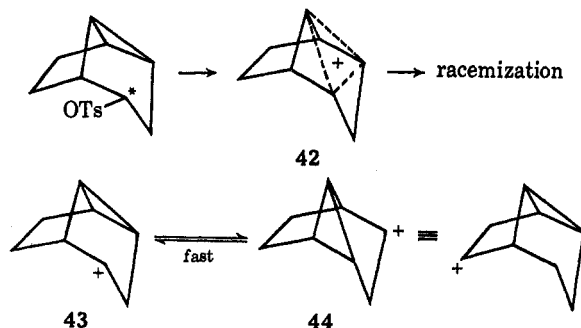
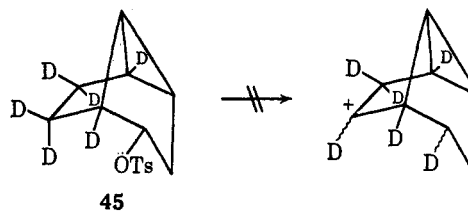


acid production (evidence for internal return). Complete racemization was observed. Our experiments showed that remaining activity, if any, was less than 2.2% in buffered acetolysis and 2.3% in buffered hydrolysis. The racemization indicates that the reaction proceeds through a symmetrical trishomocyclopropenyl cation (42), rapidly interconverting unsymmetrical cations (43 and 44), or the occurrence of the 1,3-hydride shift from C₅ to C₃. The properly polydeuterated material 45 was prepared, and its acetolysis ruled out the 1,3-hydride shift.



Our findings so far obtained are not direct evidence for the existence of the trishomocyclopropenyl ion, but



it is possible to accommodate all the results simply and economically by the formulation of the nonclassical structure. Most theories and concepts of chemistry are still built empirically by the accumulation of experimental evidence.

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Mass Spectra of Some Organometallic Molecules

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The impact of mass spectrometry in inorganic systems is just becoming apparent. The time lag between the surge of interest in the use of this technique in organic chemistry and in inorganic chemistry does not reflect the relative importance of this field in the two divisions of chemistry but more the difficulties of handling metal-containing compounds in conventional instruments. However, in our opinion, the effect of using metal complexes on the lifetime of the sources has been overemphasized in the past, and the obvious potential in this field of study is now beginning to be realized.

There are three main fields of interest in the study of inorganic systems, namely (see Figure 1): (i) the determination of molecular weights and, from isotopic patterns, with many systems, the detail composition of the molecule; (ii) the relationships between fragmentation pattern and structure; (iii) the determination of appearance and ionization potentials and the relative bond energies of similar molecules.

We have been mainly concerned with groups i and ii, although we are now involved with a study of some systems of class iii.

It is perhaps important to premise any discussion of the results obtained by emphasizing some of the main dangers that may be encountered in mass spectroscopic studies of inorganic systems. (a) In the determination of molecular weight data, it is assumed that the highest mass peak observed is the parent ion peak. In general this is true, but occasionally with electron-impact studies the parent peak is not observed; in these instances it is often possible to deduce the molecular weight from a detailed examination of the remainder of the spectrum (see discussion of hydrido metal carbonyl compounds). Alternatively, the spectrum may be determined using a field emission source, which will often give the parent ion peak. (b) The probe temperature may rise as high as 300°, a temperature at which many inorganic compounds thermally decompose or polymerize (see, for example, manganese carbonyl sulfide systems).¹ Experiments carried out with chromium carbonyl indicate that the metal produced in decomposition of the carbonyl catalytically de-

(1) K. Edgar, B. F. G. Johnson, J. Lewis, and J. M. Wilson, *J. Chem. Soc., Sect. A*, 379 (1967).

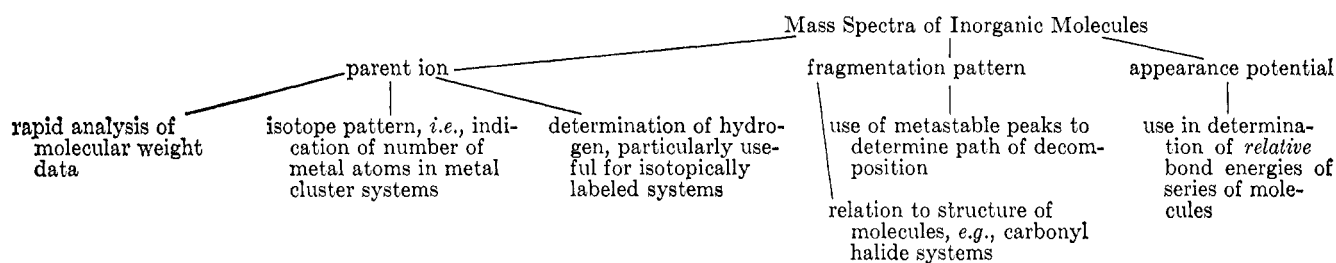


Figure 1. Application of mass spectrometry to organometallic systems.

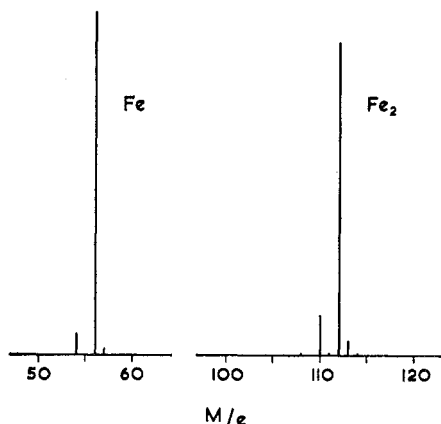


Figure 2. Isotope patterns for $[\text{Fe}]^+$ and $[\text{Fe}_2]^+$.

composes subsequent samples, at a lower temperature. (c) If the compound being studied contains a volatile impurity this will be liberated first and may be the only spectrum observed.

It is therefore of importance with respect to possibilities a-c to run spectra of complexes under a variety of conditions and operating temperatures and ensure reproducibility of the spectra.

Perhaps one of the most important points to emphasize is that, in mass spectrometry, we are investigating the properties of ionized species in which the relative abundances of the species observed may be mainly kinetically controlled, and it is dangerous to draw too many conclusions concerning the thermodynamic properties of the un-ionized parent molecule. Thus, although in most carbonyl compounds ready loss of carbon monoxide occurs, this does not necessarily indicate that carbon monoxide is weakly bonded in the neutral molecule.

A restriction that applies to mass spectrometric studies is that the compound under investigation must have an appreciable vapor pressure below 300° . This generally limits the study to covalent compounds, although occasionally ionic compounds have been studied, e.g., $\text{Cs}[\text{Y}(\text{CF}_3\text{COCH}_2\text{COCF}_3)_4]$.² This account summarizes some of our applications of mass spectrometry to (1) transition-metal hydride compounds; (2) bridging and terminal metal carbonyl halides; (3) detection of metal-metal bonds; and (4) polynuclear metal carbonyls.

Metal Hydrides

As stated above, mass spectrometry offers the tremendous advantage of accurate determination of

molecular weight. Furthermore, since most metallic elements are polyisotopic, recourse to an accurate mass measurement in the identification of ions is often unnecessary. Consider, for example, the ion m/e 224 which occurs in the spectrum of $\text{Fe}_2(\text{CO})_9$. Due to the presence of the three isotopes of iron, this may be clearly identified as $[\text{Fe}_2(\text{CO})_4]^+$ and not $[\text{Fe}(\text{CO})_6]^+$ from a consideration of the isotope peaks associated with this ion (see Figure 2). These facilities offer great practical utility in the identification of metal hydride compounds since one of the major difficulties encountered with compounds of this type is the determination of the number of hydrogen atoms present per molecule. This has been clearly demonstrated with $\text{H}_3\text{Mn}(\text{CO})_{12}$ and $\text{H}_3\text{Re}(\text{CO})_{12}$.^{3,4} We were interested in investigating (i) the feasibility of obtaining accurate molecular weight data for compounds of this type and (ii) any relationships between fragmentation pattern and structure, with particular reference to any which would allow a differentiation between terminal and bridging hydrido ligands.

To date, few transition-metal hydrides have been studied by mass spectrometric techniques. Wilkinson and his coworkers⁵ have used mass spectral data as a method of detecting the presence of hydrogen in the ruthenium carbonyl hydride, $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$, but were only able to detect two of the four hydrogens in the complex. James, *et al.*,⁶ established the presence of the hydrogen ligand in the molecule $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{H})\text{BH}_4$ from mass spectral measurements. The mass spectrum of $\text{HMn}(\text{CO})_5$ ⁷ has been reported in some detail, and very recently the spectra of the polynuclear compounds $\text{HRe}_3(\text{CO})_{14}$,⁸ $\text{HMnRe}_2(\text{CO})_{14}$,⁸ $\text{HFeCo}_3(\text{CO})_{12}$,⁹ and $\text{HRuCo}_3(\text{CO})_{12}$ ⁹ have been discussed.

We were concerned with investigating the general utility of this method. For this reason we have examined a range of well-characterized hydrido compounds. These include both mononuclear and poly-

(3) B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *J. Organometal. Chem.* (Amsterdam) **10**, 105 (1967), references therein.

(4) J. M. Smith, W. Fellman, and L. H. Jones, *Inorg. Chem.*, **4**, 1361 (1965); H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).

(5) J. W. S. Jamieson, J. V. Kingston, and G. Wilkinson, *Chem. Commun.*, 569 (1966).

(6) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *ibid.*, 849 (1966).

(7) W. F. Edgell and W. M. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 5451 (1966).

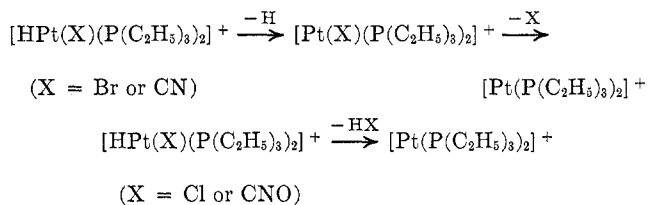
(8) W. Fellman and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 63 (1966).

(9) M. J. Mays and R. N. F. Simpson, *Chem. Commun.*, 1024 (1967).

(2) S. J. Lippard, *J. Am. Chem. Soc.*, **88**, 4300 (1966).

ion $(p - 1)^+$ also occurs in high abundance, and it is reasonable to assume that these compounds fragment with the stepwise loss of hydrogen atoms before fission of the cyclopentadienyl ring system occurs. In the spectra of all the cyclopentadienyl compounds examined, ions of the type $[C_3H_xM]^+$ ($x = 1-3$) were observed in fairly high abundance.

The hydridoplatinum compounds *trans*-Pt(H)(X)-(P(C₂H₅)₃)₂ have been well characterized. The mass spectra of these derivatives depend upon X. In all cases parent ions are observed, but where X = CNO or Cl no ion $(p - 1)^+$ is observed, and the next ion in the fragmentation process corresponds to $(p - HX)^+$.



This may be, of course, a purely kinetic effect.

Polynuclear Hydrides. Structural details on neutral polynuclear hydrides are very limited. To date only three crystal structures are known, *viz.*, HMnRe₂(CO)₁₄,¹² Mo₂(CO)₄[P(CH₃)₂](H)(C₅H₅)₂,¹³ and B₂H₇Mn₃(CO)₁₀¹⁴ (Figures 4-6). The mass spectra of HRe₃(CO)₁₄ and HMnRe₂(CO)₁₄ have been reported previously.¹⁵

In the mass spectra of H₃Mn₃(CO)₁₂¹⁶ and H₃Re₃(CO)₁₂¹⁷ (Figure 7) the parent molecular ion [H₃M₃(CO)₁₂]⁺ is observed, confirming their formulation as trimeric hydrides. Furthermore, the isotopic pattern observed for the rhenium compound (p^+) is consistent with the presence of three rhenium atoms per molecule (Figure 8). With the manganese compound the parent ion is observed in only low abundance ($\sim 2\%$) and appears to be temperature dependent, the relative abundance decreasing as the temperature is raised. However, the related ions [H₃Mn₃(CO)₄]⁺ and [H₃Mn₂(CO)]⁺ occur in appreciable amounts (18 and 90%, respectively), allowing a ready confirmation of the presence of three hydrogens. Monomeric ions [HMn(CO)]⁺ and [Mn(CO)]⁺ are also present, although few dimeric ions were observed. In contrast, with H₃Re₃(CO)₁₂ the parent ion occurs in high abundance (82%), as do other trimeric ions [H_mRe₃(CO)_m]⁺ ($m = 0-3$, $n = 0-12$); dimeric and monomeric ions are not observed in significant amounts. The stability

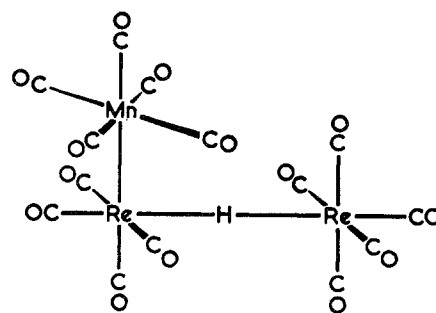


Figure 4. Structure of HMnRe₂(CO)₁₄.

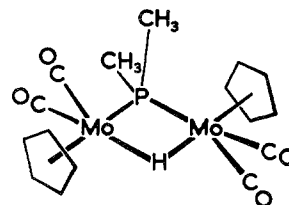


Figure 5. Structure of HMo₂(CO)₄[P(CH₃)₂](C₅H₅)₂.

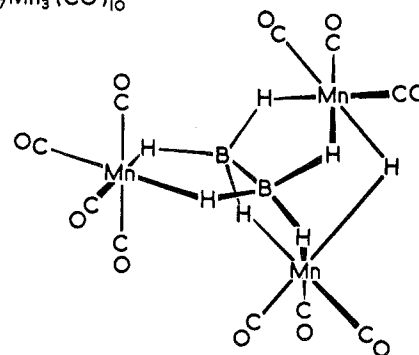
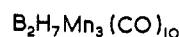


Figure 6. Structure of B₂H₇Mn₃(CO)₁₀.

of the Re₃ cluster follows the trend established for related systems (see below). Monomeric ions with more than four carbonyl groups per metal were not observed in either case. This observation is consistent with a cyclic structure involving four terminal CO groups per metal atom.

The structure of the borohydride compound H₇B₂Mn₃(CO)₁₀ has been determined by Dahl and his co-workers¹⁴ (Figure 6). Here again the parent molecular ion was observed. Stepwise loss of ten carbonyl groups then occurs, giving the ions [H₇B₂Mn₃(CO)_m]⁺ ($m = 1-10$). It is important to note that loss of H atoms does not take place until the removal of several CO groups. The first loss of hydrogen is observed from the ion [H₇B₂Mn₃(CO)₆]⁺ when the ion [H₅B₂Mn₃(CO)₆]⁺ is observed. This behavior is noted for the series of ions [H₇B₂Mn₃(CO)_m]⁺ and [H₅B₂Mn₃(CO)_m]⁺ ($m = 1-6$). At low m/e values the patterns become more complex due to the overlap of several hydrido species such as [H_xB₂Mn₃(CO)]⁺ ($x = 0-7$). Also, since

(12) M. R. Churchill and R. Brau, *Inorg. Chem.*, **6**, 2086 (1967).

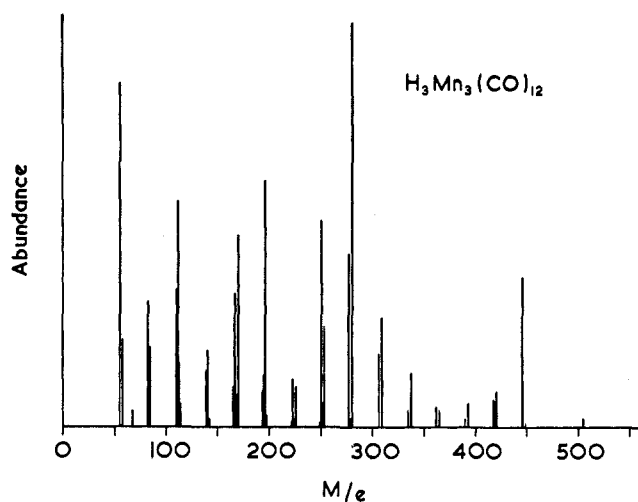
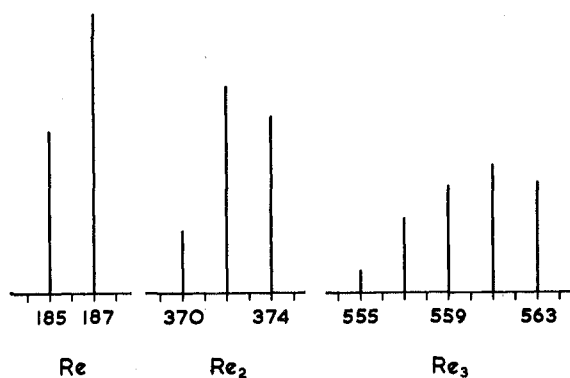
(13) R. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

(14) H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *ibid.*, **87**, 2753 (1965).

(15) J. M. Smith, K. Mehner, and H. D. Kaesz, *ibid.*, **89**, 1759 (1967).

(16) W. Fellman, D. K. Huggins, and H. D. Kaesz, Proceedings of the VIIIth International Conference on Coordination Chemistry, Vienna, 1964; E. O. Fischer and R. Altmann, *J. Organometal. Chem. (Amsterdam)*, **10**, 1 (1967); B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *ibid.*, **10**, 105 (1967).

(17) D. K. Huggins, W. Fellman, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).

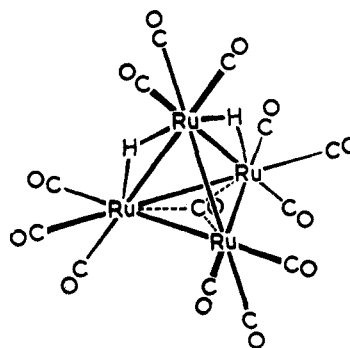
Figure 7. Mass spectrum of $\text{H}_3\text{Mn}_3(\text{CO})_{12}$.Figure 8. Isotope patterns for $[\text{Re}]^+$, $[\text{Re}_2]^+$, and $[\text{Re}_3]^+$.

manganese is monoisotopic, it is difficult to differentiate between mononuclear, dinuclear, and trinuclear ions without resorting to accurate mass measurement. Thus the ions $[\text{HMn}(\text{CO})_2]^+ = [\text{Mn}_2]^+$, etc., would occur at the same m/e values.

Recently, we have prepared the hydrido compounds α - and β - $\text{H}_4\text{M}_4(\text{CO})_{12}$ and $\text{H}_2\text{M}_4(\text{CO})_{13}$ ($\text{M} = \text{Ru}$ or Os) from the reaction of acid on the anions produced by the action of base on the carbonyl $\text{M}_3(\text{CO})_{12}$.^{5,18,19} The structures of the carbonyl hydrides are unknown; however, they are isoelectronic with $\text{Rh}_4(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$, respectively, and it is reasonable to assume that these structures will be based on a tetrahedral arrangement of four metal atoms. No bridging CO bands or metal-hydrogen bands are observed in the infrared spectra of the $\text{H}_4\text{M}_4(\text{CO})_{12}$ compounds, and on this basis it is believed that they have a pseudo- $\text{Ir}_4(\text{CO})_{12}$ structure with four bridging hydrido ligands (Figure 9). In the mass spectra, no parent ion is observed with $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ in either the α or β forms; indeed, the spectra are similar. However, ions containing at least three hydrido ligands are observed at

(18) B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *Chem. Commun.*, 851 (1966); B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc., Sect. A*, in press.

(19) B. F. G. Johnson, P. W. Kilty, and J. Lewis, *Chem. Commun.*, 180 (1968).

Figure 9a. Possible structure of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$.

lower m/e values. With $\text{H}_4\text{Os}_4(\text{CO})_{12}$ the parent ion is observed in reasonable abundance. No loss of H from $\text{H}_4\text{Os}_4(\text{CO})_{12}$ is observed until four carbonyl groups have been lost. With $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ and $\text{H}_2\text{Os}_4(\text{CO})_{13}$ parent ions are observed in both cases. Here again no loss of H radical is observed until several carbonyl groups have been removed.

Our attempts to determine the mass spectra of the bridged hydrides $\text{HMn}_2(\text{CO})_8\text{P}(\text{C}_6\text{H}_5)_2$ ²⁰ and $\text{HFe}_2(\text{CO})_2(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_2$ ²¹ were not successful, and only the fragment ions of the phosphine $(\text{C}_6\text{H}_5)_2\text{PH}$ was recorded.

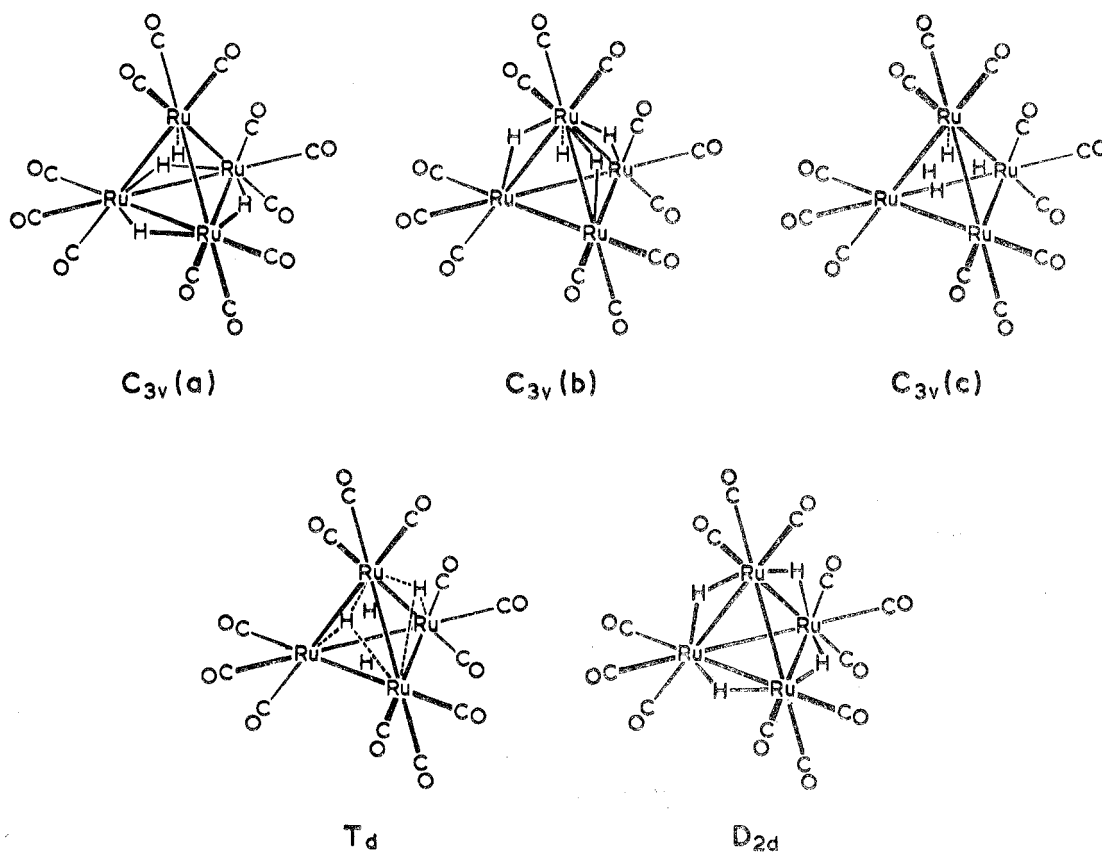
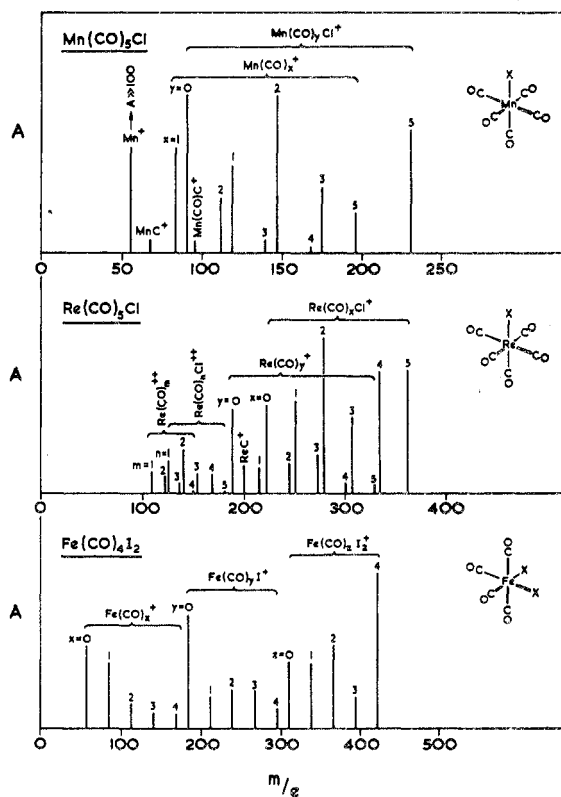
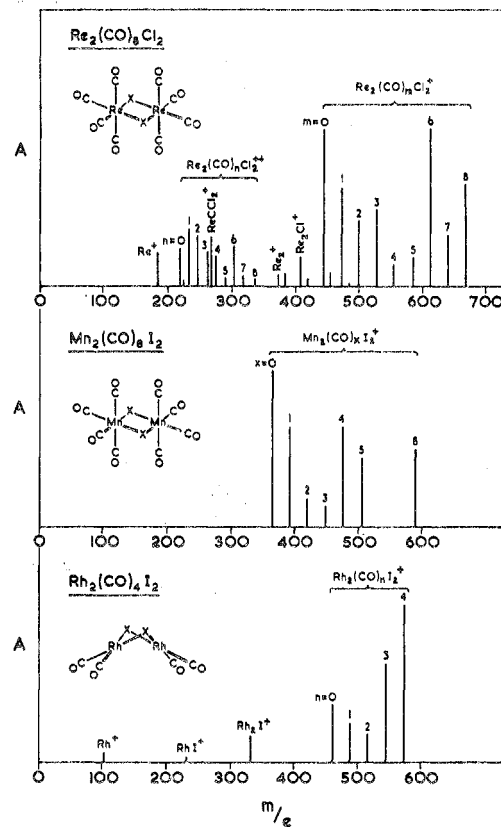
Kaesz and his coworkers¹⁵ have measured the mass spectra of $\text{HRe}_3(\text{CO})_{14}$ and $\text{HMnRe}_2(\text{CO})_{14}$. The structure of $\text{HMnRe}_2(\text{CO})_{14}$ has been determined, and it is believed to involve a Re-H-Re bridging system (Figure 4). In the spectrum of $\text{HRe}_3(\text{CO})_{14}$ stepwise loss of 14 CO groups is observed; however, no loss of hydrogen is observed except from the ions $[\text{HRe}_3(\text{CO})_2]^+$, $[\text{HRe}_3(\text{CO})]^+$, and $[\text{HRe}_3]^+$. The spectrum of $\text{HMnRe}_2(\text{CO})_{14}$ is similar. Very recently, the mass spectra of $\text{HFeO}_3(\text{CO})_{12}$ and $\text{HRuCo}_3(\text{CO})_{12}$ have been briefly mentioned;¹⁰ no loss of hydrogen from the parent ion is observed in either case. Thus, on the basis of our work and that of other workers the following points emerge: (1) with one exception, *viz.*, α - and β - $\text{M}_4\text{Ru}_4(\text{CO})_{12}$, parent molecular ions are observed in all cases allowing a convenient and accurate determination of the number of hydrogens present per molecule of compound; (2) compounds containing terminally bonded hydrogens may be differentiated from those containing bridging ligands by examination of their respective fragmentation patterns which are similar to those observed with terminal and bridging halide systems.

Bridging and Terminal Metal Carbonyl Halides

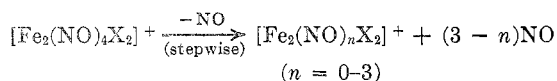
As part of our initial studies in mass spectrometry, we examined the spectra of a series of metal carbonyl halide derivatives. The compounds examined fall into two main classes, *viz.* (i) those containing terminal bonded halogens, *e.g.*, the mononuclear carbonyl halides of manganese and rhenium, $\text{M}(\text{CO})_5\text{X}$ ($\text{M} =$

(20) M. L. H. Green and J. T. Moelwyn-Hughes, *Z. Naturforsch.*, 17b, 783 (1962).

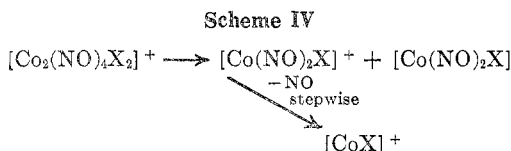
(21) J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, 11, 599 (1958).

Figure 9b. Possible structure of $H_4Ru_4(CO)_{12}$.Figure 10. Mass spectra of $M(CO)_5X$ compounds.Figure 11. Mass spectra of $M_2(CO)_8X_2$ compounds.

volves the successive removal of the nitrosyl groups before fragmentation of the Fe_2X_2 nucleus takes place.



In marked contrast, for the cobalt complexes the parent ion peak intensity is very much lower, the most abundant ions being mononuclear. In this case the predominant fragmentation scheme involves the cleavage of the dimeric molecule into the monomeric units $[\text{Co}(\text{NO})_2\text{X}]^+$ and $[\text{Co}(\text{NO})_2\text{X}]$ with subsequent fragmentation of the $[\text{Co}(\text{NO})_2\text{X}]^+$ ion (Scheme IV).



The results obtained for the bridged nitrosyl systems differ from those obtained for the bridged carbonyl compounds discussed above. With the carbonyl compounds complete loss of CO radicals occurs before rupture of the M_2X_2 nucleus takes place. Obviously, in systems of this type two possible fragmentation paths are visualized, *viz.*, loss of the terminal groups or fission into mononuclear species. From our studies of nitrosyl carbonyl compounds²² it appears that CO groups are more readily lost than nitrosyl groups in the decomposition of ions. This may be correlated with the fact that removal of a nitric oxide group requires a three-electron transfer whereas the removal of a carbon monoxide group requires only a two-electron transfer. The *primary* step of the preferential cleavage of the metal halide bridge in the $\text{Co}_2(\text{NO})_4\text{X}_2$ compounds may, therefore, be correlated with the higher stability of the metal-nitric oxide unit, and the increased stability of the Fe_2X_2 nucleus in $\text{Fe}_2(\text{NO})_4\text{X}_2$ may then be associated with the electron spin-coupling interaction between the iron atoms which stabilizes the cluster relative to the loss of nitric oxide. The significant difference in the primary fragmentation pattern for cobalt nitrosyl halides, metal carbonyl halides, and the iron nitrosyl halides may then be related to the presence of the "metal-metal" interaction in the iron complexes.

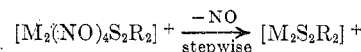
Consistent with this view, Dahl and his coworkers²³ have recently shown that in the compounds $(\text{C}_6\text{H}_5)_2\text{Co}_2(\text{P}(\text{C}_6\text{H}_5)_2)_2$ and $(\text{C}_6\text{H}_5)_2\text{Ni}_2(\text{P}(\text{C}_6\text{H}_5)_2)_2$, which bear this type of relationship to one another, the "metal-metal" interaction is sufficient not only to reduce the metal-metal distance from a nonbonding value of 3.36 Å in the nickel complex to a bonding value of 2.56 Å with the cobalt complex but also to completely change the molecular configuration. Obviously this metal-metal interaction is not weak and must be much larger than

the minimum of 2 to 3 kcal required for diamagnetism in systems of this type.

Metal Nitrosyl Thiol Compounds. In all cases the mass spectra confirm the dimeric nature of the complexes. With these compounds, however, the metal-sulfur ring structure appears to be the most stable group ring in the molecule, and the decomposition pattern is more dependent on the nature of the side chain of the thiol than on the metal ion.

In the spectrum of $\text{Co}_2(\text{NO})_4\text{S}_2(\text{C}_6\text{H}_5)_2$ there is a high abundance of dimeric ions which occur by the progressive loss of NO groups followed by ejection of phenyl groups. In addition, however, small amounts of the monomeric ions $[\text{Co}(\text{NO})_2\text{SC}_6\text{H}_5]^+$, $[\text{Co}(\text{NO})\text{SC}_6\text{H}_5]^+$, and $[\text{CoSC}_6\text{H}_5]^+$ are observed. The corresponding iron derivative does not show this behavior, there being no mononuclear ions in the spectrum. In fact, the stability of the $\text{Fe}_2\text{S}_2(\text{C}_6\text{H}_5)_2$ unit is reflected in the appearance of the doubly charged ion $[\text{Fe}_2\text{S}_2(\text{C}_6\text{H}_5)_2]^{2+}$. The behavior of these complexes can therefore be related to the corresponding halide compounds, and this difference in behavior is associated, in part at least, with the presence of the metal-metal interaction in the iron complexes.

For the ethyl and butyl nitrosyl complexes the spectra of the iron and cobalt derivatives are essentially the same, the predominant dissociation being the consecutive loss of NO groups with the preservation of the M_2S_2 nucleus.



Metal Carbonyls

The previous work in this field has been concerned with the carbonyl compounds of chromium, molybdenum, tungsten, iron, nickel, cobalt, and manganese.²⁴ More recently other studies of rhenium,²⁵ cobalt, iron, and ruthenium carbonyls¹⁰ have been reported. In our studies we have examined the homonuclear carbonyls of manganese, $\text{Mn}_2(\text{CO})_{10}$; rhenium, $\text{Re}_2(\text{CO})_{10}$; iron, $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$; ruthenium, $\text{Ru}_3(\text{CO})_{12}$; osmium, $\text{Os}_3(\text{CO})_{12}$; cobalt, $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$; rhodium, $\text{Rh}_4(\text{CO})_{12}$;²⁶ and iridium, $\text{Ir}_4(\text{CO})_{12}$;²² and the heteronuclear carbonyls $\text{MnRe}(\text{CO})_{10}$,²⁶ $\text{Ru}_2\text{Os}(\text{CO})_{12}$, $\text{RuOs}_2(\text{CO})_{12}$,²² and $\text{Mn}_2\text{Fe}(\text{CO})_{14}$.^{22,27}

Winters and Kiser²⁴ have shown that under electron impact the mononuclear metal carbonyls are first singly ionized and then progressively lose carbon monoxide until the metal cation is obtained. The binuclear carbonyls of cobalt and manganese also decompose in this way to give the ions Co_2^+ and Mn_2^+ , and may also at any stage of the process break into two mononuclear fragments, one charged and one neutral (*e.g.*, see Scheme V). Our studies indicate that this progressive loss

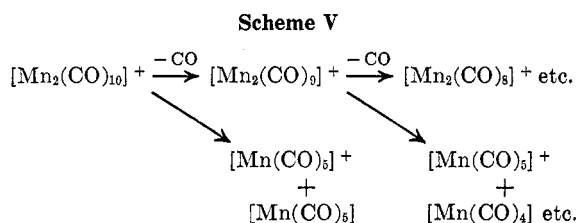
(22) B. F. G. Johnson, J. Lewis, and I. G. Williams, to be published.
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of carbon monoxide from the parent ion is a common feature with all polynuclear metal carbonyls but that the cleavage of the metal cluster is dependent upon the metal, and this tendency decreases rapidly in the order first row < second row << third row metal. Ions of the type $[\text{M}(\text{CO})_x\text{C}]^+$ are fairly common for the heavier transition metals; however, no ions of the type $[\text{M}(\text{CO})_x\text{O}]^+$ have been observed. It is generally accepted that bonding of the carbon monoxide group occurs to the metal through the carbon; these observations are consistent with this view, and it would appear that, even under the high-energy conditions operative in the mass spectrometer, no tendency to reverse this bonding pattern occurs.

Dinuclear Metal Carbonyls. $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, $\text{MnRe}(\text{CO})_{10}$, $\text{Fe}_2(\text{CO})_9$, and $\text{Co}_2(\text{CO})_8$ have been examined. These compounds fall into two distinctive types: those with bridging CO groups, *e.g.*, $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$ (Figure 13), and those in which the two halves of the molecule are joined solely by a metal-metal bond, *e.g.* $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ (Figure 14). The crystal structures of all these carbonyls have been established.²⁸

The spectrum of dimanganese decacarbonyl reported here differs from that obtained by Winters and Kiser²⁴ only in that we detected the ions $[\text{Mn}_2(\text{CO})_9]^+$ and $[\text{Mn}_2(\text{CO})_7]^+$. With $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, and $\text{MnRe}(\text{CO})_{10}$ consecutive loss of ten carbonyl groups is observed to give $[\text{M}_2]^+$. Cleavage into monomeric units is also observed, but this tendency falls off rapidly in going from $\text{Mn}_2(\text{CO})_{10}$ to $\text{Re}_2(\text{CO})_{10}$. Thus, on summation of abundance it can be shown that 59% of the ion fragments from $\text{Mn}_2(\text{CO})_{10}$ contain two metal atoms; this rises to 79% in $\text{MnRe}(\text{CO})_{10}$ and to 96% in $\text{Re}_2(\text{CO})_{10}$. With $\text{MnRe}(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ the isotope pattern of rhenium enables doubly charged ions to be clearly identified, whereas there are no ions of this type in the spectrum of $\text{Mn}_2(\text{CO})_{10}$. This may be related to the more common occurrence of metal-metal bonding in higher oxidation states of rhenium as opposed to manganese. Another feature of the spectra of $\text{MnRe}(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ is the relatively high abundance of ions such as $[\text{MnRe}(\text{CO})_x\text{C}]^+$ or $[\text{Re}(\text{CO})_x\text{C}]^+$; as found with other metal carbonyls, the abundance of these ions increases steadily as x falls. The appearance of suitable metastable peaks in the spectrum of $\text{Re}_2(\text{CO})_{10}$ allows us to conclude that both monometallic and bimetallic ions decompose with stepwise loss of carbon monoxide radicals. Rearrange-

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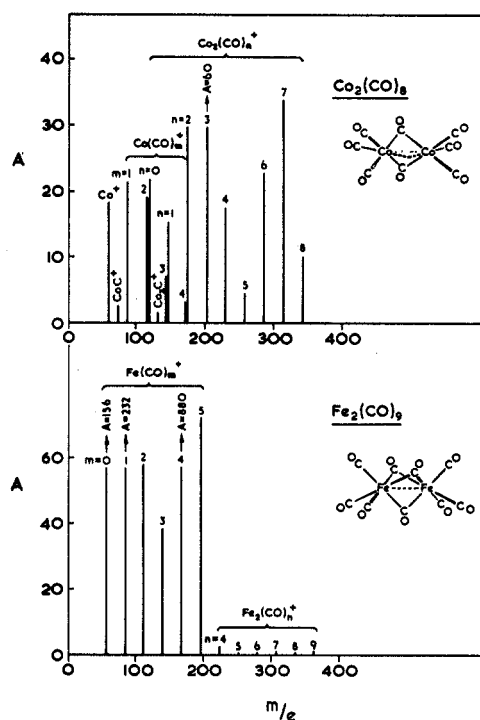


Figure 13. Mass spectra of $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$.

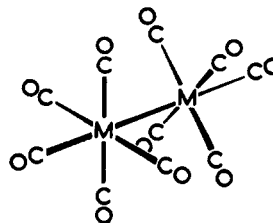
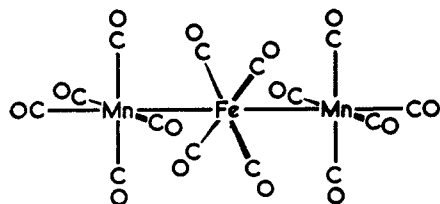


Figure 14. Structure of $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}$ or Re).

ment ions of the type $[\text{M}(\text{CO})_6]^+$ are not observed in the spectra of either $\text{Mn}_2(\text{CO})_{10}$ or $\text{Re}_2(\text{CO})_{10}$; however, the ion $[\text{Re}(\text{CO})_6]^+$ is observed in significant amounts in the spectrum of $\text{MnRe}(\text{CO})_{10}$. The migration of CO groups from the lighter to the heavier metal in the heteronuclear carbonyls as opposed to no migration in the homonuclear species has been attributed to the fact that the Re-C bond (2.07 eV) is stronger than the Mn-C bond (1.02 eV). Thus for the ion $[\text{MnRe}(\text{CO})_{10}]^+$ transfer of a CO from the manganese to rhenium can lead to a gain in bond energy.²⁵ On this basis we would not anticipate CO transfer in homonuclear systems.

The spectrum of $\text{Fe}_2(\text{CO})_9$ (Figure 13) clearly indicates that iron enneacarbonyl is a dimer in the gas phase and is consistent with the molecular weight data found for solutions in iron pentacarbonyl. No evidence was found for a higher polymeric form such as might be suggested by its general chemical inactivity and insolubility. The appearance of the ion $[\text{Fe}(\text{CO})_5]^+$ agrees with the presence of bridging carbonyl groups. The parent ion, $[\text{Fe}_2(\text{CO})_9]^+$, and the related ions $[\text{Fe}_2(\text{CO})_m]^+$ ($m = 0-8$) are observed; however, these occur in low abundances. On the other

Figure 16. Possible structure of $\text{Mn}_2\text{Fe}(\text{CO})_{14}$.

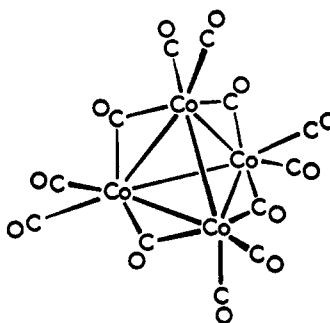
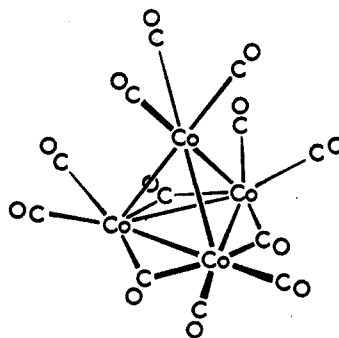
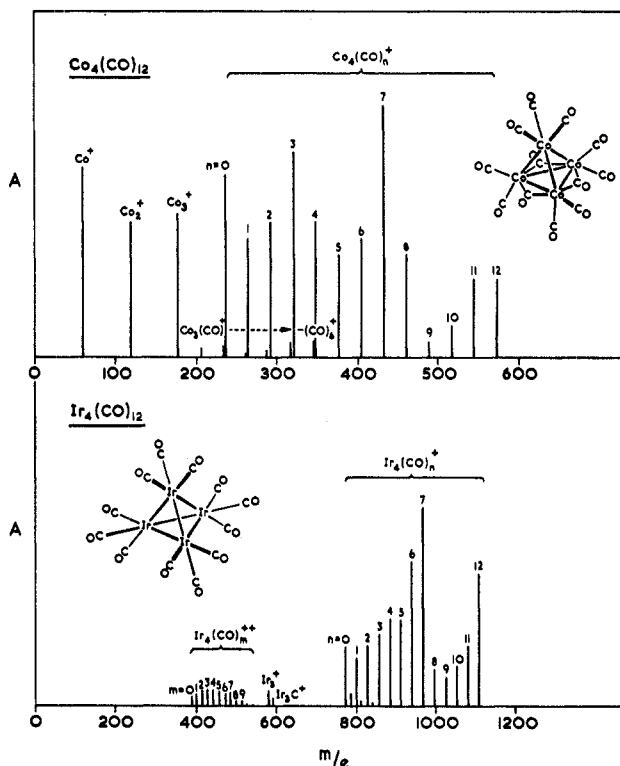
and binuclear and mononuclear species for 5 and 2%, respectively. The corresponding figures for $\text{Fe}_3(\text{CO})_{12}$ are 36, 4, and 60%. With $\text{Os}_3(\text{CO})_{12}$ neither dinuclear nor mononuclear ions were observed. Thus, these spectra follow the same trend as those of manganese and rhenium decacarbonyl and support the view that metal clusters become increasingly resistant to fragmentation down a transition-metal group. The appearance of $[\text{Os}_3(\text{CO})_n]^{2+}$ ($n = 0-12$) and $[\text{Ru}_3]^{2+}$ may be correlated with the stability of heavy metal clusters toward increased oxidation.

As the structure of $\text{Ru}_3(\text{CO})_{12}$ does not involve a ruthenium atom bonded to more than four carbonyl groups the possible appearance of $[\text{Ru}(\text{CO})_5]^+$ was of interest. Only very weak peaks ($\sim 0.05\%$) occurred in the mass range 236-244 expected for $[\text{Ru}(\text{CO})_5]^+$, and we may conclude that no significant amount of this ion is produced. This is not only consistent with the known structure of the parent compound but further confirms that carbonyl groups show no tendency to migrate in homonuclear metal carbonyls during fragmentation. The significance of $[\text{Fe}(\text{CO})_5]^+$ in the discussion of $\text{Fe}_3(\text{CO})_{12}$ is thus enhanced.

The mixed polynuclear carbonyls $\text{RuOs}_2(\text{CO})_{12}$ and $\text{Ru}_2\text{Os}(\text{CO})_{12}$ have been prepared.³¹ These have been shown to be isomorphous with $\text{Os}_3(\text{CO})_{12}$, and their infrared spectra are consistent with the absence of bridging CO groups. Their spectra are very similar to that of $\text{Os}_3(\text{CO})_{12}$: consecutive loss of twelve CO groups is observed in each case to give the trinuclear cluster ion $[\text{RuOs}_2]^+$ or $[\text{Ru}_2\text{Os}]^+$. No bi- or mononuclear ions were observed.

Few, neutral, linear trinuclear metal carbonyls are known. One of the best examples of this group is $\text{Mn}_2\text{Fe}(\text{CO})_{14}$;²⁷ crystal structure determination of this compound is not complete. The structure is believed to consist of a linear array of the three metal atoms with 14 terminal CO groups (Figure 16). The mass spectrum contains all possible trinuclear ions $[\text{Mn}_2\text{Fe}(\text{CO})_m]^+$ ($m = 0-14$), together with significant amounts of dinuclear and mononuclear species. Dinuclear ions of the type $[\text{MnFe}(\text{CO})_n]^+$ are common, but no ions containing two manganese atoms were observed, suggesting that no cyclic intermediate is produced during fragmentation. As anticipated, two types of mononuclear ions, $[\text{Mn}(\text{CO})_x]^+$ and $[\text{Fe}(\text{CO})_y]^+$, were observed. It is significant that the ion $[\text{Mn}(\text{CO})_6]^+$ was not observed, and no evidence of CO migration from the iron atom to the manganese

(31) B. F. G. Johnson, J. Lewis, and I. G. Williams, unpublished observations.

Figure 17. Structure of $\text{Co}_4(\text{CO})_{12}$ (C_{3v} and D_{2d}).Figure 18. Mass spectra of $\text{Co}_4(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$.

was obtained. However, the possibility of CO migration from the manganese to the iron cannot be entirely ruled out since ions corresponding to $[\text{Fe}_2(\text{CO})_8]^+$ were observed; however, it is possible that some thermal decomposition to produce $\text{Fe}_2(\text{CO})_9$ was taking place in the spectrometer, and subsequently some of the ions $[\text{Fe}(\text{CO})_y]^+$ ($y = 0-5$) may arise as a result of this

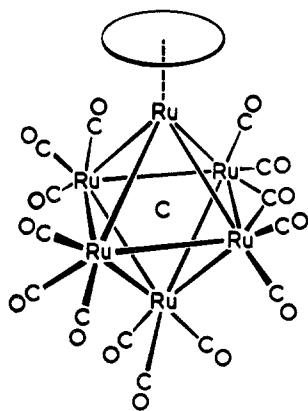


Figure 19. Structure of $\text{Ru}_6\text{C}(\text{CO})_{14}[(\text{CH}_3)_3\text{C}_6\text{H}_3]$.

decomposition path. Studies on other heteronuclear systems of this type are in progress.

Tetranuclear Metal Carbonyls. The tetranuclear carbonyls, $\text{M}_4(\text{CO})_{12}$, of cobalt, rhodium, and iridium are well-established compounds. Although there has been considerable speculation as to the structure of $\text{Co}_4(\text{CO})_{12}$, it has finally been resolved for the solid state³² (Figure 17). The main features of this molecule are the basal triangle of $\text{Co}_3(\text{CO})_9$, which contains three bridging CO groups linking the three cobalt atoms, and the over-all molecular symmetry C_{3v} . The structure of this compound in solution, however, remains uncertain.³³ On the basis of infrared data a D_{2d} molecular configuration is preferred, although the results obtained for ^{59}Co nmr measurements indicate that the C_{3v} configuration is retained³³ (Figure 18). From infrared data $\text{Rh}_4(\text{CO})_{12}$ is believed to be similar to $\text{Co}_4(\text{CO})_{12}$ (in solution).³² $\text{Ir}_4(\text{CO})_{12}$ is different, however, and following the trend observed in the iron triad has a structure (Figure 18) involving no bridging CO groups.³²

The mass spectra of the cobalt and iridium compounds are shown in Figure 18. In each case stepwise loss of 12 CO groups was observed, followed by breakdown of the M_4 cluster to give M_3^+ , M_2^+ , and M^+ . Apart from the appearance of the trimeric ions $[\text{Co}_3(\text{CO})_n]^+$ ($n = 0-6$) in low abundance with $\text{Co}_4(\text{CO})_{12}$, the spectra of $\text{Co}_4(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$ were very similar, and no further structural information concerning bridging CO groups was obtained in contrast to $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$. $\text{Rh}_4(\text{CO})_{12}$ decomposed rapidly in the spectrometer, and only limited information was obtained. This was sufficient, however, to confirm the

tetrameric formulation $\text{Rh}_4(\text{CO})_{12}$ and suggest that the fragmentation pattern is similar to those of the cobalt and rhodium analogs.

From these studies on the polynuclear metal carbonyls the following points emerge: (1) parent molecular ions are observed in all cases; (2) loss of CO occurs in a stepwise fashion to give ultimately the polynuclear metal cation; (3) CO transfer does not occur in homonuclear systems; (4) ions of the type $[\text{M}(\text{CO})_x\text{C}]^+$ are fairly common for the heavier transition metals but only appear after several CO groups have been ejected; (5) no ions of the type $[\text{M}(\text{CO})_x\text{O}]^+$ are observed, consistent with the view that CO is bonded *via* the carbon in all carbonyls studied.

We have been able to utilize this information in the identification of a number of new polynuclear carbonyl compounds. The recently reported carbide complexes of ruthenium,³⁴ $\text{Ru}_6\text{C}(\text{CO})_{17}$ and $\text{Ru}_6\text{C}(\text{CO})_{14}(\text{arene})$ [arene = $\text{CH}_3\text{C}_6\text{H}_5$, $(\text{CH}_3)_2\text{C}_6\text{H}_4$, or $(\text{CH}_3)_3\text{C}_6\text{H}_3$], provide an especially good example of the value of mass spectrometry in the determination of the molecular formula of "unusual" organometallic complexes. The differentiation between, *e.g.*, $\text{Ru}_6\text{C}(\text{CO})_{17}$ and $\text{Ru}_6(\text{CO})_{18}$ would be difficult by analytical and other usual techniques. However, the appearance of the ion $[\text{Ru}_6\text{C}(\text{CO})_{17}]^+$ and the related ions $[\text{Ru}_6\text{C}(\text{CO})_n]^+$ ($n = 0-16$) is consistent with the formulation of this compound as a "carbide" compound. This is further supported by observation 4 (see above) that in *all* other polynuclear carbonyls examined "carbide" ions are not produced until several CO groups have been removed from the parent ion. It is significant that a recent X-ray study of the mesitylene complex, $\text{Ru}_6\text{C}(\text{CO})_{14}[\text{C}_6\text{H}_3(\text{CH}_3)_3]$, has fully confirmed our formulation (Figure 19).³⁵

Conclusion

This account emphasizes the general utility of mass spectrometry to a variety of structural problems in inorganic chemistry. The main approach is essentially one of correlation of fragmentation pattern with known molecular structure and suffers from the disadvantage that the structures assumed are from crystallographic data whereas the spectra are obtained from gaseous samples. The main advantage offered by this technique is the rapid determination of accurate molecular weights and molecular formulas. This is obviously a technique which is rapidly gaining popularity in a wide field of interest.

(32) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

(33) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966), and references therein.

(34) B. F. G. Johnson, R. D. Johnston, and J. Lewis, *Chem. Commun.*, 1057 (1967).

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