

# Mass Spectra of Organometallic Compounds

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The basic theory<sup>1</sup> and organic aspects<sup>2</sup> of mass spectrometry have been summarised recently and sufficient is known of the behaviour of organometallic compounds under electron impact to show the major differences from organic molecules.

Problems connected with the identification of ions containing polyisotopic elements are first considered and this is followed by a discussion of appearance potential measurements. General aspects of the fragmentation behaviour of organometallic compounds are then summarised, and this is followed by a treatment of first main group and then transition-metal compounds. The range of compounds covered includes the metalloids (Si and As) and transition-metal carbonyls, but excludes boron and phosphorus.

Aston<sup>3</sup> used the volatile alkyls and carbonyls of metals to determine their isotopic constitution, and for compounds containing polyisotopic metals the relative isotope abundances produce characteristic patterns of ions which are readily recognised,<sup>4</sup> and can assist in identifying species in low-resolution spectra. With increasing numbers of polyisotopic atoms the calculation of abundance patterns and mass combinations is more readily performed by computer methods.<sup>5</sup> In comparing the abundances of ions containing polyisotopic elements with other types, the contributions from each isotope combination must be summed. For example a spectrum showing three peaks of relative height 2 : 1 : 1 due to  $^{127}\text{I}^+$ ,  $^{81}\text{Br}^+$ , and  $^{79}\text{Br}^+$  corresponds to a 1 : 1 ratio of  $\text{I}^+$  to  $\text{Br}^+$  ( $^{81}\text{Br} = 49\%$ ,  $^{79}\text{Br} = 51\%$ ). Similarly in obtaining relative ion abundances allowance must be made for the  $^{13}\text{C}$  content of each ion.

Although much information can be obtained by studying mass spectra at low resolution (1 : 1000), there are some problems for which high resolution (1 : 10,000) facilities are essential since these allow distinctions to be drawn based on packing-fraction mass differences. Fragmentation processes of ions containing polyisotopic elements sometimes produce overlapping patterns and identification of each component then requires high-resolution mass measurements on selected ions. This situation arises even in simple molecules such as tetramethylgermane where the ions  $\text{GeCH}_5^+$ ,  $\text{GeCH}_4^+$ ,  $\text{GeCH}_3^+$ ,

<sup>1</sup> R. I. Reed, *Quart. Rev.*, 1966, 20, 527 and refs. therein.

<sup>2</sup> H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds', Holden-Day Inc., San Francisco, 1967.

<sup>3</sup> F. W. Aston, 'Mass Spectra and Isotopes', 2nd edn., Edward Arnold and Co., London, 1942.

<sup>4</sup> D. B. Chambers and F. Glockling, *J. Chem. Soc. (A)*, 1968, 735; J. R. C. Light and F. Glockling, *J. Chem. Soc. (A)*, 1968, 717; D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc. (A)*, 1967, 1759 or refs. therein.

<sup>5</sup> A. Carrick and F. Glockling, *J. Chem. Soc. (A)*, 1967, 40.

$\text{GeCH}_2^+$ ,  $\text{GeCH}^+$ , and  $\text{GeC}^+$  form a complex pattern at low resolution. Identification can also be a problem with compounds of monoisotopic metals. For example the spectrum of diethylberyllium shows a fragment ion at mass 37 which, in the absence of high-resolution facilities, could reasonably be assigned to  $\text{C}_2\text{H}_4\text{Be}^+$  or  $\text{C}_3\text{H}^+$ .

Diffuse 'metastable' peaks of low abundance often appear in low-resolution mass spectra, usually at non-integral masses. These result from the decomposition of ions in the field-free region between the magnetic and electrostatic analysers (in a double-focusing instrument) and, for a transition (1), if there is no internal



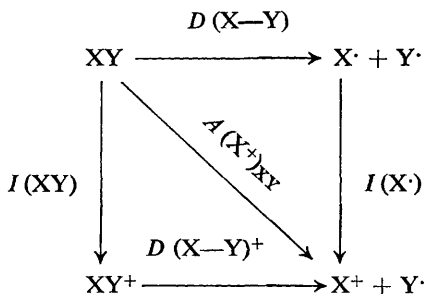
energy release the apparent mass<sup>1</sup> of the metastable peak  $m^*$  is given by (2).

$$m^* = m_2^2/m_1 \quad (2)$$

Metastable peaks are not always symmetrical,<sup>6</sup> and for ions containing polyisotopic elements the isotope abundance pattern appears in the metastable peak. If  $m_1$  is of high mass, or if the neutral fragment ( $m_1 - m_2$ ) eliminated is large individual peaks coalesce. If the neutral fragment contains a polyisotopic element the pattern is distorted in various ways.<sup>4</sup> Variations in the ionizing energy between 30 and 70 eV does not generally alter ion abundances significantly. Below 30 eV fragment ions disappear from the spectrum as the threshold energy for a given process is reached.

### Appearance Potentials

Heats of formation and bond dissociation energies can be measured or compared from appearance-potential measurements using the cycle shown in Scheme 1,<sup>1</sup>



Scheme 1

in which  $I(\text{X}\cdot)$  is the ionisation potential of  $\text{X}\cdot$ ;  $A(\text{X}^+_{\text{XY}})$  is the appearance potential of  $\text{X}^+$  from the molecule  $\text{XY}$ ; and  $D(X-Y)$  and  $D(X-Y)^+$  are the dissociation energies of the molecule and molecular ion. This gives the following relationships (3) and (4) in which  $E_1$  and  $E_2$  represent excess of kinetic energy

<sup>6</sup> J. H. Beynon and A. E. Fontaine, *Z. Naturforsch.*, 1967, 22, 334 or refs. therein.

$$A(X^+)_{XY} = I(XY) + D(X-Y)^+ + E_1 \quad (3)$$

$$= I(X\cdot) + D(X-Y) + E_2 \quad (4)$$

produced in the dissociation process together with any excitation energy of the products  $X^+$  and  $Y\cdot$ . A similar cycle can be written for the formation of  $Y^+$  and  $X\cdot$ . There is a considerable body of evidence<sup>1</sup> that if  $I(X\cdot) < I(Y\cdot)$  then the ion  $X^+$  and radical  $Y\cdot$  are formed without excess of energy;  $E_1$  and  $E_2$  may then be taken as zero, but in general bond energies derived from appearance potentials are likely to be upper limits. The appearance potentials of metal ions  $M^+$  in the spectra of many organometallic compounds have also been used to determine heats of formation and mean metal-carbon bond energies. The validity of using appearance-potential measurements for the derivation of thermodynamic quantities depends on the correct assignment of the process involved in the threshold measurement, and in general more reliance can be placed on values derived from appearance potentials of ions formed by less extensive dissociative processes.

Ionisation potentials of organometallic compounds obtained from electron-impact measurements decrease as the size of the attached organic group increases. For methyl derivatives of the main-group metals ionisation requires less energy as the atomic number of the metal atom increases.<sup>7</sup> For perfluoroalkylarsines<sup>8</sup> variations of the observed ionisation potentials have been correlated with the inductive and electron-withdrawing effects of groups attached to arsenic. Ionisation potentials of metal carbonyls are approximately the same as those of the free metal which suggests that the electron is removed from an essentially non-bonding orbital.<sup>9</sup> This is further substantiated by mean metal-carbon bond dissociation energies which are slightly lower in the molecular ion than in the molecule (Table 1).

Ionisation potentials of bicyclopentadienyl metal complexes also lead to the conclusion that an electron is removed from a non-bonding orbital localised

**Table 1** Mean metal-carbon bond dissociation energies in neutral molecules and molecular ions (kcal. mole<sup>-1</sup>) (from ref. 9)

|                     | $\bar{E}(M-CO)^+$ | $\bar{E}(M-CO)$ | Thermo <sup>a</sup><br>chemical |
|---------------------|-------------------|-----------------|---------------------------------|
| Ni(CO) <sub>4</sub> | 37                | 43              | 35.2                            |
| Fe(CO) <sub>5</sub> | 32                | 33              | 27.7                            |
| Cr(CO) <sub>6</sub> | 31                | 31              | 27.1                            |
| Mo(CO) <sub>6</sub> | 39                | 42              | 35.9                            |
| W(CO) <sub>6</sub>  | 48                | 50              | 42.1                            |
| V(CO) <sub>6</sub>  | 31                | 34              |                                 |

<sup>a</sup>F. A. Cotton, A. K. Fischer, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1959, **81**, 800.

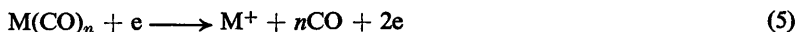
<sup>7</sup> R. E. Winters and R. W. Kiser, *J. Organometallic Chem.*, 1967, **10**, 7 or refs. therein.

<sup>8</sup> W. R. Cullen and D. C. Frost, *Canad. J. Chem.*, 1962, **40**, 390.

<sup>9</sup> D. R. Bidinosti and N. S. McIntyre, *Canad. J. Chem.*, 1967, **45**, 641 or refs. therein.

on the metal, and this is in agreement with the calculated molecular orbital energy levels in ferrocene.<sup>10</sup>

Comparatively few absolute bond dissociation energies have been determined by electron-impact methods since ionisation potentials of organometallic radicals are mostly unknown. The ionisation potential of the  $\text{Mn}(\text{CO})_5\cdot$  radical (9.26 eV) has been determined directly and, combined with the appearance potential of  $\text{Mn}(\text{CO})_5^+$ , leads to a value of 19–22 kcal. mole<sup>-1</sup> for  $D$  [ $(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_5$ ]. Although this is the energy to form two  $\text{Mn}(\text{CO})_5\cdot$  radicals, the radicals may not have the same geometrical configuration.<sup>11</sup> Thermal decomposition of iron pentacarbonyl at a high source temperature (250–300°) produces  $\text{Fe}(\text{CO})_4\cdot$  radicals and their ionisation potential (8.48 eV) can be measured. At low source temperatures (60–70°) the appearance potential of the ion  $\text{Fe}(\text{CO})_4^+$  may be found giving  $D$  [ $(\text{CO})_4\text{Fe}-\text{CO}$ ] as 6.1–6.9 kcal. mole<sup>-1</sup>.<sup>12</sup> Mean metal–carbon bond dissociation energies for metal carbonyls, obtained from the appearance potential of the metal ion, assuming its formation to be as in eqn. (5) are shown in Table 1. The differences from thermochemically determined bond energies may be ascribed to the fragmentation process occurring with release of excess of energy. Average metal–ring bond energies in biscyclopentadienyl complexes have been derived in the same way<sup>10,13</sup> [ $E(\text{M}-\text{C}_5\text{H}_5) = 90 \pm 6$  (V, Cr);  $72 \pm 6$  (Mn);  $75 \pm 6$  (Fe);  $112 \pm 6$  (Ru);  $79 \pm 6$  (Co);  $71 \pm 6$  (Ni) kcal. mole<sup>-1</sup>]. The values for ferrocene and nickelocene are in



good agreement with the thermochemically determined value of 77 kcal. mole<sup>-1</sup>.

Heats of formation of molecules can be calculated from appearance-potential measurements if the heat of formation of the ligand or ligands is known. Applied to biscyclopentadienyls the values agree well with calorimetric measurements.<sup>10</sup> There are some examples where appearance potentials provide evidence for a particular decomposition process occurring at the threshold energy. For example in cyclopentadienylmetal carbonyls,  $\text{C}_5\text{H}_5\text{M}(\text{CO})_n$  (M = Co, Mn, V) the appearance potential of the metal ion suggests that the overall process leading to its formation is (6).<sup>14</sup>



Appearance potentials of trimethylsilyl ions  $\text{Me}_3\text{Si}^+$  derived from various trimethylsilyl compounds have been determined, but it is only recently that dissociation energies of  $\text{Me}_3\text{Si}-\text{X}$  bonds have been evaluated.<sup>15</sup> The ionisation potential of trimethylsilyl radicals (7.1 eV) has been determined from the appearance potential of the trimethylsilyl ion derived from hexamethyldisilane

<sup>10</sup> J. Müller and L. D'Or, *J. Organometallic Chem.*, 1967, **10**, 313 or refs. therein.

<sup>11</sup> L. I. B. Haines, D. Hopgood, and A. J. Poë, *J. Chem. Soc. (A)*, 1968, 421 or refs. therein.

<sup>12</sup> S. Pignataro and F. P. Lossing, *J. Organometallic Chem.*, 1968, **11**, 571; 1967, **10**, 531 or refs. therein.

<sup>13</sup> H. S. Hull, A. F. Reid, and A. G. Turnbull, *Inorg. Chem.*, 1967, **6**, 805 or refs. therein.

<sup>14</sup> R. E. Winters and R. W. Kiser, *J. Organometallic Chem.*, 1965, **4**, 190.

<sup>15</sup> S. J. Band, I. M. T. Davidson, I. L. Stephenson, and C. A. Lambert, *Chem. Comm.*, 1967, 723 and refs. therein.

and the kinetically determined dissociation energy of the Si—Si bond in  $\text{Me}_6\text{Si}_2$ . An alternative method of determining ionisation potentials and heats of formation of organometallic radicals is applicable to metal-metal compounds such as  $\text{Me}_3\text{Sn}\cdot\text{SnMe}_3$ .<sup>16</sup> The heat of formation of the ion  $\text{SnMe}_3^+$  is first found from the appearance potential of  $\text{SnMe}_3^+$  derived from a trimethylstannyl compound whose standard heat of formation is known. The heat of formation of the trimethylstannyl radical can then be obtained from the appearance potential of  $\text{SnMe}_3\cdot$  derived from hexamethyldistannane, and the heat of formation of hexamethyldistannane (7). The ionisation potential of  $\text{SnMe}_3\cdot$  [ $\Delta H_f(\text{SnMe}_3^+) - \Delta H_f(\text{SnMe}_3\cdot)$ ] has been estimated as  $6.54 \text{ eV}^{16}$  and that of the triphenyltin radical as  $5.51 \pm 0.5 \text{ eV}^{17}$ .

$$A(\text{SnMe}_3^+)_{\text{Sn}_2\text{Me}_6} = \Delta H_f(\text{SnMe}_3^+) + \Delta H_f(\text{SnMe}_3\cdot) - \Delta H_f(\text{Sn}_2\text{Me}_6) \quad (7)$$

In cases where the ionisation potential of organometallic radicals is unknown it is still possible to compare bond dissociation energies from appearance potential differences and it has been shown for example that the Ge—Sn bond strength in  $\text{Ph}_3\text{Sn}\cdot\text{GeMe}_3$  is  $12 \pm 3.2 \text{ kcal. mole}^{-1}$  stronger than the phenyltin bond in tetraphenyltin.<sup>4</sup> Bond energies in molecular ions are obtained directly from eqn. (3) by measuring the ionisation potential of the molecular ion  $I(\text{XY})$  in addition to  $A(\text{X}^+)_{\text{XY}}$ . Illustrative examples are given in Table 2 and for mono-nuclear metal carbonyls wide variations have been reported; these may be due to thermal decomposition at the source temperature used.<sup>12</sup>

**Table 2** Approximate bond-dissociation energies in molecular ions (kcal. mole<sup>-1</sup>)\*

|   | V                    | Cr    | Mn                  | Fe   | Co                  | Ni  | Mo    | W   |
|---|----------------------|-------|---------------------|------|---------------------|-----|-------|---|
| $D(\text{C}_5\text{H}_5\text{M}^+ - \text{C}_5\text{H}_5)^{10, 12}$ | 123                  | 151   | 87                  | 153  | 180                 | 125 |       |   |
| $D(\text{C}_6\text{H}_6\text{M}^+ - \text{C}_6\text{H}_6)^{12}$     |                      | 81    |                     |      |                     |     |       |   |
| $D(\text{C}_5\text{H}_5\text{M}^+ - \text{C}_6\text{H}_6)^{12}$     |                      |       | 122                 |      |                     |     |       |   |
| $D[(\text{CO})_x\text{M}^+ - \text{CO}]^9$                          |                      | 11–28 |                     | 5–34 |                     | 16  | 22–34 | 32  |
| $D(\text{MeM}^+ - \text{Me})$                                       | 45(Be) <sup>17</sup> |       | 53(Zn) <sup>7</sup> |      | 30(Hg) <sup>7</sup> |     |       |   |
| $D(\text{Me}_2\text{M}^+ - \text{Me})^7$                            | 23(Al)               |       | 58(Sb)              |      |                     |     |       |   |
| $D(\text{Et}_3\text{Sn}^+ - \text{Et})^4$                           | 14                   |       |                     |      |                     |     |       | $D(\text{PhEt}_2\text{Sn}^+ - \text{Ph}), 10$ |

\*For references, see text.

### General Discussions of Spectra

The importance of mass spectroscopic studies on organometallic compounds, apart from the derivation of thermodynamic quantities, lies in establishing molecular formulae and providing information on molecular structure. Most of the following discussion is concerned with the fragmentation behaviour of different types of compound. It is only when a number of compounds of a given type have been examined that one can proceed with any confidence to

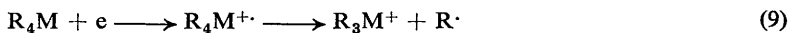
<sup>16</sup> A. L. Yergey and F. W. Lampe, *J. Amer. Chem. Soc.*, 1965, **87**, 4204 or refs. therein.

assign a unique structure when various isomers are possible, and this is the main justification for the empirical approach to mass spectrometry. For example the digermane  $\text{Et}_5(\text{C}_6\text{H}_{11})\text{Ge}_2$  shows a metastable transition for the elimination of hexene which confirms its constitution. However in the absence of a background knowledge of how alkyl digermanes fragment, elimination of hexene could be attributed to the isomeric structure  $\text{Et}_4(\text{Bu})_2\text{Ge}_2$ .<sup>17</sup> Many of the differences between electron-impact behaviour of organometallic and organic compounds arise from the low M—C and M—H bond strengths compared with those of C—C and C—H. The greater electronegativity of carbon and hydrogen than of metals means that when a positive ion decomposes the charge is likely to remain with the metal-containing fragment, and for most organometallic compounds a high proportion of the ion-current is carried by metal-containing species. There are nevertheless examples of transitions in which a metal-containing fragment is eliminated either as a neutral molecule or a radical. Compounds in which hydrocarbon ions feature extensively (*e.g.*, mercury- and beryllium-alkyls) are those which decompose thermally at the source temperature before ionisation. Hence the experimental conditions under which spectra are recorded can profoundly affect ion abundances. There are instances where the ionisation potential of a hydrocarbon radical is lower than that of the metal, and this may account for the high abundance of the  $\text{C}_7\text{H}_7^+$  (tropylium) ion in the mass spectrum of tetrabenzylgermane (equation 8).

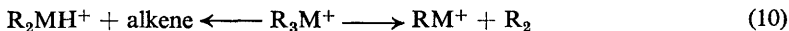


The question of whether a bonding or non-bonding electron is removed in the primary ionisation process is not clearly reflected in ion abundances. Organo-derivatives of the Group IVB elements generally show low-abundance molecular ions, compatible with removal of an electron from an M—C bond. However, molecular ions are of high abundance in beryllium alkyls where it *must* be a bonding electron which is removed. Mercury, zinc, and aluminium alkyls also produce abundant molecular ions.

With main-group organometallic compounds molecular ions usually decompose by radical elimination, thereby producing even-electron ions



*e.g.*, reaction (9). In subsequent fragmentation processes the dominant feature (as in organic compounds) is the tendency to form further even-electron ions. Thus  $\text{R}_3\text{M}^+$  ions ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) lose alkene or  $\text{R}_2$  molecules to a greater extent than a further radical which would give the odd-electron ion  $\text{R}_2\text{M}^{\cdot+}$  (reaction 10).



<sup>17</sup> D. B. Chambers, G. E. Coates, F. Glockling, J. R. C. Light, and P. D. Roberts, unpublished observations.

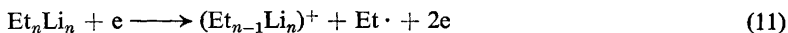
Although there is a paucity of bond-energy data it appears that with unsymmetrical organometallic compounds of Group IV the weakest bond in the molecular ion is the same as in the molecule, and this is the bond most susceptible to cleavage. The abundance of metal ions,  $M^+$ , depends on the strengths of  $M-C$ ,  $M-H$ , and  $M-M$  bonds as well as on the ionisation potential of the metal, and among the Group IV metals these ions are only abundant for tin and lead where bond energies and ionisation potentials are low. The variety and abundance of metal hydride ions formed from almost all types of organometallic compound is quite striking, especially with metals such as mercury and lead.

Transition-metal complexes such as carbonyls and cyclopentadienyls often show molecular ions of high abundance and the fragmentation behaviour is not dominated by odd- and even-electron considerations. This difference may be accounted for if primary ionisation involves the removal of an electron from an essentially non-bonding orbital. Relative metal-carbon bond strengths profoundly influence fragmentation as in  $\pi$ -cyclopentadienylmetal carbonyls which fragment by successive loss of carbon monoxide before cleavage or fragmentation of the cyclopentadienyl group; [ $D(\pi-C_5H_5-M) > D(M-CO)$ ]. Similarly in metal-metal bonded carbonyls the way the  $M-M$  bond strength increases with atomic weight in series such as  $Mn_2 < MnRe < Re_2$  is reflected in the proportion of the ion-current carried by ions having the  $M-M$  bond intact.

The extent to which structures can be assigned to ions is quite limited. The high energy of the electron beam (normally 70 eV) means that unimolecular rearrangement processes readily occur, and these can invalidate structural conclusions. Metal-metal bonded compounds are particularly prone to undergo rearrangement processes especially in compounds where the metal-metal bond is strong relative to others in the molecule. Despite these limitations mass spectrometry has provided substantiating evidence for novel structures, in addition to being the most definitive method of establishing molecular compositions.

### Main-group Metals

**Lithium.**—The mass spectra of lithium alkyls are of interest since their vapours are associated. None of the compounds so far reported<sup>18</sup> produces a molecular ion, but the identity of parent ions can be deduced from appearance-potential measurements of fragment ions. In this way it has been demonstrated that ethyl-lithium vapour consists of tetramer and hexamer units, both of which decompose (11) upon ionisation. Similar observations show that lithiomethyl-trimethylsilane,  $LiCH_2SiMe_3$ , vapour is tetrameric.



In the mass spectra of lithium alkyls the most abundant ions are  $Li_2R^+$ ;

<sup>18</sup> G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, 1966, 5, 1257 and refs. therein.

ion abundances and appearance potentials suggest that the decomposition processes (12) are most favourable when  $x$  is even.

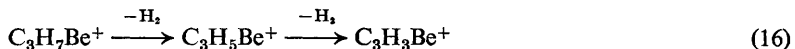
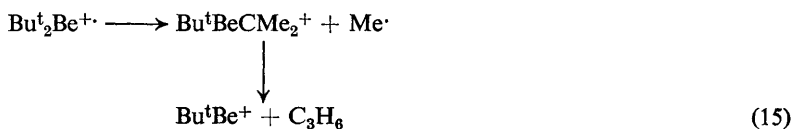


**Beryllium, Magnesium, Zinc, and Mercury.**—This group of metal alkyls shows many trends which reflect changes in ionisation potential and M—C and M—H bond energies. With the exception of the di-*t*-butyl, all beryllium alkyls are associated through Be—C—Be bridging-bonds, usually forming cyclic dimers, in the vapour state. The low energy of these bridge-bonds (probably less than 10 kcal. per C—Be) means that only under the most carefully controlled spectrometer conditions are dimer or trimer ions observed. The abundance of all beryllium-containing ions, but especially dimeric and trimeric species, falls with increasing source temperature owing to dissociation of bringing bonds and thermal decomposition before ionisation.<sup>17</sup>

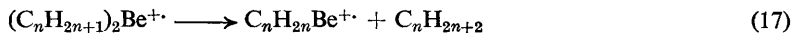
Mass spectrometry has provided the only direct evidence that beryllium dialkyls ( $\text{R} = \text{Et}, \text{Pr}^n, \text{Pr}^l$ ) are associated in the vapour phase.<sup>17</sup> Diethylberyllium even shows the trimeric ion  $\text{Et}_5\text{Be}_3^+$  whilst  $\text{Et}_3\text{Be}_2^+$  is extremely abundant at low source temperature ( $< 50^\circ$ ). The fragmentation of beryllium alkyls reflects the greater stability of even-electron ions, as in the sequences (13) and (14). The higher alkyls also show transitions in which C—C and C—H



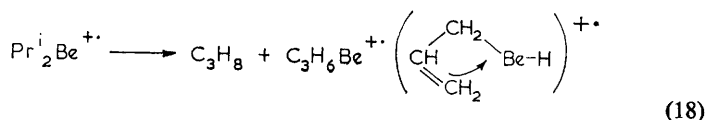
bonds are cleaved, as in (15) and (16). Alkane elimination from odd-electron



monomer ions is a favoured process (17) in marked contrast to the behaviour

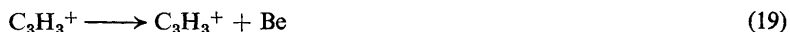


of Group IV<sub>B</sub> metal alkyls. With di-isopropylberyllium the  $\text{C}_3\text{H}_6\text{Be}^+$  ion is the most abundant in the spectrum but appearance-potential measurements suggest that its formation is accompanied by considerable rearrangement, possibly to an allylberyllium hydride, as in (18). Alkene elimination from the monomer





is always observed, although the hydride ion produced is usually of low abundance. Where the ionisation potential of a hydrocarbon radical is less than that of beryllium, elimination (19) of the metal may be observed.



$$[I(\text{C}_3\text{H}_3^{\cdot}) = 8.25; I(\text{Be}) = 9.32 \text{ eV}]$$

Biscyclopentadienylmagnesium<sup>10</sup> is mentioned under transition metals. Several zinc<sup>7,17</sup> and mercury<sup>7</sup> alkyls have been examined. They form molecular ions of high abundance and with mercury alkyls (Me, Et, Bu<sup>n</sup>) hydrocarbon ions make a large contribution to the total ion current, though part of this may arise from thermal decomposition before ionisation. Low-abundance hydride ions (MH<sup>+</sup> and RMH<sup>+</sup>) are observed, but the major processes are simple bond cleavages (20).

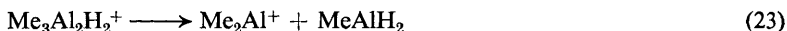


**Aluminium.**—Aluminium alkyls are also associated in the vapour phase and dimeric ions have been detected for Me<sub>3</sub>Al<sup>7,17</sup> at low source temperature but not for Et<sub>3</sub>Al. By contrast, compounds with strongly bridging groups<sup>19</sup> such as (Et<sub>2</sub>AlOEt)<sub>2</sub> and (R<sub>2</sub>AlNCPh<sub>2</sub>)<sub>2</sub> produce parent dimer ions in high abundance even at a source temperature of 200°.

Trimethylaluminium fragments mainly by successive loss of methyl radicals,<sup>7</sup> but metastable peaks are observed for more complex rearrangement processes<sup>17</sup> such as (21) and (22). Dimethylaluminium hydride vapour contains dimeric



and trimeric species at 80°, but its mass spectrum shows only a minute amount of trimer ion, Me<sub>5</sub>Al<sub>3</sub>H<sub>3</sub><sup>+</sup> whereas dimer ions, presumably hydrogen-bridged, are of high abundance.<sup>17</sup> These fragment partly by elimination (23,24) of methylaluminium hydride molecules.



**Silicon, Germanium, Tin, and Lead.**—Organo-derivatives of silicon,<sup>4,7,15,20–24</sup> germanium,<sup>4,7,17,20</sup> tin<sup>4,7,16,20</sup> and lead<sup>4,7,20</sup> have been the subject of

<sup>19</sup> K. Wade and B. K. Wyatt, *J. Chem. Soc. (A)*, 1967, 1339.

<sup>20</sup> J. J. Ridder and G. Dijkstra, *Rec. Trav. chim.*, 1967, **86**, 737.

<sup>21</sup> C. A. Hird, *Analyt. Chem.*, 1961, **33**, 1786.

<sup>22</sup> G. Fritz, H. J. Buhl, and D. Kummer, *Z. anorg. Chem.*, 1964, **327**, 165 and refs. therein.

<sup>23</sup> F. Aulinger, *Colloq. Spectros. Intern.* 8th, Lucerne Switzerland, 1960, 1959, 267 and refs. therein.

<sup>24</sup> J. Silbiger, C. Lifshitz, J. Fuchs, and Mandelbaum, *J. Amer. Chem. Soc.*, 1967, **89**, 4308 and refs. therein.

numerous studies. Their mass spectra have many features in common; the differences observed are qualitatively related to the decrease in ionisation potential of the metal with increasing atomic number, and to a progressive decrease in the metal-carbon and -hydrogen bond strengths. For example, metal hydride ions are least abundant with lead, and tetraethyl-lead eliminates butane from the  $\text{Et}_3\text{Pb}^+$  ion whereas a similar process is rarely observed with the lighter Group IVB metal alkyls. Molecular ions are usually of low abundance and radical elimination by  $\text{M}-\text{X}$  bond cleavage (25) is a dominant decomposition path for molecular and other odd-electron ions.



In unsymmetrical molecules such as  $\text{R}_3\text{MR}'$  the relative probability of the various bond-cleavage processes depends on the bond strengths in the molecule ion and on the relative stabilities of the radicals and ions produced. Even so it appears that the radical most readily eliminated is that which is most weakly bonded to the metal in the neutral molecule. For example, in  $\text{Me}_2\text{SnEt}_2$  and  $\text{Ph}_2\text{SnEt}_2$  the major ion is produced by ethyl loss from the parent, whilst in  $\text{Me}_2\text{SiCl}_2$  the ion  $\text{MeSiCl}_2^+$  is more abundant than  $\text{Me}_2\text{SiCl}^+$ . The relative bond dissociation energies are  $D(\text{Me}_3\text{Sn}-\text{Me}) > D(\text{Me}_3\text{Sn}-\text{Et})$ ,  $D(\text{Me}_3\text{Sn}-\text{Ph}) > D(\text{Me}_3\text{Sn}-\text{Et})$ ,<sup>16</sup>  $D(\text{Ph}_3\text{Sn}-\text{Ph}) > D(\text{Ph}_3\text{Sn}-\text{Et})$ ,<sup>4</sup> and  $D(\text{Me}_3\text{Si}-\text{Cl}) > D(\text{Me}_3\text{Si}-\text{Me})$ .<sup>15</sup> Similarly in metal-metal bonded compounds of the type  $\text{R}_3\text{M}\cdot\text{M}'\text{R}'_3$  ( $\text{M}, \text{M}' = \text{Si}, \text{Ge}, \text{Sn}$ ) extensive cleavage of the metal-metal bond occurs only when it is the weakest in the neutral molecule. For  $\text{R}_3\text{M}-\text{M}'\text{Ph}_3$  compounds the  $\text{Ph}_3\text{M}'^+$  ion is always the more abundant irrespective of the metal. This may be ascribed to the combined effect of various factors: the ionisation potential of  $\text{Ph}_3\text{M}'$  radicals may be lower than those of  $\text{R}_3\text{M}$ ; charge delocalisation over the phenyl groups will stabilise the  $\text{Ph}_3\text{M}'^+$  ion and there are fewer low-energy decomposition routes available for  $\text{Ph}_3\text{M}'^+$  than for  $\text{R}_3\text{M}^+$ . In methylpolygermanes  $\text{Me}_{2n+2}\text{Ge}_n$  ( $n = 2, 4, 5$  or  $6$ ) loss of a methyl radical is followed by successive elimination of  $\text{Me}_2\text{Ge}$  units. Whereas cyclic organosilanes  $(\text{Me}_2\text{SiCH}_2)_3$  produce only one major fragment ion due to loss of methyl from the parent, linear silanes of the type  $\text{Me}_3\text{SiCH}_2(\text{SiMe}_2\text{CH}_2)_{0-2}-\text{SiMe}_3$  also fragment by cleavage of methylene-silicon bonds.

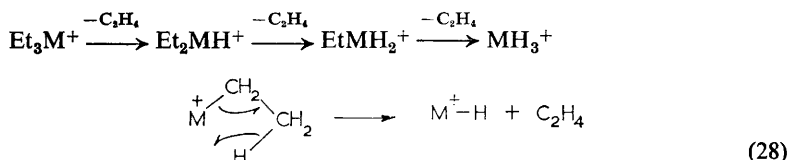
Radical elimination from even-electron ions is rarely observed and only a few examples are supported by metastable peaks such as (26) and (27).



Fragmentation by cleavage of  $\text{C}-\text{C}$  and  $\text{C}-\text{H}$  bonds is most apparent with organosilanes although tolylgermanes produce ions owing to methyl loss. In  $\text{R}_4\text{M}$  compounds doubly- and triply-charged ions are either absent or of low abundance but with methylsiloxanes, silazanes, and related compounds having more than one metal atom they are quite intense, indicating the removal of a

methyl group together with one electron per silicon atom. In germoxanes  $(R_3Ge)_2O$  doubly charged ions are more apparent than in digermanes,  $R_6Ge_2$ .

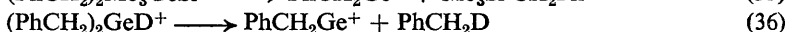
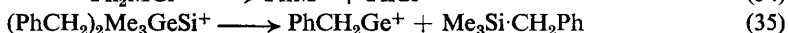
Alkene elimination is an important fragmentation process for all  $\sigma$ -bonded metal alkyls frequently giving strong metastable ions. It is a general reaction for even-electron ions containing the grouping  $R_2CHCH_2M$ , and is probably a  $\beta$ -elimination process (28).



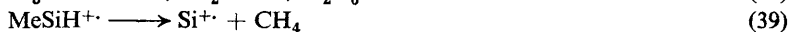
Alkene elimination from odd-electron parent ions has not been observed; on mechanism (28) it requires a pentaco-ordinate intermediate which may be energetically unfavourable compared with radical elimination. More complex alkene-elimination processes (29) are shown by benzyl and methyl compounds.



Molecule elimination by cleavage of two  $M-X$  bonds is most favourable for the heavier metals and comparatively few organosilanes show metastable peaks for alkane or hydrogen elimination. This again is a reflection of  $M-C$  and  $M-H$  bond energy changes in the group. The reactions (30–35) show the range of neutral molecules formed in this way. For reactions such as

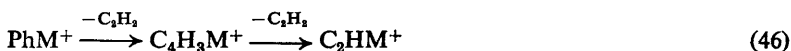
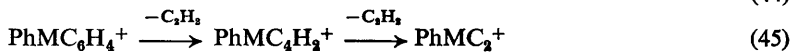
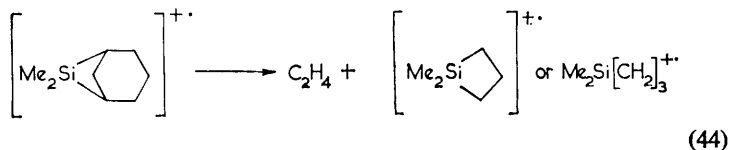


(32) it is almost certainly the  $M-H$  bond which is cleaved since this decomposition (36) is metastable-confirmed for tribenzyldeuteriogermane. This type of fragmentation is sometimes observed from odd-electron ions when the product (also odd-electron) ions are often of high abundance, as in reactions (37–40). Cleavage of one  $M-X$  bond in even-electron metal aryl ions (41) occurs to a slight extent. A similar decomposition involving methane loss is observed with methylsilazanes and cyclic silicon-methylene compounds. The only odd-electron ions showing a parallel process (42) are the triphenyltin halides.





Many low-abundance ions are formed by processes which do not involve cleavage of bonds to the metal. For example, the higher alkyls eliminate smaller alkene fragments (43). Lead alkyls in particular show abundant ions formed by rearrangement of alkyl groups, and in tetra-*n*-propyl-lead the  $\text{MePb}^+$  ion is the most abundant in the spectrum. In some cases it is not possible to determine whether metal-carbon bonds are cleaved. For example, dimethylsilacyclohexane produces an abundant ion owing to loss of ethylene (44). Similarly, phenylmetal ions degrade partly by successive elimination (45), (46) of acetylene



Acetylene loss is a high-energy process which disappears at 20 eV and diminishes in the order  $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$ . The extent of hydrogen-molecule elimination (47), (48) follows the same order and may be ascribed to the progressive decrease in  $\text{M}-\text{C}$  bond strength.



Methylene elimination from the trimethyltin ion is a metastable-supported process and tetraethyl derivatives of germanium, tin, and lead show low-abundance ions which are best ascribed to elimination of methylene (49).



**Arsenic, Antimony, and Bismuth.**—The triphenyl-<sup>25</sup> and trimethyl-derivatives<sup>26</sup> have been examined and molecular ion abundances diminish in the order  $\text{As} > \text{Sb} > \text{Bi}$  whereas the metal-ion abundances  $\text{M}^+$  follow the reverse order, as expected. Loss of  $\text{H}_2$  (or  $2\text{H}\cdot$ ) from  $\text{R}_2\text{M}^+$  ions is observed for the arsenic and antimony compounds, but not with bismuth.

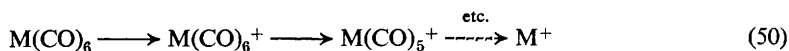
### Transition Metals

The mass spectra of organotransition metal compounds are classified according to the types of ligand present since these produce the main characteristics of the spectra, the influence of the metal being more subtle.

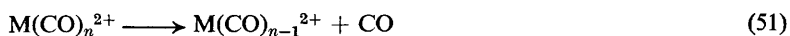
<sup>25</sup> D. E. Bublitz and A. W. Baker, *J. Organometallic Chem.*, 1967, 9, 383.

<sup>26</sup> R. G. Kostyanovsky and V. V. Yakshin, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1967, 2363.

**Carbonyls.**—The mononuclear carbonyls of iron, nickel, chromium, molybdenum, tungsten, and vanadium<sup>3,9,12</sup> show prominent molecular ions decomposing by successive loss (50) of carbon monoxide. Appearance-potential measurements



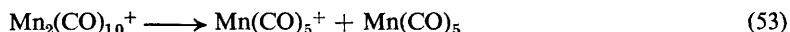
indicate that electron-impact ionisation of carbonyls occurs by removal of an essentially non-bonding electron,<sup>9</sup> and stepwise loss of carbonyl groups is often confirmed by the presence of metastable peaks.<sup>27</sup> Metal ions  $\text{M}^+$  are commonly the most abundant in the spectra, but doubly-charged molecular- and fragment-ions are also formed and these decompose by stepwise loss (51) of carbon monoxide.<sup>9,27</sup>



The heavier metal carbonyls show carbide ions,  $\text{M}(\text{CO})_n\text{C}^+$ , and these decompose by loss (52) of carbonyl.<sup>9,12,27,28</sup>



Differences in the fragmentation of bi- and poly-nuclear carbonyls provides evidence about the extent of metal-metal bonding. For purely metal-metal bonded carbonyls [such as  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Re}_2(\text{CO})_{10}$  and  $\text{ReMn}(\text{CO})_{10}$ ]<sup>12,28</sup> a high proportion of the ion current is carried by ions containing the metal-metal bond, and this increases with the atomic weight of the metal (Table 3). This trend, and the observation that doubly-charged dimetallic ions are more abundant for the heavier metals, reveals the greater ability of the heavier metals to sustain metal-metal bonding in higher oxidation states. Of this series only manganese has a metastable peak for cleavage (53) of the M—M bond.



Compounds with bridging carbonyl groups and only weak metal-metal interaction show extensive cleavage to mononuclear ions. For example, in  $\text{Fe}_2(\text{CO})_9$  the ions  $\text{Fe}_2(\text{CO})_{0-9}^+$  are all of low abundance and the spectrum is dominated by the ions  $\text{Fe}(\text{CO})_{0-5}^+$ . In dicobalt octacarbonyl, although there are bridging carbonyl groups, the metal-metal interaction is stronger, and dimetallic species are more abundant.<sup>12,28</sup> Differences in bonding are implied by the mass spectra of the carbonyls  $\text{M}_3(\text{CO})_{12}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ )<sup>12</sup> (Table 3), and only the iron complex has bridging carbonyl groups. In  $\text{Co}_4(\text{CO})_{12}$  a high proportion of the ion-current is carried by  $\text{Co}_4$  species.<sup>12</sup>

Osmium tetroxide and  $\text{Os}_3(\text{CO})_{12}$  form a complex  $\text{Os}_4\text{O}_4(\text{CO})_{12}$  which has been identified solely from its mass spectrum. The molecular ion forms the base peak, and ions due to successive loss of all 12 carbonyl groups are of high abundance, but the corresponding doubly-charged ions are absent. However, doubly-charged ions  $\text{Os}_3(\text{CO})_n^{2+}$  ( $n = 0-11$ ) are present, but not the singly-

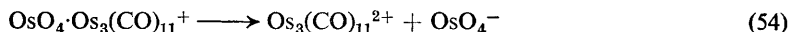
<sup>27</sup> R. E. Winters and J. H. Collins, *J. Phys. Chem.*, 1966, **70**, 2057 or refs. therein.

<sup>28</sup> R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, 1965, **69**, 1618 or refs. therein.

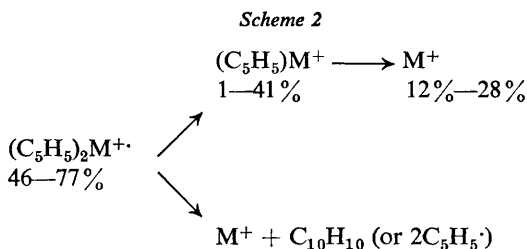
**Table 3** Relative ion-abundances of  $M_3$ ,  $M_2$ , and  $M$  species (from ref. 12)

|                 | $M_3$ | $M_2$ | $M$ |
|-----------------|-------|-------|-----|
| $Mn_2(CO)_{10}$ | —     | 59    | 41  |
| $ReMn(CO)_{10}$ | —     | 71    | 29  |
| $Re_2(CO)_{10}$ | —     | 96    | 4   |
| $Fe_3(CO)_{12}$ | 36    | 4     | 60  |
| $Ru_3(CO)_{12}$ | 93    | 5     | 2   |
| $Os_3(CO)_{12}$ | 100   | 0     | 0   |

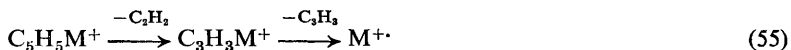
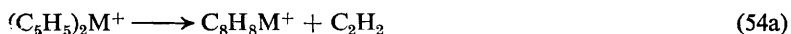
charged species. These unusual observations can be explained by elimination (54) of the negative  $OsO_4^-$  ion, and subsequent carbonyl elimination.<sup>12,29</sup>



**Hydrocarbon Complexes.**—Bis- $\pi$ -cyclopentadienyl compounds have been extensively studied (Fe, Co, Ni, V, Cr, Ru, Re, Os).<sup>10, 30</sup> The molecular ion is always of high abundance and metal-ring bond cleavage processes also produce ions of high abundance (Scheme 2). Fragmentation of the cyclopentadienyl



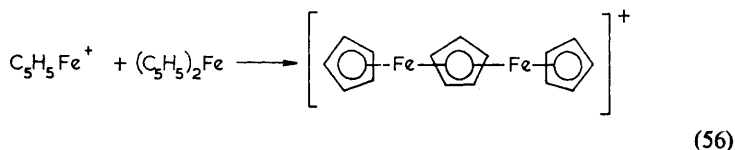
groups occurs mainly by elimination of acetylene, but minor ions are produced by loss (54a), (55) of  $H^+$ , and  $CH_3^+$  and other hydrocarbons. The isoelectronic



cyclopentadienyls of Fe, Ru, and Os, and the isoelectronic hydrides  $(C_5H_5)_2TcH$ ,  $(C_5H_5)_2ReH$ , and  $(C_5H_5)_2WH_2$ <sup>10</sup> produce similar abundances for ion groups containing the same number of carbon atoms. Some biscyclopentadienyls show ions at higher mass than the molecular ion which have been ascribed to ion-molecule reactions (56). Examination of the mass spectrum of a mixture of ferrocene and nickelocene reveals ions such as  $(C_5H_5)_3FeNi^+$  whilst ferrocene also shows ions resulting from fragmentation of  $(C_5H_5)_3Fe_2^+$ .

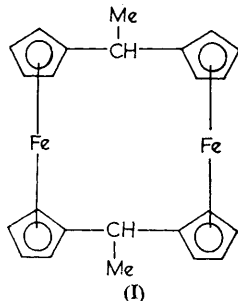
<sup>29</sup> B. F. G. Johnson, J. Lewis, I. G. Williams, and J. Wilson, *Chem. Comm.*, 1966, 391.

<sup>30</sup> F. W. McLafferty, *Analyt. Chem.*, 1956, **28**, 306.



The ionic cyclopentadienyls  $(\text{C}_5\text{H}_5)_2\text{Mn}$  and  $(\text{C}_5\text{H}_5)_2\text{Mg}$  produce similar fragment ions to those of the  $\pi$ -bonded complexes, although in very different relative abundance, indicative of the structural differences<sup>10</sup> [ $(\text{C}_5\text{H}_5)_2\text{Mn}^+$ , 19;  $\text{C}_5\text{H}_5\text{Mn}^+$ , 29;  $\text{Mn}^+$ , 25%;  $(\text{C}_5\text{H}_5)_2\text{Mg}^+$ , 21;  $\text{C}_5\text{H}_5\text{Mg}^+$ , 38;  $\text{Mg}^+$ , 31%]. With increasing ring substitution in ferrocene the abundance of metal-containing ions diminishes.<sup>31</sup>

The weaker metal-ring bonding in benzene complexes is probably reflected in the isoelectronic series  $(\text{C}_5\text{H}_5)_2\text{Fe}$ ,  $\text{C}_5\text{H}_5\text{MnC}_6\text{H}_6$ , and  $(\text{C}_6\text{H}_6)_2\text{Cr}$  for which the most abundant metal-containing species are  $(\text{C}_5\text{H}_5)_2\text{Fe}^+$ ,  $\text{C}_5\text{H}_5\text{Mn}^+$ , and  $\text{Cr}^+$ . In bisbenzenechromium the abundance of ions produced by fragmentation of benzene is high, and the doubly-charged molecular ion [a chromium(II) species] has also been reported.<sup>10,12</sup> Mass spectrometry has proved important in the characterisation of more complex cyclopentadienyls such as (I) for which the molecular ion forms the base peak, and metastable transitions are observed for successive loss of two methyl groups.<sup>32</sup> Similarly the zirconium oxide complex<sup>33</sup>  $[(\text{C}_5\text{H}_5)_2\text{ZrCl}]_2\text{O}$  gives many ions containing the  $\text{Zr}_2\text{O}$  unit.



Some  $\pi$ -allyl complexes are too unstable to show molecular ions under electron-impact, and field-ionisation mass spectrometry has been used to minimise fragmentation processes. Electron-impact fragmentation of the bis- $\pi$ -allyl complexes of nickel causes ethylene elimination and loss of allyl radicals from the parent, whereas in the platinum analogue elimination of propene predominates.<sup>34</sup>

<sup>31</sup> D. T. Roberts, W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, 1967, **89**, 4917 or refs. therein.

<sup>32</sup> W. E. Watts, *J. Organometallic Chem.*, 1967, **10**, 191 or refs. therein.

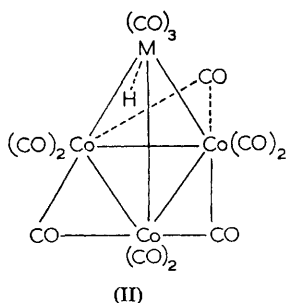
<sup>33</sup> A. F. Reid, J. S. Shannon, J. H. Swann, and P. C. Wailes, *Austral. J. Chem.*, 1965, **18**, 173.

<sup>34</sup> J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc. (A)*, 1967, 423.

**Carbonyl Hydrides.**—In the mass spectra of metal carbonyl hydrides hydrogen is strongly retained by parent and fragment ions. Manganese carbonyl hydride shows two series of ions,  $\text{HMn}(\text{CO})_{0-5}^+$  and  $\text{Mn}(\text{CO})_{0-5}^+$  in which elimination of a hydrogen radical competes with loss of carbon monoxide.<sup>12</sup>

Polynuclear carbonyl hydrides lose carbon monoxide more readily than hydrogen as in  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$  where the base peak is due to  $\text{H}_3\text{Mn}_3(\text{CO})_4^+$ . In similar rhenium and ruthenium hydrides [ $\text{H}_3\text{Re}_3(\text{CO})_{12}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{12}$ ] the molecular ions are of high abundance.<sup>35,36</sup> Polynuclear carbonyl hydrides pose an acute analytical problem and the number of hydrogen atoms attached to a metal cluster cannot usually be predicted. For most compounds of this type molecular compositions are convincingly established from their mass spectra. In the complex borohydride  $\text{H}_7\text{B}_2\text{Mn}_3(\text{CO})_{10}$ , six of the hydrogen atoms form bridging B—H—Mn bonds whilst the other occupies a bridging position across an Mn—Mn bond. Its mass spectrum shows that all of the hydrogen atoms are retained until four carbonyl groups have been lost, and in general it appears that bridging hydrogen atoms are even more strongly retained than those occupying terminal positions.<sup>36</sup>

The structures of several unusual compounds derive support from their mass spectra. For example, the iron and ruthenium complexes,  $\text{HMC}_3(\text{CO})_{12}$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) have been assigned structure (II) in which the hydrogen atom is enclosed in the metal cage. Their mass spectra show the molecular ion followed by successive loss of six carbonyl groups. Slight hydrogen loss is then observed while the remaining six carbonyl groups are cleaved. Only when the tetrahedron of metal atoms  $\text{Co}_3\text{M}$  is broken does hydrogen loss become an important process. Although hydrogen is initially bonded to iron or ruthenium, low abundance cobalt hydride ions ( $\text{HC}_3^+$  and  $\text{HC}_2^+$ ) are observed.<sup>37</sup>



**Hydrocarbon–Metal Carbonyls.**—The mass spectra of complexes having different ligands bonded to a transition metal reflect differences in metal–ligand

<sup>35</sup> B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *J. Organometallic Chem.*, 1967, **10**, 105 or refs. therein.

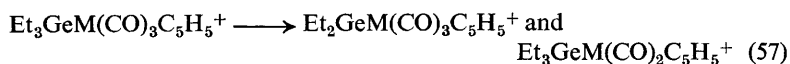
<sup>36</sup> J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1967, **89**, 1759 or refs. therein.

<sup>37</sup> M. J. Mays and R. N. F. Simpson, *Chem. Comm.*, 1967, 1024 or refs. therein.



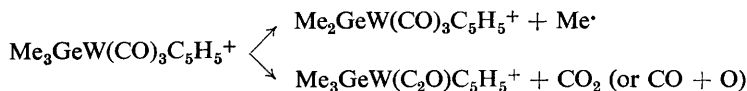
bond strengths. In cyclopentadienylmetal carbonyls the carbonyl groups are lost before cyclopentadienyl although in some cases the ion  $\text{MCO}^+$  can be detected.<sup>14</sup> Cyclobutadieneiron tricarbonyl is similar in that carbonyl groups are lost before fragmentation or cleavage of cyclobutadiene.<sup>38</sup> In benzenechromium tricarbonyl the ions  $\text{Cr}(\text{CO})_{0-3}^+$  are of low abundance, whilst in cyclopentadienylnickel nitrosyl the ion  $\text{NiNO}^+$  is only 1.5% as abundant as the base peak  $\text{C}_5\text{H}_5\text{Ni}^+$ .<sup>12</sup> In  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$  both carbonyl groups are lost before the nitrosyl group.<sup>39</sup>

In molybdenum and tungsten complexes such as  $\text{Et}_3\text{GeM}(\text{CO})_3\text{C}_5\text{H}_5$  a high proportion of the ion current is carried by species containing the  $\text{GeM}$  group and molecular ions are of high abundance. The first fragment ions are those formed by loss of carbonyl or an ethyl radical and further degradation (57) takes place by ethylene and carbonyl elimination.



A most unusual feature in the spectrum of the trimethylgermyltungsten complex is that the parent ion decomposes by loss of a methyl radical or carbon dioxide<sup>40</sup> (Scheme 3). The influence of bridging carbonyl groups on the proportion of

Scheme 3



dimetallic ions has been referred to and further illustrations are provided by the dimeric compounds  $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$  and  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ . In the former the most abundant ion is  $(\text{C}_5\text{H}_5)_2\text{Mo}_2^+$  whereas in the carbonyl-bridged iron complex dimer ions are of low abundance and the base peak is  $\text{C}_5\text{H}_5\text{Fe}^+$ .<sup>12</sup> These complexes form ion-molecule associates as with ferrocene.<sup>10</sup> In cyclohexadieneiron tricarbonyl loss of molecular hydrogen is a significant process, probably yielding  $\pi$ -benzenecarbonyl ions.<sup>39</sup>

**Carbonyl Halides.**—Manganese- and rhenium-carbonyl halides  $(\text{CO})_5\text{MX}$  and  $\text{Fe}(\text{CO})_4\text{I}_2$  show comparable loss of carbonyl and halide from the molecular ions, although  $\text{MX}^+$  ions are of considerable abundance. In halogen-bridged dimers such as  $(\text{CO})_8\text{Mn}_2\text{X}_2$  the  $\text{Mn}_2\text{X}_2$  unit persists unfragmented until loss of carbonyl groups is complete. As with the hydrides there seems to be an appreciable difference between ease of elimination of terminal and bridging ligands.<sup>12,35</sup>

**Carbonyl-phosphorus Complexes.**—Differences in the donor-acceptor properties of phosphines relative to carbon monoxide influence fragmentation behaviour

<sup>38</sup> R. G. Amiet, P. C. Reeves, and R. Pettit, *Chem. Comm.*, 1967, 1208.

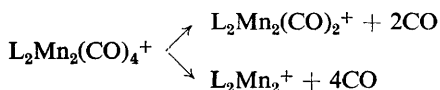
<sup>39</sup> M. A. Haas and J. M. Wilson, *J. Chem. Soc. (B)*, 1968, 104 or refs. therein.

<sup>40</sup> A. Carrick and F. Glockling, *J. Chem. Soc. (A)*, 1968, 913.

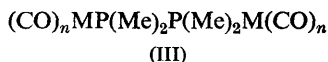
considerably. In carbonyltriphenylphosphine complexes of molybdenum and tungsten,  $\text{Ph}_3\text{PM}(\text{CO})_5$ , the triphenylphosphine group is eliminated only after complete loss of carbon monoxide, and there is little fragmentation of the phosphine. By contrast the chelating phosphine complexes  $(\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2)\text{M}(\text{CO})_4$  lose ethylene forming the ion  $(\text{Ph}_2\text{P})_2\text{M}^+$ .

In binuclear complexes with tertiary phosphines,  $[\text{R}_3\text{PMn}(\text{CO})_4]_2$ , the abundance of dimetallic species is low compared with unsubstituted binuclear carbonyls, and arylphosphines enhance this effect more than alkylphosphines. Binuclear phosphite complexes  $[(\text{RO})_3\text{PMn}(\text{CO})_4]_2$  lose carbonyl groups more readily than phosphite and metastable peaks are apparent for the loss of four and two carbonyl groups<sup>12</sup> (Scheme 4).

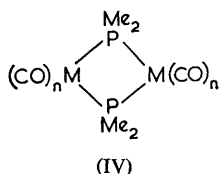
Scheme 4



Several phosphino-bridged complexes of Cr, Fe, Mn, Mo, and W have been examined (III and IV) and loss of carbonyl groups leaves the  $\text{M}_2\text{P}_2\text{Me}_4$  nucleus



intact. For compounds of the type (IV) mononuclear metal ions, present in low abundance, are probably formed by the process (57).<sup>41</sup>



**Carbonyl-sulphur Complexes.**—Sulphur is a very strong ligand to many transition metals and the trinuclear complex  $\text{Fe}_3(\text{CO})_9\text{S}_2$  loses all the carbonyl groups leaving the ion  $\text{Fe}_3\text{S}_2^+$  as the base peak of the spectrum.<sup>42</sup> Similarly thio-bridged metal carbonyls such as  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{R}_2$ ,  $\text{Mn}_2(\text{CO})_8\text{S}_2\text{R}_2$ , and  $\text{Re}_2(\text{CO})_8\text{S}_2\text{Ph}_2$  resemble phosphorus and halide analogues in retaining the  $\text{M}_2\text{S}_2\text{R}_2$  structure until loss of carbonyl groups is completed. Alkene loss is then observed if R is ethyl or butyl. Trimeric and tetrameric compounds show similar features.<sup>35,43</sup>

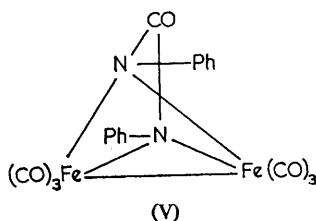
<sup>41</sup> B. F. G. Johnson, J. Lewis, J. M. Wilson, and D. T. Thompson, *J. Chem. Soc. (A)*, 1967 1445 or refs. therein.

<sup>42</sup> S. R. Smith, R. A. Krause, and G. O. Dudek, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1533.

<sup>43</sup> M. Ahmad, G. R. Knox, F. J. Preston, and R. I. Reed, *Chem. Comm.*, 1967, 138.

**Other Substituents.**—Elimination of nitric oxide from complexes such as  $\text{Co}(\text{CO})_3\text{NO}$  and  $\text{Fe}(\text{CO})_2(\text{NO})_2$  competes with carbonyl loss at all stages. In the phosphorus trichloride complex  $\text{Co}(\text{CO})_2(\text{NO})\text{PCl}_3$  the molecular ion loses a chloride radical as well as the three neutral ligands.<sup>12</sup> In transition-metal-Group IVB metal complexes, like  $(\text{Me}_3\text{Sn})_2\text{Ru}(\text{CO})_4$ , a methyl radical is lost before a carbonyl group<sup>44</sup> whereas in  $\text{Ph}_3\text{SnMn}(\text{CO})_5$  the ion of highest mass,  $\text{Ph}_3\text{SnMn}^+$ , shows successive loss of phenyl radicals.<sup>5</sup>

Mass spectrometry has provided support for a number of unusual structures. The compound  $(\text{PhN})_2\text{Fe}_2(\text{CO})_7$  formed in the reaction between  $\text{Fe}_3(\text{CO})_{12}$  and phenyl isocyanate shows the molecular ion and fragments involving loss of only six carbonyl groups followed by the elimination of phenyl isocyanate. This behaviour is completely compatible with structure (V).<sup>45</sup> A further novel



example is the ruthenium carbonyl carbide  $\text{Ru}_6(\text{CO})_{17}\text{C}$  in which the 'carbide' atom lies close to the centre of an irregular octahedron of ruthenium atoms with both bridging and terminal carbonyl groups.<sup>45a</sup> The mass spectrum is understandable in terms of this structure since the molecular ion is observed followed by stepwise elimination of all 17 carbonyl groups giving finally the very abundant ion,  $\text{Ru}_6\text{C}^+$ . No singly-charged ions of lower mass were present but abundant doubly-charged ions,  $\text{Ru}_6\text{C}(\text{CO})_{0-17}^{2+}$  were observed.<sup>46</sup>

**$\sigma$ -Bonded Complexes.**—Comparison of the mass spectrum of the  $\sigma$ -benzyliron complex  $\text{C}_5\text{H}_5(\text{CO})_2\text{FeCH}_2\text{Ph}$  with that of the pentafluorophenyl analogue suggests that on ionisation only the former is transformed into the  $\pi$ -bonded tropylium group.<sup>47</sup> Methylmanganese pentacarbonyl loses a methyl radical and carbonyl groups competitively, and several manganese hydride ions are produced in low abundance. The trifluoromethyl analogue behaves differently in that the molecular ion is far more abundant and the highest-mass fragment ion is formed by loss of  $\text{F}^+$ . Rearrangement ions containing  $\text{Mn}-\text{F}$  bonds are of appreciable abundance. Methylsulphonylmanganese pentacarbonyl  $\text{MeSO}_2\text{Mn}(\text{CO})_5$  does not show ions due to successive elimination of carbonyl groups, most of the

<sup>44</sup> J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *Chem. Comm.*, 1967, 965.

<sup>45</sup> J. A. J. Jarvis, B. E. Job, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Comm.*, 1967, 1149.

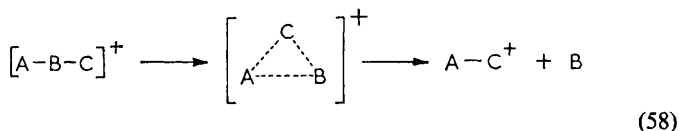
<sup>45a</sup> R. Mason and W. R. Robinson, *Chem. Comm.*, 1968, 468.

<sup>46</sup> B. F. G. Johnson, R. D. Johnston, and J. Lewis, *Chem. Comm.*, 1967, 1057.

<sup>47</sup> M. I. Bruce, *J. Organometallic Chem.*, 1967, **10**, 495 or refs. therein.

ion current being carried by the species  $\text{SO}_2\text{Mn}(\text{CO})_5^+$ ,  $\text{Mn}(\text{CO})_5^+$ ,  $\text{Mn}(\text{CO})_4^+$ , and  $\text{Mn}^+$ .<sup>48</sup>

**Rearrangement Ions.**—The fragmentation processes so far discussed involve simple bond cleavage with in some cases migration of a hydrogen atom. However, as with organic compounds,<sup>49</sup> electron-impact induced migration (58) of function groups is quite common.

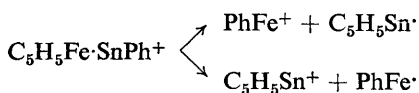


Rearrangement ions are often of high abundance and this makes the use of mass spectrometry ambiguous for distinguishing isomers of, for example,  $\text{A}_3\text{M}\cdot\text{MB}_3$  and it also poses problems for 'element mapping' by computer.<sup>49</sup>

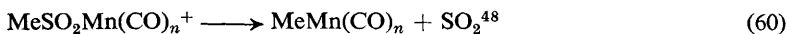
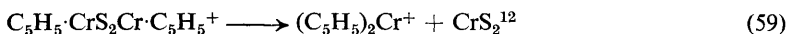
Compounds of the type  $\text{A}_3\text{M}\cdot\text{M}'\text{B}_3$  ( $\text{M}, \text{M}' = \text{Si}, \text{Ge}, \text{Sn}$ ) show all possible rearrangement ions  $\text{A}_2\text{MB}^+$ ,  $\text{AMB}_2^+$ ,  $\text{MB}_3^+$ ,  $\text{B}_2\text{M}'\text{A}^+$ ,  $\text{BM}'\text{A}_2^+$ , and  $\text{M}'\text{A}_3^+$ . Rearrangement may occur in the molecular ion or in fragment ions containing the metal-metal bond. It is also possible that rearrangement ions are formed by a synchronous process in which transfer or interchange of groups is accompanied by fission of the metal-metal bond. In the above series of compounds ( $\text{M} \neq \text{M}'$ ) rearrangement ions are most abundant for silicon and least for tin.<sup>4</sup>

Migration reactions are observed in other types of metal-metal bonded compounds such as the iron-tin complex  $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}\cdot\text{SnPh}_3$  (Scheme 5).

Scheme 5



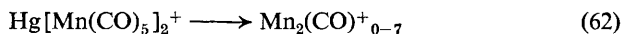
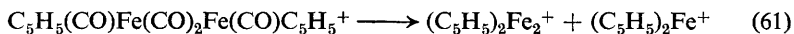
Similarly the  $\text{PhMn}^+$  ion is observed in the spectrum of  $\text{Ph}_3\text{Sn}\cdot\text{Mn}(\text{CO})_5$ . Transfer of an initially  $\pi$ -bonded cyclopentadienyl group from a transition- to a non-transition-metal is a common process, and for  $[\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}]_2\text{SnCl}_2$  the cyclopentadienyltin ion is the most abundant in the spectrum.<sup>12</sup> Trialkylgermyl-molybdenum and -tungsten complexes  $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{M}\cdot\text{GeR}_3$  behave similarly forming the ion  $\text{C}_5\text{H}_5\text{Ge}^+$ .<sup>40</sup> Transfer of carbonyl groups must occur in various rhenium carbonyls  $[\text{Re}_2(\text{CO})_{10}, (\text{CO})_5\text{Re}\cdot\text{Mn}(\text{CO})_5, \text{H}_3\text{Re}_3(\text{CO})_4]$  since  $\text{Re}(\text{CO})_6^+$  is formed in low abundance.<sup>12,36</sup> Phosphorus-, sulphur-, and oxygen-metal complexes show ions which result from rearrangement processes, *e.g.*, (59), (60).



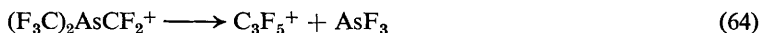
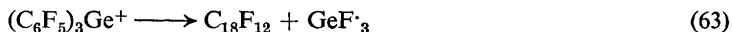
<sup>48</sup> M. J. Mays and R. N. F. Simpson, *J. Chem. Soc. (A)*, 1967, 1936 or refs. therein.

<sup>49</sup> P. Brown and C. Djerassi, *Angew. Chem. Internat. Edn.*, 1966, **6**, 477.

Migration of groups from carbon to a metal has also been observed. For example, Si-O and Si-N compounds such as  $\text{Me}_3\text{Si}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$  and  $\text{Me}_3\text{Si}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$  produce phenylsilyl ions<sup>2</sup> whilst substituted arene complexes of the type  $\pi\text{-C}_6\text{H}_5\cdot\text{CORM}(\text{CO})_3$  ( $\text{M} = \text{Mn}, \text{Cr}$ ) form  $\text{RM}^+$  and  $\text{C}_6\text{H}_5\text{MR}^+$  ions.<sup>12</sup> Rearrangement processes can also result in the formation of metal-metal bonds as in examples (61), (62), although thermal decomposition followed by ionisation may also occur.<sup>48,49</sup>



Group-migration reactions are common in fluorocarbon-metal compounds, presumably because of the high strength of metal-fluorine bonds. Tetrakis-(pentafluorophenyl)germane<sup>4</sup> produces  $(\text{C}_6\text{F}_5)_2\text{GeF}^+$  in high abundance contrasting with the low abundance of  $\text{Ph}_2\text{GeH}^+$  derived from tetraphenylgermane. Migration of fluorine from carbon to metal produces high abundance ions in the mass spectra of fluorocarbon derivatives of silicon,<sup>4</sup> arsenic,<sup>50</sup> iron,<sup>4,39,47,51</sup> manganese,<sup>12,48</sup> and rhenium,<sup>12</sup> and elimination of the neutral metal fluoride is often observed, as in (63) and (64).



<sup>50</sup> R. C. Dobbie and R. G. Cavell, *Inorg. Chem.*, 1967, **6**, 1450.

<sup>51</sup> R. B. King, *J. Amer. Chem. Soc.*, 1967 **89**, 6368.