pt(III)–Pt(III) complex $Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-}$. The NO$_2$ ligands coordinate the axial positions in this Pt(III)–Pt(III) complex, and this has been confirmed by X-ray crystallography. Crystals grown from an acidic aqueous solution of $Pt_2(P_2O_5H_2)_4{}^{4-}$ and NaNO$_2$ have the formula $H_{40}N_2O_{42}P_8Pt_2Na_8$. The compound crystallizes in the monoclinic space group $C2/c$ with $a = 13.958$ (3) Å, $b = 19.413$ (2) Å, $c = 15.538$ (5) Å, $\beta = 106.19$ (2)°, and $Z = 4$. The molecular structure shows respective Pt–Pt and Pt–N distances of 2.7333 (3) and 2.153 (6) Å, with half the ligand protons replaced by hydrated sodium ions. Reductive elimination of NO$_2$ gives $Pt_2(P_2O_5H_2)_4{}^{4-}$. Halide ion X$^-$ (X = Cl, Br) reacts with $Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-}$ to give $Pt_2(P_2O_5H_2)_4X(NO_2)^{4-}$. Excess iodide ion gives $Pt_2(P_2O_5H_2)_4I_2{}^{4-}$, and 1 equiv of *N*-iodosuccinimide reacts with $Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-}$ to give $Pt_2(P_2O_5H_2)_4I(NO_2)^{4-}$. Nitric oxide does not add to $Pt_2(P_2O_5H_2)_4{}^{4-}$, and nitrosyl chloride gives $Pt_2(P_2O_5H_2)_4Cl_2{}^{4-}$. Carbonylation of $Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-}$ gives CO$_2$ and $Pt_2(P_2O_5H_2)_4{}^{4-}$ with no observable nitrosyl intermediate.

The coordination chemistry of platinum is dominated by complexes with Pt in oxidation states 0, II, and IV.[2] Interconversions between these complexes involve two-electron changes, and consequently, reactions of monomeric platinum complexes with one-electron reagents have received considerably less study.[3] Nevertheless, for multimetallic chain complexes of platinum the odd-electron mixed-valence compounds are quite commonly found, because the paramagnetic form is stabilized by intermetallic delocalization.[4] Using the delocalization concept with binuclear complexes, we have carried out pairwise one-electron oxidations at each platinum in the Pt(II)–Pt(II) complex $Pt_2(P_2O_5H_2)_4{}^{4-}$ in the presence of Cl$^-$ to convert it to the Pt(III)–Pt(III) complex $Pt_2(P_2O_5H_2)_4Cl_2{}^{4-}$ with outer-sphere oxidants.[5] This next paper now describes the reactions of the binuclear complex $Pt_2(P_2O_5H_2)_4{}^{4-}$ with the one-electron *inner*-sphere oxidant NO$_2$, and for the first time, we show how addition and elimination reactions of the stable NO$_2$ radical can be used to interconvert between Pt(II)–Pt(II) and Pt(III)–Pt(III) complexes.[6] Lippard et al. have

used nitrous acid to convert Pt(II)–Pt(II) complexes into axially disubstituted nitro Pt(III)–Pt(III) complexes.[7] With Lippard's μ-pyridonato complexes, however, NO$_2$ elimination does not appear to be facile, and this paper for the first time shows how to prepare Pt(III)–Pt(III) complexes with both nitro and halo ligands in the axial positions.

Experimental Section

^{31}P NMR spectra were measured at 80.98 MHz on a Nicolet NTC 200 NMR spectrometer. Samples were dissolved in D$_2$O contained in 12-mm tubes. Chemical shifts are reported in ppm with positive shifts to high frequency of 85% H$_3$PO$_4$. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Model 383 spectrometer. Reagents and solvents were commercial samples and were used without further purification. The complex K$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$]·2H$_2$O was prepared by the literature method,[8] and solutions of this compound and K$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$X$_2$] are strongly acidic.

K$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$(NO$_2$)$_2$] (1). Method A. The complex K$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$]·2H$_2$O (200 mg, 0.17 mmol) was dissolved in deionized water (3 mL). Nitrogen dioxide was slowly bubbled through the solution for 10 min, during which time the solution turned from green to orange-brown. The reaction is complete when no green emission (514 nm) is observable.[8] Dropwise addition of acetone (20 mL) precipitated the complex as an orange powder, which was filtered and air-dried; yield 110 mg (51%). A

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