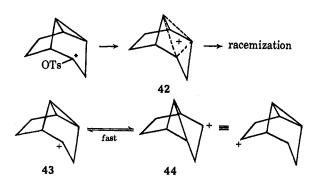
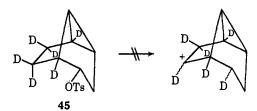
acid production (evidence for internal return). Complete racemization was observed. Our experiments showed that remaining activity, if any, was less than 2.2% in buffered acetolysis and 2.3% in buffered hydrolysis. The racemization indicates that the reaction proceeds through a symmetrical trishomocyclopropenyl cation (42), rapidly interconverting unsymmetrical cations (43 and 44), or the occurrence of the 1,3-hydride shift from C_5 to C_8 . 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.

This paper is based on lectures given at Universität München, Università di Roma, École Nationale Supérieure de Chimie, Institut de Chimie des Substances Naturelles, Université D'Aix-Marseille, Harvard University, State University of New York at Albany, University of Ottawa, Case Western Reserve University, Michigan State University, Loyola University, University of California at Santa Cruz, and University of Alberta during the fall of 1967. The author thanks Professors R. Huisgen, G. Illuminati, M. Julia, H. Felkin, B. Waegell, P. D. Bartlett, W. D. Closson, R. R. Fraser, G. A. Olah, H. Hart, J. W. Wilt, J. F. Bunnett, and S. Masamune of the respective universities and, in addition, Professor M. Hanack of Tübingen for their invitations, hospitality, and helpful discussions. It is a pleasure to acknowledge the contribution of my coworkers, whose names are to be found in the references.

Mass Spectra of Some Organometallic Molecules

J. LEWIS AND B. F. G. JOHNSON

Department of Chemistry, University College, London, W.C. 1, England
Received March 28, 1968

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).

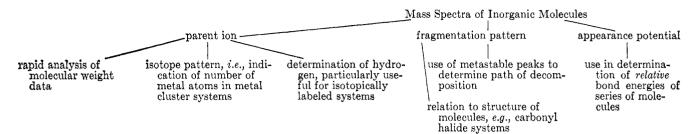


Figure 1. Application of mass spectrometry to organometallic systems.

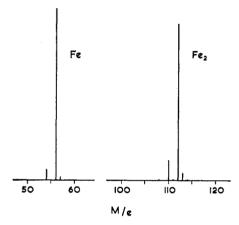


Figure 2. Isotope patterns for [Fe] + and [Fe2] +.

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., Cs[Y(CF₃COCH₂COCF₃)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

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

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 $Fe_2(CO)_9$. Due to the presence of the three isotopes of iron, this may be clearly identified as $[Fe_2(CO)_4]^+$ and not $[Fe(CO)_6]^+$ 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 $H_3Mn_3(CO)_{12}$ and $H_3Re_3(CO)_{12}$. 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, α -H₄Ru₄(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 $(C_5H_5)_2Zr(H)BH_4$ from mass spectral measurements. The mass spectrum of $HMn(CO)_5$ ⁷ has been reported in some detail, and very recently the spectra of the polynuclear compounds $HRe_3(CO)_{14}$,⁸ $HMnRe_2(CO)_{14}$,⁸ $HFeCo_3(CO)_{12}$,⁹ and $HRuCo_3(CO)_{12}$, 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).

nuclear derivatives and were of various types ranging from the acidic carbonyl hydrides, e.g., HMn(CO)₅, HRe(CO)₅, and HCo(CO)₄, to the basic cyclopentadienyl hydrides, e.g., (C₅H₅)₂ReH and (C₅H₅)₂WH₂. We will discuss the mononuclear and polynuclear compounds separately.

Mononuclear Hydrides. With all the mononuclear hydrides, parent molecular ions were observed, confirming their formulation in all cases. The simplest spectra were observed with the carbonyl compounds HMn(CO)₅, HRe(CO)₅, and HCo(CO)₄ (Figure 3). The spectrum of HMn(CO)₅ has been reported previously by Edgell and Risen.⁷ Their spectrum differed from ours in that they observed no metastable peaks; however, by analogy with other carbonyl systems, they suggested that competitive loss of hydrogen and carbon monoxide groups was taking place. In our spectrum metastable peaks were observed, and we were able to confirm the suggested mechanism (Scheme I). The spectra

$$[HMn(CO)_{\delta}] + \xrightarrow{CO} [HMn(CO)_{4}] + \xrightarrow{-4CO} [MnH] + \xrightarrow{-5CO} [Mn] +$$

$$[Mn(CO)_{\delta}] + \xrightarrow{-5CO} [Mn] +$$

of HRe(CO)₅ and HCo(CO)₄ were similar except that no metastable peaks were observed. In a comparison of the manganese and rhenium compounds, the ratio of hydrogen-containing metal ions to the total ion abundance has been determined. The value of 48% with HMn(CO)₅ increases to 60% with HRe(CO)₅, and it is tempting to equate these figures with a more stable metal-hydrogen bond with the rhenium compound; however, as mentioned above, it must be realized that these figures may merely reflect the rate at which the fragmentation takes place.

With the weakly acidic cyclopentadienyl compounds $HM_0(CO)_3(C_5H_5)$ and $HW(CO)_3(C_5H_5)$, consecutive loss of CO and H radicals is again observed, to give ultimately the ion [M(C₅H₅)]+. Fission of this ion then occurs to give $[MC_xH_y]^+$ (x = 1-5; y = x). Again, a comparison of the hydrogen-containing metal ions was made. In this case the figures obtained were similar, being 70% with HMo(CO)₃(C₅H₅) and 75% with HW(CO)₃(C₅H₅). King¹⁰ has reported that in the spectrum of $(C_5H_5)_2Cr_2(CO)_6$ two of the most intense peaks correspond to the ions [C₅H₅Cr(CO)₃]+ and [C₅H₅Cr(CO)₃H]+. The mechanism by which the hydrido ion was produced was unknown. We examined the spectra of the molybdenum and tungsten analogs, therefore, to investigate whether or not this is a general phenomenon with compounds of this type. In both cases the ion [(C₅H₅)M(CO)₈H]+ was observed in very small amounts, as were the ions [(C₅H₅)M- $(CO)_nH$]⁺ (n = 0-2). In the absence of metastable peaks it is not possible to decide the mechanism by

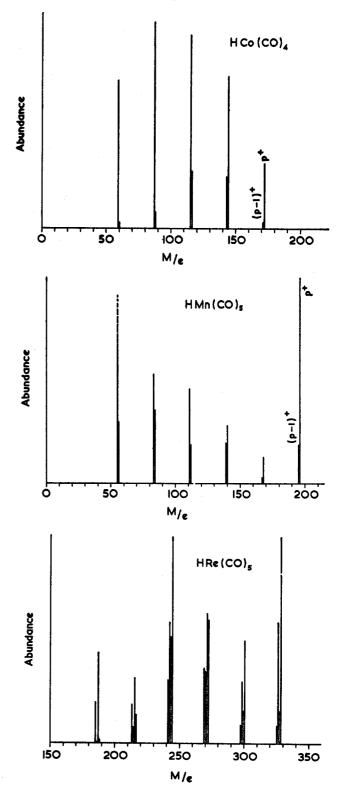


Figure 3. Mass spectra of HMn(CO)₅, HRe(CO)₅, and HCo-(CO)₄.

which this hydrogen transfer takes place. In the iron derivative (C₅H₅)₂Fe₂(CO)₄ no hydrido ions were observed.

In the spectra of the more basic compounds $(C_5H_5)_2$ -ReH and $(C_5H_5)_2WH_2$, parent ions were observed in high abundance. This has been previously noted by Fischer and his coworkers¹¹ with $(C_5H_5)_2TcH$. The

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)⁺.

$$\begin{split} [HPt(X)(P(C_2H_5)_3)_2] &\overset{-H}{\longrightarrow} [Pt(X)(P(C_2H_5)_3)_2] \overset{-X}{\longrightarrow} \\ (X = Br \ or \ CN) & [Pt(P(C_2H_5)_3)_2] \overset{+}{\longrightarrow} \\ [HPt(X)(P(C_2H_5)_3)_2] &\overset{-HX}{\longrightarrow} [Pt(P(C_2H_5)_3)_2] \overset{+}{\longrightarrow} \\ (X = Cl \ or \ CNO) \end{split}$$

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 B₂H₇-Mn₃ $(CO)_{10}$ (Figures 4–6). The mass spectra of HRe₃- $(CO)_{14}$ and HMnRe₂ $(CO)_{14}$ have been reported previously. 15

In the mass spectra of $H_3Mn_3(CO)_{12}^{16}$ and H_3Re_3 -(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 $[H_3Mn_3(CO)_4]^+$ and $[H_3Mn_3-$ (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 $[H_m Re_3(CO)_m]^+$ (m = 0-3, n = 0-12); dimeric and monomeric ions are not observed in significant amounts. The stability

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

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

Figure 4. Structure of HMnRe₂(CO)₁₄.

Cp2Mo2(CO)4(PMe2)H

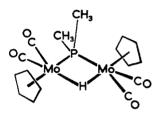


Figure 5. Structure of $HMo_2(CO)_4[P(CH_3)_2](C_5H_5)_2$.

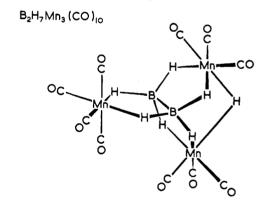


Figure 6. Structure of B₂H₇Mn₃(CO)₁₀.

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 H_7B_2 - $Mn_3(CO)_{10}$ has been determined by Dahl and his coworkers¹⁴ (Figure 6). Here again the parent molecular ion was observed. Stepwise loss of ten carbonyl groups then occurs, giving the ions $[H_7B_2Mn_3(CO)_m]^+$ (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 $[H_7B_2Mn_3(CO)_6]^+$ when the ion $[H_5B_2Mn_3(CO)_6]^+$ is observed. This behavior is noted for the series of ions $[H_7B_2Mn_3(CO)_m]^+$ and $[H_5B_2Mn_3(CO)_m]^+$ (m=1-6). At low m/e values the patterns become more complex due to the overlap of several hydrido species such as $[H_zB_2Mn_3(CO)]^+$ (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).

⁽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).

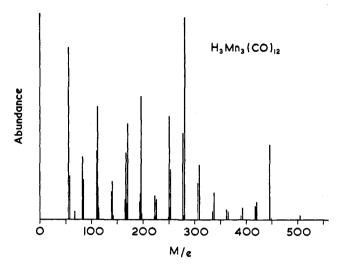


Figure 7. Mass spectrum of H₃Mn₃(CO)₁₂.

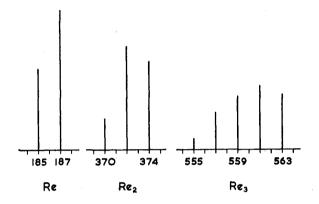


Figure 8. Isotope patterns for [Re] +, [Re2] +, and [Re3] +.

manganese is monoisotopic, it is difficult to differentiate between mononuclear, dinuclear, and trinuclear ions without resorting to accurate mass measurement. Thus the ions $[HMn(CO)_2]^+ = [Mn_2]^+$, etc., would occur at the same m/e values.

Recently, we have prepared the hydrido compounds α - and β -H₄M₄(CO)₁₂ and H₂M₄(CO)₁₃ (M = Ru or Os) from the reaction of acid on the anions produced by the action of base on the carbonyl $M_3(CO)_{12}$. 5,18,19 The structures of the carbonyl hydrides are unknown: however, they are isoelectronic with Rh₄(CO)₁₂ and Ir₄(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 H₄M₄(CO)₁₂ compounds, and on this basis it is believed that they have a pseudo-Ir₄-(CO)₁₂ structure with four bridging hydrido ligands (Figure 9). In the mass spectra, no parent ion is observed with $H_4Ru_4(CO)_{12}$ in either the α or β forms; indeed, the spectra are similar. However, ions containing at least three hydrido ligands are observed at

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

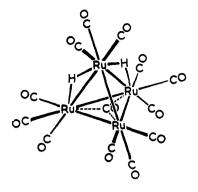


Figure 9a. Possible structure of H₂Ru₄(CO)₁₃.

lower m/e values. With $H_4Os_4(CO)_{12}$ the parent ion is observed in reasonable abundance. No loss of H from $H_4Os_4(CO)_{12}$ is observed until four carbonyl groups have been lost. With $H_2Ru_4(CO)_{13}$ and $H_2Os_4(CO)_{13}$ 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 $\mathrm{HMn_2(CO)_8P(C_6H_5)_2^{20}}$ and $\mathrm{HFe_2-(CO)_2(C_5H_5)_2P(C_6H_5)_2^{21}}$ were not successful, and only the fragment ions of the phosphine $(C_6H_5)_2\mathrm{PH}$ was recorded.

Kaesz and his coworkers¹⁵ have measured the mass spectra of HRe₃(CO)₁₄ and HMnRe₂(CO)₁₄. The structure of HMnRe₂(CO)₁₄ has been determined, and it is believed to involve a Re-H-Re bridging system (Figure 4). In the spectrum of HRe₃(CO)₁₄ stepwise loss of 14 CO groups is observed; however, no loss of hydrogen is observed except from the ions [HRe3- $(CO)_2$]+, $[HRe_3(CO)]$ +, and $[HRe_3]$ +. The spectrum of HMnRe₂(CO)₁₄ is similar. Very recently, the mass spectra of HFeCo₃(CO)₁₂ and HRuCo₃(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-M₄Ru₄(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, $M(CO)_5X$ (M =

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

⁽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.

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

$$C_{3v}(a)$$
 $C_{3v}(b)$ $C_{3v}(c)$ C_{3

Figure 9b. Possible structure of H₄Ru₄(CO)₁₂.

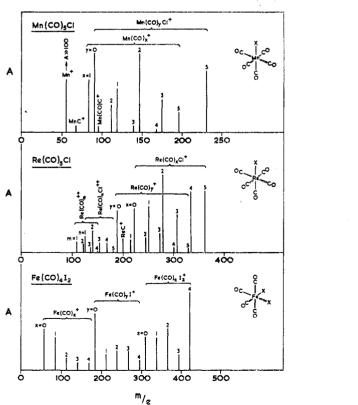


Figure 10. Mass spectra of $\mathrm{M}(\mathrm{CO})_5\mathrm{X}$ compounds.

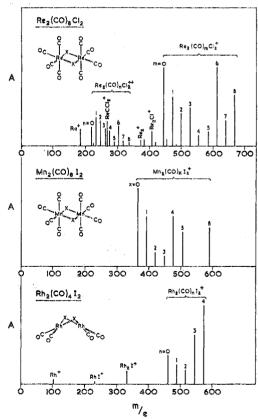


Figure 11. Mass spectra of $M_2(CO)_8X_2$ compounds.

Mn or Re; X = Cl, Br, or I), and of iron and ruthenium, cis-M'(CO)₄X₂ (M' = Fe or Ru; X = Cl, Br, or I) (Figure 10), and (ii) those containing bridging halogens, e.g., the dimeric compounds $M_2(CO)_8X_2$ (M = Mn or Re; X = Cl, Br, or I) and $Rh_2(CO)_4X_2$ (X = Cl, Br, or I) (Figure 11). This problem of differentiation of bridging and terminal ligands is often encountered in this area of chemistry. For these carbonyl halide compounds parent molecular ions were observed in all cases, but the fragmentation patterns of the two classes of compound were substantially different. With the mononuclear complexes loss of CO or X radicals occurs with equal ease, and the spectra are characterized by the appearance of ions of the types $[M(CO)_m]^+$, $[M(CO)_nX]^+$, or $[M(CO)_tX_2]^+$, e.g., Scheme II.

Scheme II

$$[M(CO)_{5}X] + \xrightarrow{-CO} [M(CO)_{4}X] + \xrightarrow{-4CO} [MX] + \\ (M = Mn \text{ or Re}) \xrightarrow{-X} \sqrt{-X} \\ [M(CO)_{5}] + \xrightarrow{-5CO} [M] + \\ (stepwise)$$

Loss of halogen from the intermediate ions $[M(CO)_nX]^+$ (n = 0-4) to give $[M(CO)_n]^+$ may also occur at any stage of the fragmentation process (Scheme III; Figure 10).

Scheme III

[M'(CO)₄X₂] +
$$\xrightarrow{-\text{CO}}$$
 [M'(CO)₃X₂] $\xrightarrow{-3\text{CO}}$ [M'X₂] + $\xrightarrow{-X}$ $\xrightarrow{-X}$ $\xrightarrow{-X}$ $\xrightarrow{-X}$ [M'(CO)₄X] + $\xrightarrow{-4\text{CO}}$ [M'X] + $\xrightarrow{-X}$ [M'(CO)₄] + $\xrightarrow{-4\text{CO}}$ [M'] +

These decomposition paths are confirmed by the appearance of the appropriate metastable peaks.

On the other hand, with the dinuclear bridged systems carbonyl groups are lost in a stepwise fashion with the retention of the M_2X_2 nucleus (Figure 11). No loss of halogen is observed until the breakdown of this nucleus occurs, e.g.

$$[M_2(CO)_xX_2] + \xrightarrow{-xCO} [M_2X_2] + \xrightarrow{-X} [M_2X] + \text{etc.}$$

Thus, compounds containing terminal halogeno ligands may be readily differentiated from those containing bridging halogens by an examination of their respective fragmentation patterns. The related compounds $(C_2H_5)_3PMn(CO)_4Cl$, $C_5H_5Mo(CO)_3X$, and $C_5H_5W-(CO)_3X$ behave similarly.

Metal-Metal Bonds

Two distinct types of compound containing metalmetal bonds are known, viz., those in which the metal atoms are joined together without bridging groups and those in which metal-metal bonding occurs in conjunction with bridging groups. For the first group of compounds many examples occur in the metal carbonyl series, and it is convenient to discuss this aspect of the structure in conjunction with other factors

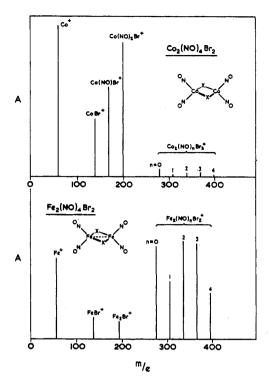


Figure 12. Mass spectra of M₂(NO)₄X₂ compounds.

related to the fragmentation of metal carbonyl derivatives later.

In this latter group there exist a number of organometallic complexes of neighboring transition metals containing bridging ligand groups which differ only in the necessity of invoking "metal-metal" interaction in one of the complexes to maintain the inert gas configuration of the metal ions. Thus, on the basis of dipole moment, infrared, and molecular weight data. iron and cobalt dinitrosyl derivatives $M(NO)_2X$ (M = Fe or Co; X = Cl, Br, I, SCH_3 , SC_2H_5 , SC_4H_9 , or SC₆H₅) have dimeric structures involving either halogen or thiol bridges. This structure has been confirmed for Roussins's red salt, $Fe_2(NO)_4S_2(C_2H_5)_2$, 21 by single-crystal X-ray structure determination. For the iron complexes it is generally postulated that the odd electrons on the metal atoms interact directly to form a "metal-metal" bond. It has been pointed out. however, that for dinuclear metal complexes with bridging groups the observed diamagnetism may not necessarily be attributable to the formation of a definite metal-metal bond but rather the result of a super exchange mechanism operating through the bridging ligand and the iron-iron distance merely reflects the geometry of the bridging system. We were, therefore, particularly interested in studying the manner of the breakdown of $Fe_2(NO)_4X_2$ and $Co_2(NO)_4X_2$ under electron impact to see if the fragmentation pattern reflected the presence of this metal-metal bond.

Nitrosyl Halide Compounds, $M_2(NO)_4X_2$. The spectra of these compounds are relatively simple (Figure 12), and in all cases the binuclear nature of the compounds was confirmed. For the iron compounds the most abundant ions were $[Fe_2(NO)_nX_2]^+$ (n = 0-4), indicating that the primary fragmentation scheme in-

volves the successive removal of the nitrosyl groups before fragmentation of the Fe₂X₂ nucleus takes place.

$$[\text{Fe}_2(\text{NO})_4\text{X}_2] + \frac{-\text{NO}}{(\text{stepwise})} [\text{Fe}_2(\text{NO})_n\text{X}_2] + + (3 - n)\text{NO}$$

$$(n = 0-3)$$

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 $[Co(NO)_2X]^+$ and $[Co(NO)_2X]$ with subsequent fragmentation of the $[Co(NO)_2X]^+$ ion (Scheme IV).

Scheme IV
$$[\text{Co}_2(\text{NO})_4\text{X}_2]^+ \longrightarrow [\text{Co}(\text{NO})_2\text{X}]^+ + [\text{Co}(\text{NO})_2\text{X}]^- \\ \text{NO} \\ \text{stepwise}$$

$$[\text{Co}_2\text{X}]^+$$

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 M₂X₂ 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 Co₂(NO)₄X₂ compounds may, therefore, be correlated with the higher stability of the metal-nitric oxide unit, and the increased stability of the Fe₂X₂ nucleus in $Fe_2(NO)_4X_2$ 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 $(C_5H_5)_2$ -Co₂ $(P(C_6H_5)_2)_2$ and $(C_5H_5)_2Ni_2(P(C_6H_5)_2)_2$, which bear this type of relationship to one another, the "metalmetal" interaction is sufficient not only to reduce the metalmetal 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 metalmetal interaction is not weak and must be much larger than

(22) B. F. G. Johnson, J. Lewis, and I. G. Williams, to be published. (23) J. M. Coleman and L. F. Dahl, J. Am. Chem. Soc., 89, 542 (1967).

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 $\mathrm{Co_2(NO)_4S_2(C_6H_5)_2}$ 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 $[\mathrm{Co(NO)_2SC_6H_5}]^+$, $[\mathrm{Co(NO)S-C_6H_5}]^+$, and $[\mathrm{CoSC_6H_5}]^+$ 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 $\mathrm{Fe_2S_2(C_6H_5)_2}$ unit is reflected in the appearance of the doubly charged ion $[\mathrm{Fe_2S_2-(C_6H_5)_2}]^{2+}$. The behavior of these complexes can therefore be related to the corresponding halide compounds, and this difference in behavor 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.

$$[M_2(NO)_4S_2R_2] + \xrightarrow{NO} [M_2S_2R_2] +$$

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, Mn₂(CO)₁₀; rhenium, Re₂(CO)₁₀; iron, Fe₂(CO)₉ and Fe₃(CO)₁₂; ruthenium, Ru₃(CO)₁₂; osmium, Os₃(CO)₁₂; cobalt, Co₂(CO)₈ and Co₄(CO)₁₂; rhodium, Rh₄(CO)₁₂;²⁶ and iridium, Ir₄(CO)₁₂;²² and the heteronuclear carbonyls MnRe(CO)₁₀,²⁶ Ru₂Os(CO)₁₂, RuOs₂(CO)₁₂,²² and Mn₂Fe(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 Co₂⁺ and Mn₂⁺, 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

⁽²⁴⁾ R. E. Winters and R. W. Kiser, *Inorg. Chem.*, 4, 157 (1965); 3, 699 (1964); *J. Phys. Chem.*, 69, 1618 (1965).

 ⁽²⁵⁾ H. J. Svec and G. A. Junk, J. Am. Chem. Soc., 89, 2836 (1967).
 (26) B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson,
 J. Chem. Soc., Sect. A, 341 (1967).

⁽²⁷⁾ E. H. Schubert and R. H. Sheline, Z. Naturforsch., 20b, 1366 (1965).

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 $[M(CO)_zC]^+$ are fairly common for the heavier transition metals; however, no ions of the type $[M-(CO)_zO]^+$ 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. Mn₂(CO)₁₀, Re₂(CO)₁₀, MnRe(CO)₁₀, Fe₂(CO)₉, and Co₂(CO)₈ have been examined. These compounds fall into two distinctive types: those with bridging CO groups, e.g., Co₂(CO)₈ and Fe₂(CO)₉ (Figure 13), and those in which the two halves of the molecule are joined solely by a metalmetal bond, e.g. Mn₂(CO)₁₀ and Re₂(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 [Mn₂(CO)₉]⁺ and $[Mn_2(CO)_7]^+$. With $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Mn_2(CO)_{10}$ Re(CO)₁₀ consecutive loss of ten carbonyl groups is observed to give [M₂]+. Cleavage into monomeric units is also observed, but this tendency falls off rapidly in going from $Mn_2(CO)_{10}$ to $Re_2(CO)_{10}$. Thus, on summation of abundance it can be shown that 59% of the ion fragments from Mn₂(CO)₁₀ contain two metal atoms; this rises to 79% in MnRe(CO)₁₀ and to 96% in Re₂(CO)₁₀. With MnRe(CO)₁₀ and Re₂(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 $Mn_2(CO)_{10}$. This may be related to the more common occurrence of metalmetal bonding in higher oxidation states of rhenium as opposed to manganese. Another feature of the spectra of MnRe(CO)₁₀ and Re₂(CO)₁₀ is the relatively high abundance of ions such as $[MnRe(CO)_xC]^+$ or $[Re(CO)_xC]^+$; 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 Re₂(CO)₁₀ allows us to conclude that both monometallic and bimetallic ions decompose with stepwise loss of carbon monoxide radicals. Rearrange-

(28) H. M. Powell and R. V. G. Evans, J. Chem. Soc., 286 (1939);
G. Sumner, H. P. Klug, and L. Alexander, Acta Cryst., 17, 732 (1964);
L. F. Dahl and R. E. Rundle, J. Chem. Phys., 26, 1750 (1957);
Acta Cryst., 16, 419 (1963).

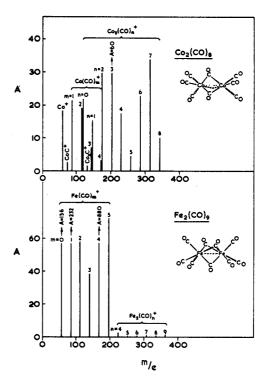


Figure 13. Mass spectra of Fe₂(CO)₉ and Co₂(CO)₈.

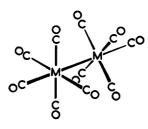


Figure 14. Structure of $M_2(CO)_{10}$ (M = Mn or Re).

ment ions of the type $[M(CO)_6]^+$ are not observed in the spectra of either $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$; however, the ion $[Re(CO)_6]^+$ is observed in significant amounts in the spectrum of $MnRe(CO)_{10}$. 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 $[MnRe-(CO)_{10}]^+$ transfer of a CO from the manganese to rhenium can lead to a gain in bond energy. 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 [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

hand, mononuclear ions of the type $[Fe(CO)_n]^+$ (n = 0-5) occur in high abundance, suggesting that, on initial fragmentation, cleavage of bridging CO bonds occurs in preference to the cleavage of terminal CO bonds and the stability of the $Fe(CO)_3Fe$ nucleus is low. This behavior is in contrast to that of the halogen-bridged carbonyl halides, e.g., $[M(CO)_4X]_2$ (M = Mn or Re; X = Cl, Br, or I), where the M_2X_2 nucleus resists fragmentation until all the terminal CO groups have been removed.

The spectrum of $\text{Co}_2(\text{CO})_8$ has been studied previously using a time-of-flight spectrometer; we have measured it under the conditions used for the other polynuclear carbonyls discussed here. The parent ion occurs in the spectrum (Figure 13) and, significantly, the most abundant ions contain the Co_2 nucleus, although mononuclear ions also occur in comparatively high abundance. The predominance of binuclear ions may be attributed to the stability of the $\text{Co}_2(\text{CO})_2$ nucleus which contains two bridging CO groups together with a Co-Co bond, and in this respect the reasoning applied to the binuclear nitrosyl halide compounds, $\text{M}_2(\text{NO})_4\text{X}_2$, may be applied here. Thus, the breakdown pattern may be represented as Scheme VI,

Scheme VI

$$[Co_{2}(CO)_{8}]^{+} \longrightarrow [Co(CO)_{4}]^{+} + [Co(CO)_{4}]$$

$$\downarrow^{-4CO}_{(stepwise)}$$

$$[Co]^{+}$$

in which a symmetrical fragmentation takes place. It must be emphasized that in this case a structure (OC)₄Co-Co(CO)₄, which does not involve bridging CO groups, cannot be ruled out on the basis of these results alone. Indeed, it has been shown from infrared measurements that a nonbridged form of cobalt carbonyl does exist at higher temperatures.

It is of interest to compare the fragmentation patterns of $Co_2(CO)_8$ and $Fe_2(CO)_9$. The two complexes have related structures (Figure 13):28 in Fe₂(CO)₉ each iron has three terminal and three bridging carbonyl groups and an iron-iron distance of 2.46 Å, while in Co₂(CO)₈ there are three terminal and two bridging carbonyl groups, the Co-Co distance being 2.51 Å. The extra bridging group in the iron complex may be considered to be replaced by a "lone-electron pair" in the cobalt structure. It is possible that the metal-metal distance in the iron complex may reflect the bonding of the bridging carbonyl groups rather than the optimum distance for bonding between the metal atoms. It is significant in this respect that in all bridging carbonyl compounds reported the metalcarbon-metal bond angle is in the range 80-87°. In the cobalt complex the presence of two rather than three bridging carbonyls gives a larger degree of flexibility in maintaining the favorable angles of the metalcarbon-metal grouping with bonding between the metal centers. It is unfortunate that the details of the iron structure are not sufficient to allow a comparison of the two sets of bond angles. The higher abundance of the

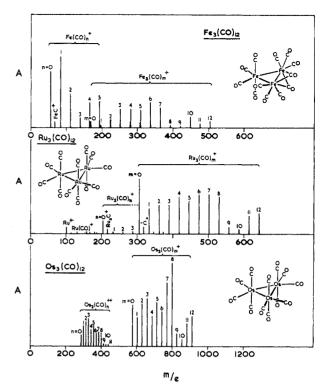


Figure 15. Mass spectra of Fe $_3(CO)_{12}$, Ru $_3(CO)_{12}$, and Os $_3$ -(CO) $_{12}$.

binuclear species in the mass spectrum of the cobalt complex may thus reflect this greater stability of this bridging system in the cobalt compound.

Trinuclear Metal Carbonyls. These may be conveniently divided into cyclic and noncyclic systems. Possibly the best known example of a cyclic system is Fe₃(CO)₁₂. The structure of this compound has recently been established and may be described simply as Fe₂(CO)₉ with one bridging CO group replaced by an Fe(CO)₄ unit²⁹ (Figure 15). The structures of Ru₃-(CO)₁₂ and Os₃(CO)₁₂ are different, consisting of an equilateral triangle of metal atoms with 12 terminal carbonyl groups³⁰ (Figure 15).

In the spectrum of Fe₃(CO)₁₂ (Figure 15) all possible trimeric ions [Fe₃(CO)_n]⁺ (n = 0–12) were observed; in addition dinuclear and mononuclear ions were found. The occurrence of [Fe(CO)₅]⁺ in high abundance is of considerable interest, as in all homonuclear compounds studied to date no migration of a CO group from one metal to another has been observed. Thus, the presence of this ion may be readily correlated with a structure from the parent carbonyl in which the presence of five carbonyl groups around an iron atom occurs. It must be emphasized, however, that in a complex molecule such as Fe₃(CO)₁₂ the migration of a CO group may have occurred in the intermediate ions.

The spectra of the corresponding ruthenium and osmium carbonyls (Figure 15) are much simpler. In the spectrum of Ru₃(CO)₁₂ singly charged trinuclear species account for 92% of metal-containing fragments,

(30) E. R. Corey and L. F. Dahl, ibid., 1, 521 (1962).

⁽²⁹⁾ L. F. Dahl and J. F. Blount, Inorg. Chem., 4, 1373 (1965).

Figure 16. Possible structure of Mn₂Fe(CO)₁₄.

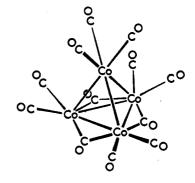
and binuclear and mononuclear species for 5 and 2%, respectively. The corresponding figures for Fe₃(CO)₁₂ are 36, 4, and 60%. With Os₃(CO)₁₂ neither dinuclear nor mononuclear ions were observed. Thus, these spectra follow the same trend as those of manganese and rhenium decacarbonyl and support the view that metal clusters become increasingly resistant to fragmentation down a transition-metal group. The appearance of $[Os_3(CO)_n]^{2+}$ (n=0–12) and $[Ru_3]^{2+}$ may be correlated with the stability of heavy metal clusters toward increased oxidation.

As the structure of $\mathrm{Ru_3(CO)_{12}}$ does not involve a ruthenium atom bonded to more than four carbonyl groups the possible appearance of $[\mathrm{Ru(CO)_5}]^+$ was of interest. Only very weak peaks ($\sim 0.05\%$) occurred in the mass range 236–244 expected for $[\mathrm{Ru(CO)_5}]^+$, 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 $[\mathrm{Fe(CO)_5}]^+$ in the discussion of $\mathrm{Fe_3(CO)_{12}}$ is thus enhanced.

The mixed polynuclear carbonyls RuOs₂(CO)₁₂ and Ru₂Os(CO)₁₂ have been prepared.³¹ These have been shown to be isomorphous with Os₃(CO)₁₂, and their infrared spectra are consistent with the absence of bridging CO groups. Their spectra are very similar to that of Os₃(CO)₁₂: consecutive loss of twelve CO groups is observed in each case to give the trinuclear cluster ion [RuOs₂]⁺ or [Ru₂Os]⁺. No bi- or mononuclear ions were observed.

Few, neutral, linear trinuclear metal carbonyls are known. One of the best examples of this group is Mn₂Fe(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 $[Mn_2Fe(CO)_m]^+$ (m = 0-14), together with significant amounts of dinuclear and mononuclear species. Dinuclear ions of the type $[MnFe(CO)_n]^+$ 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, $[Mn(CO)_x]^+$ and [Fe- $(CO)_y$]+, were observed. It is significant that the ion [Mn(CO)₆]+ was not observed, and no evidence of CO migration from the iron atom to the manganese

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



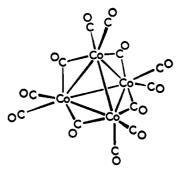


Figure 17. Structure of Co₄(CO)₁₂ (C_{3v} and D_{2d}).

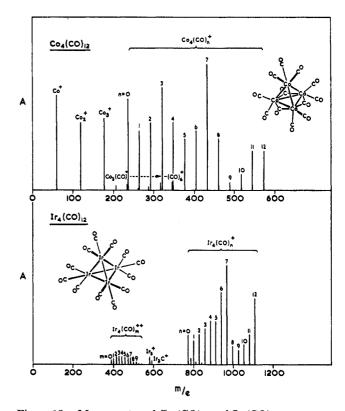


Figure 18. Mass spectra of Co₄(CO)₁₂ and Ir₄(CO)₁₂.

was obtained. However, the possibility of CO migration from the manganese to the iron cannot be entirely ruled out since ions corresponding to $[Fe_2(CO)_8]^+$ were observed; however, it is possible that some thermal decomposition to produce $Fe_2(CO)_9$ was taking place in the spectrometer, and subsequently some of the ions $[Fe(CO)_y]^+$ (y = 0-5) may arise as a result of this

Figure 19. Structure of $Ru_6C(CO)_{14}[(CH_3)_8C_6H_3]$.

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

Tetranuclear Metal Carbonyls. The tetranuclear carbonyls, M₄(CO)₁₂, of cobalt, rhodium, and iridium are well-established compounds. Although there has been considerable speculation as to the structure of Co₄(CO)₁₂, it has finally been resolved for the solid state³² (Figure 17). The main features of this molecule are the basal triangle of Co₃(CO)₉, which contains three bridging CO groups linking the three cobalt atoms, and the over-all molecular symmetry C_{3v}. 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 ⁵⁹Co nmr measurements indicate that the C_{3v} configuration is retained³³ (Figure 18). From infrared data Rh₄(CO)₁₂ is believed to be similar to Co₄(CO)₁₂ (in solution).³² Ir₄(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 $[Co_{3-}(CO)_n]^+$ (n=0-6) in low abundance with $Co_4(CO)_{12}$, the spectra of $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$ were very similar, and no further structural information concerning bridging CO groups was obtained in contrast to $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$. $Rh_4(CO)_{12}$ decomposed rapidly in the spectrometer, and only limited information was obtained. This was sufficient, however, to confirm the

tetrameric formulation Rh₄(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 $[M(CO)_xC]^+$ are fairly common for the heavier transition metals but only appear after several CO groups have been ejected; (5) no ions of the type $[M(CO)_xO]^+$ 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 Ru₆C(CO)₁₇ and Ru₆C(CO)₁₄(arene) [arene = $CH_3C_6H_5$, $(CH_3)_2C_6H_4$, or $(CH_3)_3C_6H_3$], 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., Ru₆C(CO)₁₇ and Ru₆(CO)₁₈ would be difficult by analytical and other usual techniques. However, the appearance of the ion [Ru6C- $(CO)_{17}$] + and the related ions $[Ru_6C(CO)_n]$ + (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, Ru₆C(CO)₁₄- $[C_6H_3(CH_3)_3]$, 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. Com-

⁽³⁵⁾ R. Mason and W. Robinson, *ibid.*, 468 (1968).