SOME APPLICATIONS OF MASS SPECTROSCOPY IN INORGANIC AND ORGANOMETALLIC CHEMISTRY

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I. Introduction

Mass spectroscopic studies of organometallic compounds are almost as old as the field of mass spectrometry: nickel tetracarbonyl was studied by J. J. Thomson (*1*) and Aston (*2, 3*) in their work on the isotope ratios of nickel. Following this early flurry of specialized interest, however, inorganic and organometallic mass spectral studies were delayed until the late 1950s, at which time commercial "organic" mass spectrometers offered suitable inlet systems and extended mass range. Routine use of these instruments by inorganic chemists was postponed a further decade by the fear, unfortunately still prevalent today in many laboratories, that metal-containing compounds will decompose and thus contaminate the instrument. We hope to illustrate in this review, aimed at the inorganic or organometallic chemist considering the use of mass spectroscopy as a routine technique in his work, that this fear is groundless. Certainly these compounds may cause problems, but with care these are no worse than those encountered at times in the mass spectral studies of organic heterocycles, biological materials, or environmental samples.

The field of organometallic mass spectroscopy has been covered by a series of general reviews (*4–6*), whereas more specific reports include those on metallocenes (*7*), transition metal carbonyl derivatives (*8*), Group IV (*8a*), germanium compounds (*9*, *10*), and boron compounds (*11*). King (*12*) reviewed his work with transition metal derivatives, whereas Müller (*13*) attempted to classify decomposition types for organometallic chemistry. More inorganic in nature are the proceedings of a 1966 American Chemical Society Symposium (*14*). A most comprehensive reference source for both inorganic and organometallic compounds is the recent book by Litzow and Spalding (*15*). Organometallic and coordination compounds are covered by Bruce in the Chemical Society's *Specialist Periodical Reports* (*16*, *17*), and the monthly *Mass Spectrometry Bulletin* (*18*) indexes articles, books, and conference proceedings for mass spectrometry-related material, including organometallic and inorganic subsections. Mass spectrometry of metal-containing compounds has formed the topic of both ASMS (*19*) and international (*20*) symposia.

Several of the standard organic mass spectrometry reference works (*21–24*) also contain material useful to the inorganic/organometallic chemist, as do some of the more general mass spectrometry works, which also contain greater discussion of theory and instrumentation (*25–31*), Kiser's book (*25*) in particular referring to much of the early work in the field. The beginner in the field of inorganic/organometallic mass spectrometry should be familiar with the basics of organic mass spectra such as can be obtained from McLafferty's (*31*) and other books (*32*, *33*).

In this review we point out briefly the various instrumentation factors important in obtaining mass spectra of inorganic and organometallic compounds and in affecting the quality of spectra observed. Selected examples are chosen, admittedly with a personal bias, to illustrate the various types of information available from mass spectra. We have deliberately not discussed elemental analysis by spark-source mass spectrometry (*34*, *35*) nor detailed thermochemical studies possible with the Knudsen cell (*36*, *37*), but we do point out some of the new ionization techniques which may be of potential use in the future.

II. Instrumentation and Sample Handling

A. MASS ANALYZERS

Most of the mass spectrometers used for the work that we are describing use sector magnetic mass analyzers; descriptions of the ion optics, etc., may be found in most of the standard works referenced in the Introduction. The minimum mass analyzer requirements for an instrument to be used routinely for inorganic and organometallic compounds are an upper mass range of m/e 1000, but preferably higher and medium resolution,* i.e., a resolution of 1000 to 5000, although some studies may require high resolution (commercial instruments now readily achieve resolutions of 10,000 to 150,000). Until recently only magnetic analyzers met the mass range and medium-resolution requirements.

The mass spectrometers most commonly used for the work described have been 60° and 90° single-focusing instruments (*38*), and double-focusing instruments of Nier-Johnson (*39*), reversed Nier-Johnson (*40*), and Mattauch-Herzog (*41*) geometry, the double-focusing instruments generally producing higher resolution. Older instruments all had nonlinear mass scans, but newer designs incorporate either Hall effect feedback loops in the magnet scan control or variable chart speed to give a pseudolinear spectrum presentation.

Quadrupole or radio-frequency mass analyzers have only recently become available with the mass range and resolution (*42*) to be of general use in inorganic and organometallic mass spectrometry, although they have been popular as small mass spectrometers built into specific systems as reaction monitors. They do have the advantage of essentially linear

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* Resolution in mass spectrometry is defined as $R = M/\Delta M$, where M is the mass under consideration and ΔM the mass difference between adjacent peaks. Unlike most other forms of spectroscopy where width at half height would be used as ΔM, the mass spectrometry convention is the 10% valley definition, i.e., for two peaks of equal height ΔM would be the peak separation producing a valley between them, whose height above the base line is equal to 10% of the peak heights. To a first approximation, therefore, for an isolated peak, ΔM corresponds to the width at 5% maximum height. Some manufacturers still use width at half height, which gives an apparent resolution of about twice that of the 10% valley definition. Magnetic instruments have essentially constant resolution throughout the mass range, whereas quadrupole mass analyzers have variable resolution, e.g., $R = 250$ at m/e 250 and $R = 25$ at m/e 25.

mass scans. Time-of-flight instruments (*43*) have never really achieved the mass range or resolution to become popular in their field. However, much early work, especially that involving appearance potential studies (*25*) was facilitated by time-of-flight instruments where open ion source design offers particular adaptability to special problems or very dirty systems. The cycloidal double-focusing designs were not a commercial success (*44*) for routine work and are no longer manufactured. Of the various types, the magnetic analyzer is to be preferred for another reason, namely, the ready observation of metastable ions (see Section VI).

B. ION SOURCES

The details of ion sources, recently reviewed by Chait (*45*), and adequately covered in the major mass spectrometry texts will just be mentioned briefly, and the potential mass spectrometer user is advised to investigate the facilities in his laboratories.

1. *Electron Impact Sources*

Most mass spectrometers available to the routine user are equipped with electron impact (EI) sources. In these sources, a heated filament of rhenium or tungsten produces electrons that are accelerated to a "trap" anode with energies typically variable from 5 to 100 eV, adjustable energies permitting appearance potential studies. Unless otherwise specified, most laboratories run spectra at 70 eV. Collimating slits and magnets pass the electron beam through the "cage" or ion source proper where ionization occurs by the following process:

$$M + e^- \longrightarrow M^{+\cdot} + 2e^- \tag{1}$$

The positive ions formed are extracted from the cage by a repeller plate with a small variable positive charge, collimated and focused by slits and electrostatic lenses, and finally accelerated to a high potential (1000–10,000 volts depending on the instrument and mass range). Decreasing the accelerating voltage increases the mass range of a particular magnetic analyzer but decreases both resolution and sensitivity.

Most common ion sources are categorized as "closed" or "tight," the inside of the cage typically being on the order of a 5-mm cube, the only passages to its interior being the electron entrance and exit slits, the positive ion exit slit, and one or more small holes for the sample inlet devices such as a solid probe, batch inlet, and gas chromatograph (GC) interface. These sources maximize sample pressure in the region of the electron beam and typically have sensitivities several orders of magnitude greater than "open" sources (*46*), where all components are open to the source housing and thus rapid pumping. Time-of-flight and quadrupole instruments are often designed with open sources, as are specialized units for studies in fast kinetics where pumping speed is important. In closed source instruments the user must be aware that the sample pressure in the ion source is not that read from the ion-source pressure gauge, which measures pressure in either the source housing or source pumping line, and it is necessary to calculate the actual pressure (*47*) in the cage, typically several orders of magnitude higher than the gauge reading.

2. *Chemical Ionization*

Chemical ionization (CI) sources (*48*, *49*) use electron bombardment of a reagent gas at higher pressures than normally found in a mass spectrometer ion source, i.e., ~1 torr. Sample ionization follows via an ion–molecule reaction, often accompanied by a proton transfer to yield a "quasi-molecular ion":

$$\underset{\text{reagent gas}}{CH_4 + e^-} \xrightarrow[\text{1 torr}]{CH_4} CH_5^+ \quad \text{etc.} \tag{2}$$

$$\underset{\text{sample}}{CH_5^+ + M} \longrightarrow \underset{\text{quasi-molecular ion}}{MH^+ + CH_4} \tag{3}$$

This method of ionization usually causes minimum fragmentation of the molecule under investigation, and thus can be useful in establishing molecular weights, but as little fragmentation occurs it may be of less use as an aid in structure elucidation.

Hunt's group (*50*, *51*) have pioneered the application of the CI source to organometallics such as the iron tricarbonyl complex of heptafulvene, whose electron impact spectrum shows $(M—CO)^+$ as the heaviest ion, in contrast to the methane CI spectrum with the MH^+ ion as base peak. Boron hydrides (*52*) and borazine (*53*) have also been studied. The methane CI spectrum of arenechromium and -molybdenum (*54*) show protonation at the metal giving a protonated parent or molecular ion. Risby *et al.* have studied the isobutane CI mass spectra of lanthanide 2,2,6,6-tetramethylheptane-3,5-dionates[$Ln(thd)_3$] (*55*) and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione [H(fod)] lanthanide complexes (*56*). These latter complexes have been suggested as a means of analysis for the lanthanide elements.

3. *Field Ionization/Field Desorption*

Field ionization (FI) mass spectrometry (*57*, *58*) (produced by a high electric field gradient between a sharp blade and the first source slit) is another technique useful for obtaining parent molecular ions without undue fragmentation. The sample, however, must still be volatilized into the source, so there may be no advantage for thermally sensitive materials. The recently developed field desorption (FD) technique of Beckey (*59*, *60*) involves the use of a wire emitter, similar to that in an FI source, which has been activated by growing of carbon microneedles on its surface. The sample is deposited, usually from solution, onto the emitter, and then desorbed under the influence of a high field gradient. For example, biological species that cannot normally be thermally volatilized may be introduced into the ion source in this manner. The technique has been used as well in conjunction with liquid chromatography (*61*) and with heated emitters (*62*). To date, no inorganic or organometallic compounds have been investigated by this promising technique although inorganic salts have been alluded to (*62a*). The few commercial instruments (*63*) delivered to date have been used mainly for biochemical applications. If, as proposed, the double-beam MS-30 mass spectrometer can be fitted with an FD source on one side and a standard EI source on the other, the problem of mass marking and exact mass measurement, important at the high molecular weights to be expected for organometallic polymers, etc., will be greatly simplified (*64*, *65*).

Hass *et al.* (*65a*) have observed no ion current from an emitter coated with hexaquocobalt(II)chloride, but on the admission to the ion source of gaseous acetylacetone (Hacac) the ion $[Co(acac)Cl]^+$ was observed. Trifluoroacetic acid produced an analogous ion and when $FeCl_2$ was coated on the emitter the corresponding iron chelate was observed. Sodium from sodium chloride has also been detected by volatilization with acetic acid.

Phthalocyanines and metal phthalocyanines which require high probe (and often high source) temperatures (>350°C) in conventional EI mass spectrometry, readily give molecular ions as the base peak (*65b*) in FD spectra and minimal fragmentation occurs, providing a rapid method for the qualitative examination of mixtures of phthalocyanines.

Organic complex salts of the type $[LM(CO)_3]^+BF_4^-$ [M = Fe, L = cyclo-C_6H_7, cyclo-C_7H_9, cyclo-$C_{10}H_{11}$, 2MeO-cyclo-C_6H_7; M = W, L = cyclo-C_7H_7], $[(Ar)Fe(C_5H_5)]^+PF_6^-$ [Ar = C_6H_6, $CH_3C_6H_5$, $(CH_3)_3C_6H_3$], and $[(\text{cyclo-}C_8H_{11})Co(C_5H_5)]^+BF_4^-$ have been studied by FD mass spectrometry (*65c*). They show molecular or quasimolecular ions, usually the base peak, and fragment ions corresponding to metal ligand cleavages. (The last 3 paragraphs were added in proof.)

4. *Other Sources*

Several other types of ion source under development should be watched closely for potential inorganic/organometallic use. Ionization by electrons from a ^{63}Ni source has been used in an external ion source that is at atmospheric pressure (*66*, *67*) giving a reported sensitivity in the subpicogram range.

A second type of source worth watching is the electrohydrodynamic (EHD) ionization source (*68–70*). This source, built into both AEI MS-7 and MS-902 mass spectrometers, was originally applied to the analysis of liquid metal systems (*68*, *69*), such as the Ga–In eutectic alloy, which showed not only Ga^+ and In^+ ions but also species such as Ga_2^+, $GaIn^+$, In_2^+, Ga_2In^+, Ga_4^+, and Ga_5^+ as well as five metallic impurities. Similar results were observed for GaInSn and Cerrolow 117 alloy containing Bi, In, Pb, Sn, Cd, and Hg. This work has now been extended to a nonmetallic liquid, glycerol (*70*), which in the presence of dissolved metallic salts gives ions such as $[\text{glycerol} + \text{cation} - \text{H}]_n^+$. Complex inorganic salts may become amenable to study by EHD ionization.

Spark, photoionization, surface, thermionic, and laser ionization sources are not considered in this review.

C. BASIC INLET SYSTEMS

1. *Direct Insertion or "Solids" Probe*

As relatively high volatility (≈ 1 torr), thermal stability, and a fairly large sample size (1–10 μl liquid) are required of samples to be introduced via the batch inlet system, the development of the direct insertion probe makes possible much of modern mass spectroscopic work. The probe may be rapidly loaded and inserted through a sliding-seal vacuum lock such that the sample, usually contained in a glass or quartz cup, may be evaporated directly into the "tight" ion chamber. Older units were heated indirectly by the hot ion source, but newer probes are electrically heated with temperature control independent of source temperature, and in some cases coolable as well; the latter is useful in lowering the volatility of, for example, some metal carbonyls. Separate temperature control of the solids probe is a must for any new mass spectrometer. It should be noted that a solids probe can readily be used for relatively nonvolatile liquids, simply by transferring a small quantity to the sample cup with fine wire. For both solids or liquids, if the sample is visible, then there is enough in the probe.

2. *Gases/Liquids Probe*

Many manufacturers now offer other sample injection systems compatible with the vacuum lock used for the solids probe. These include small (e.g., 75-ml) heatable batch inlet systems, usually accessible via syringe (gas syringe or GC microliter syringe for liquids), which can be particularly useful as inlets for mass reference compounds. Other probes are designed as flexible, easily removed connections to a gas chromatograph via some form of interface.

3. *Batch Inlet System*

Batch inlet systems are in many ways the most convenient for gases and volatile, thermally stable liquids or solids, provided there is sufficient sample available. They consist of reservoirs, varying in volume from 20 ml to several liters, which are connected to the ion source via a "molecular leak," usually a porous ceramic material, or a pinhole in thin gold foil or glass. The leak serves to reduce the pressure from 10^{-2} torr in the inlet system to $\sim 10^{-5}$ torr in the ion source. Large ballast bulbs valved to the system allow a constant pressure feed to the source for long duration, such as appearance potential studies. Batch inlets for room temperature work were traditionally constructed of glass, whereas heated inlets were of metal, and later glass-coated metal. Today, however, most manufacturers offer all-glass heated inlet systems (AGHIS), valves being of the magnetically operated "optical flat" type with no lubricant or sealant. Gases are admitted via some form of pressure reduction manifold, gases and liquids may be admitted by syringe (*71*, *72*), and liquids and solids by some form of removable sample cup.

4. *GC/MS Interfaces*

Combined gas chromatography/mass spectrometry (GC/MS), which is likely to be of increasing importance to inorganic and organometallic chemistry (Section VII), is discussed in detail in both a recent book (*30*) and review (*73*). Not only can complex reaction products be studied, but reactions may be monitored and trace by-products identified. The gas chromatograph has the advantage of concentrating a sample so that it has all eluted from the column and entered the mass spectrometer in a matter of seconds. This is no problem for modern fast-scanning mass spectrometers. The question of GC/MS interfacing is of prime importance, however, as the sample must be introduced into the source through a large pressure differential, from 1 atm to 10^{-6} torr, requiring the preferential removal of carrier gas. Early solutions involved capillary columns (most mass spectrometers will accept 1–3 ml/min of helium without undue pressure rise), stream splitters, and capillary "sniffers." Maximum detection limits (10^{-10}–10^{-11} gm) were obtained only when various molecular separators were employed as sample-enrichment devices.

The most common separators include the Ryhage or jet diffusion separator (*74*), the Watson–Biemann or pore diffusion separator (*75*), and the membrane solution diffusion separator originally developed by Llewellyn (*76*). The first two separators involve direct passage of the sample into the mass spectrometer; the low molecular weight helium diffuses more readily and is pumped away. The membrane separator involves diffusion of the sample through a silicone membrane while the carrier gas vents to the atmosphere; carrier gas is thus not confined to helium. There is no "best separator"; the choice depends on the nature of the compounds, the temperature range over which it will be operated, and most usually what is available in a particular laboratory. A convenient configuration for a double-beam mass spectrometer such as the AEI MS-30 is two different separators, one into each beam, which permits rapid evaluation of separator performance.

Of all the inlets, the GC is the most foolproof, since operation of high vacuum valving, the chief danger with probe and batch inlets, is not necessary. Thus, once the instrument is properly tuned and operating, even novices may run their own GC/MS with minimum supervision.

D. HANDLING AIR- AND MOISTURE-SENSITIVE COMPOUNDS

One problem arising with inorganic and organometallic samples is the air and/or moisture sensitivity of many of these compounds. With ingenuity such problems can usually be overcome. The greatest hurdle is to convince the person in charge of the mass spectrometer that the minor modifications will only enhance the capability of the instrument. To quote Cooks and Beynon (*77*): "commercial scientific instruments are anything but sacrosanct. They should be modified, rearranged, run backwards, prodded, and coaxed to perform tasks other than those envisaged by the designer. One can hardly be doing something new if one is using an instrument in a manner foreseen when the instrument was designed." Labels "organic" and "inorganic (spark-source)" mass spectrometer in no way justify limited use, to the exclusion of the organometallic sample or to the modification of the instrument to meet changing problems. Because various specialized inlets have been reviewed by Beynon (*78*) and others, we only indicate a few current techniques of particular use.

For many workers, the handling of samples under anhydrous or oxygen-free conditions is of primary importance. The speed and efficiency of solids probe sample introduction need not be lost, as two simple techniques are applicable to this problem. Since most probes have sample holders made of glass or quartz of similar cross-section to melting point tubing, samples loaded in a dry box into either actual sample cups or pieces of capillary may be transported to the mass spectrometer sealed under an inert atmosphere. The sample cup can then be transferred to the probe and the assembly inserted into the vacuum lock by the use of an inexpensive disposable plastic glove bag, which is readily erected over the vacuum lock and purged with nitrogen, aided, if necessary, by the vacuum pump of the lock. We have readily handled anhydrous organotin nitrates (*79*) and spontaneously inflammable phosphines in this manner with no signs of hydrolysis or oxidation. Use of a concentric tube sample cup (Fig. 1), easily fabricated by a glassblower, can eliminate the need of the glove bag. If such tubes are loaded in a dry box and transported to the instrument under nitrogen, the few seconds required to transfer to the probe and pump down are insufficient for air to diffuse significantly through the narrow opening. Again, when tested with spontaneously inflammable phosphines, no phosphine oxide was observed in the mass spectra. The concentric tube is also useful in limiting sample quantity entering the ion source in the case of more volatile solids. Other workers have built modified probes (*80*) for handling specific compounds and describe (*81*) useful methods for concentrating microsamples for probe insertion.

FIG. 1. Concentric sample cup for a direct probe. Typical dimensions: 1.7 mm O.D. × 9 mm long.

For more volatile compounds, the simplest procedure is to build a small vacuum line to handle sensitive materials. Depending on the mass spectrometer this may either be permanently attached or portable, connecting through the batch inlet which also supplies the vacuum source. Modern greaseless stopcocks plus use of glass "break seals" allow the most sensitive compounds to be handled. One can also readily build small breakers for sealed capillaries for use with the AGHIS (*82*), so that the entire device fits into the sample-heating oven. Others have built simple heated inlet systems by replacing the column in a GC interfaced to the MS (*83*, *84*). Sensitive liquids are readily handled via GC syringes (*72*) and even inflammable gases can be handled readily by syringe. An expensive gas syringe is useful, but we found that we could handle PH_3–organophosphine mixtures, sampled from an autoclave, very readily in 2-ml disposable plastic syringes (*85*), which for some purposes were more successful than the gas syringes. Syringes for injection of solids are also available and can be loaded in a dry box for transport to the mass spectrometer.

Spots from thin-layer chromatography (TLC) plates may often be used directly in the mass spectrometer without eluting thus for air-sensitive compounds, when TLC is done in a glove box, a "concentric" tube may be directly loaded with the unknown plus support; the concentric tube is recommended because it minimizes loss of silica gel into the ion source.

III. Inorganic and Organometallic Mass Spectra: Practice and Pitfalls

The initial stimulus to submit a sample for mass spectrometric analysis, is usually a desire for confirmation of the molecular weight and elemental composition of a compound. Although much additional structural information is contained in the fragmentation pattern, the novice may be discouraged by a few unsuccessful attempts at interpretation. Perseverance at this point often results in the discovery of interesting new phenomena and in an interest in mass spectrometry beyond confirmation of a molecular weight. Another potential area of interest, bond strength as determined by appearance potentials, is far more difficult and uncertain experimentally, but should not be neglected.

A. MOLECULAR IONS, POLYMERS, AND FRAGMENTS

In seeking to identify a newly prepared compound by mass spectrometry, the observation of the "parent" or "molecular" ion isotopic cluster is usually greeted with satisfaction, but observation of apparently lower or higher m/e values for the parent ion causes initial confusion. However, even in a series of closely related compounds, run in the same mass spectrometer under identical conditions, some compounds may show molecular ions and others only fragments as a result of cleavage. For example, loss of an R· group, from R_4M compounds, to give the R_3M^+ ion as base peak, is very common for hydrocarbon derivatives of Group IV elements (*86*, *87*), but, in a series of pentafluorophenyl derivatives of tin (*88*), it is not possible to predict, *a priori*, which derivative will show a parent ion in its 70-eV spectrum (Table I) (*88*, *89*). There is no immediately apparent reason why the parent ion should be lacking if there are one or three $—C_4H_9$ groups, but be present if there are two $—C_4H_9$ groups in the molecule.

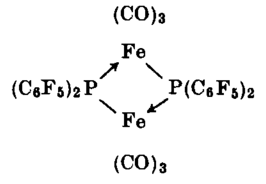
TABLE I

MOLECULAR IONS FOR A SERIES OF C_6F_5Sn DERIVATIVES

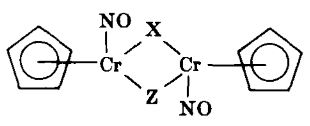
Ion	Abundance as percent of total positive ion current				
	$R{=}C_6H_5$[a]	$R{=}C_6F_5$[b]	$R{=}C_4H_9$[a]	$R{=}CH_3$[a]	$R{=}CH{=}CH_2$[a]
$(C_6F_5)_3SnR^{+\cdot}$	1.8	7.2	0	6.5	N.D.[c]
$(C_6F_5)_2SnR_2^{+\cdot}$	0.8	7.2	3.6	8.4	0
$C_6F_5SnR_3^{+\cdot}$	0.3	7.2	0	3.3	N.D.[c]

[a] Chivers *et al.* (*88*).
[b] Miller (*89*).
[c] Not determined.

There are many examples today of polynuclear metal complexes yielding a parent ion in the mass spectra, but initially their observation for high molecular weight compounds, such as di[bis(pentafluorophenyl)-phosphidoirontricarbonyl] (I), having a molecular ion of *m/e* 1010 (*90*) was considered unusual, as were the binuclear chromium complexes (II)



(I)



(X = Z = SMe;
X = Z = SPh;
X = SMe, Z = OH;
X = Z = OMe;
X = Z = NMe₂)

(II)

studied by Preston and Reed (*91*). Mass spectra proved invaluable in the determination of the molecular formula of carbide complexes of ruthenium (*8*, *92*), since the differentiation between the actual compound,

$Ru_6C(CO)_{17}$ and $Ru_6(CO)_{18}$, would be difficult using classic analytical methods.

Examples of large polymetallic molecules that readily give molecular ions are $Co_3(CO)_{10}BH_2$—$N(CH_3)_3$ (*93*), $(CO)_5MnAs(CH_3)_2Cr(CO)_4$-$As(CH_3)_2Mn(CO)_5$ with m/e 764 (*94*), and $(C_5H_5)Fe(CO)_2SnX_2Ni(CO)$-$(C_5H_5)$ (where X = Cl or Br) (*95*). Interestingly, the germanium analog of the foregoing tin compound shows as its highest m/e peaks those assignable to the P—CO ion (P = parent ion; P—CO indicates the parent that has lost CO), another example of the unpredictability of the mass spectra of a homologous series. Even heavy atoms such as uranium give volatile complexes and parent ions, e.g., (salicylideneiminato)bis-(dipivaloylmethanato)uranium(IV), m/e 870 (*96*). The mass spectrum similarly proved invaluable in assigning one of the by-products in the polyrecombination of ferrocene to a 1,2-diferrocenylethene (*97*). The mass spectra do not show parent ions for phosphorus selenides such as $P_4Se_7 \cdot 2py$, the $P_2Se_5^+$ ion being the highest m/e ratio observed (*98*), although for the sulfur selenides, parent ions $S_xSe_{8-x}^+$ are observed (*99*) as they are for the simple phosphorus selenide P_4Se_3 and for the sulfides P_4S_3, P_4S_5, P_4S_7, and P_4S_{10} (*100*).

Many species also give dimeric or polymeric ions in the gas phase. For example, in the spectrum of BiF_5 and SbF_5 the highest m/e values observed correspond to $Bi_2F_9^+$ and $Sb_2F_9^+$, i.e., loss of a fluorine from the simple dimer (*101*). Copper (I) carboxylates, which show dimeric units in their crystal structures show dimers in their mass spectra, i.e., $Cu_2L_2^{+\cdot}$ (*102*). Metal alkoxides form low polymers in solution and many alkoxy-bridged oligomers survive the impact of 70-eV electrons. Although not all compounds in the series $Ti_4(OMe)_{16}$, $Zr_4(OEt)_{16}$, $Nb_2(OEt)_{10}$, $Ta_2(OEt)_{10}$, and $MAl_3(OPr^i)_{12}$ (where M = Fe, La, Ce, Pr, Nd, Eu, Gd, Ho, and Yb) exhibited parent ions (*103*), $LaAl_3(OPr^i)_{12}^{+\cdot}$ is observed in good abundance at m/e 928 (*104*).

Both monomers and polymers have been reported in the mass spectra of metal acetylacetonates (*105*, *106*), depending on the nature of the metal, and its oxidation state; different laboratories have reported conflicting results. Undergraduates in our freshman laboratory (*107*) recently discovered $Cr_2(acac)_5^+$ ions in the spectrum of $Cr(acac)_3$ but found that this dimer was removed if the sample was carefully purified, thus casting doubt on the purity of some of the previously reported (acac) derivatives showing dimers.

Alkali metals may also form stable complexes for which parent ions are observed in the mass spectra; species such as $NaHo(C_8H_{10}O_2F_3)_4^{+\cdot}$ (m/e = 968) (*108*) and metal β-diketones (*109*) have been observed. In the latter case, the 1 : 1 complexes have spectra complicated by polymeric ions such as $Li_2L_2^{+\cdot}$, $Li_3L_3^{+\cdot}$, $NaKL_2^{+\cdot}$, and $K_2L_2^{+\cdot}$. Thus, even the most unexpected species are sufficiently volatile for mass spectral study; in some cases no parent ion is observed, while in orders, one observes unexpected polymers.

B. FACTORS AFFECTING SPECTRA

Attention to the following factors is essential to success in the use of mass spectrometry.

1. *Source and Inlet Temperatures*

Perhaps the most common problem is that of thermal decomposition of the sample, either in the batch inlet, for which the cure is a lower inlet temperature or use of the direct probe, or in the source itself. A common misconception among mass spectroscopists, often promulgated by manufacturers, is that if the source is kept hot, the decomposition of contaminants is minimized. The ion source should routinely be run no hotter than 180°–200°C. A source at the common temperature of 250°C is much more likely to result in decomposition of sample and contamination of the source, and should be used only rarely. On our AEI MS-30 we run ~200 samples per month, many of which are organometallic or inorganic, and we are seldom forced to exceed 200°C more than once a month. If some sample condenses into the source it is far better to sublime it away slowly by carefully raising the temperature than to pyrolyze it.

An example of the effect of source temperature is seen for TiF_4oxH (*110*), for which, at 180°C, the highest m/e corresponds to TiF_3ox^+ (i.e., P—HF), whereas at 240°C the thermal decomposition product, $TiF_2ox_2^+$, is observed. Compound $Cu(NO_3)_2$ shows a parent ion (*111, 112*) [unlike $Sn(NO_3)_4$ (*79*)], but thermal decomposition occurs even at source temperatures of ~100°C resulting in much of the NO_2^+ and NO^+ observed. As samples are volatilized from the probe at temperatures of up to 350°C, serious thermal decomposition or polymerization may result (*8, 113–116*). Even with the source at a low temperature, there is still the very hot region in the vicinity of the filament that can cause pyrolysis.

2. *Influence of Metal Parts*

Glass or glass-lined heated batch inlet systems and transfer lines are to be preferred to the older metal systems since metals tend to accelerate decomposition, although metal deposited by decomposing compounds does have a particularly strong catalytic action (*8, 13, 114,* *116*). Not only the complexes themselves, but potential ligands can be shown to rearrange in contact with hot metallic surfaces of an inlet system (*117*).

Unusual exchange reactions are observed with or on the metal surfaces of a source itself. Sherwood and Turner (*118*) in their studies of the spectra of iodine pentoxide observed peaks due to copper oxygen, copper iodine, and copper oxygen iodine species (Cu_2^+, Cu_2I^+, $Cu_3I_2^+$, $Cu_4I_3^+$, $Cu_4I_4^+$, . . . , $Cu_6I_3^+$, CuO^+, Cu_2O^+, $Cu_5O_5^+$, $Cu_5IO_5^+$, etc.) as well as ions assignable to silver- and lead-containing species. These extraneous metal-containing species were observed in four different mass spectrometers with both open and closed sources. The authors report unsuccessful attempts to find a mass spectrometer with no trace of copper in its source system. Terlouw and de Ridder (*119*) observed metal–metal chelate exchange in their study of metal chelates of diethylthiocarbamate ligands. The pure iron chelate shows pronounced peaks due to the nickel complex. The amount of nickel complex was dependent on the source condition, being greatest for a clean source and diminished as the source was coated with a layer of decomposition products. The nickel spectrum was eliminated only by plating the stainless steel source components with layers of rhodium and gold. Similar effects were observed for β-diketonate complexes when a metal inlet system was used (*120*). Metal substitutions can be caused by source memory effects; for example, when $[Cr(CO)_4P(CF_3)_2]_2$ was run after $Zn(acac)_2$, a weak ion corresponding to the highly unusual $[Zn(CO)_4P(CF_3)_2]_2$, was observed (*121*).

One of the most serious areas of exchange involves metal halides, for which there are definite source memory effects. After running many bromo compounds, followed by a chloro compound, the chloro compound will often show contamination by its bromo derivative. This can be minimized by source cleaning, or more simply by treating the source with a reactive halide, such as $SiCl_4$ for 15 to 30 min (*122*). One of the most severe cases of halogen exchange involves methyl mercuric halides, of particular importance in the identification of organomercury derivatives in environmental and biological materials. It is virtually impossible to eliminate CH_3HgI^+ from the spectrum of CH_3HgCl (*122–124*).

3. *Sample Size and Instrument Background*

Great care must be exercised when dealing with compounds that may decompose, so as to minimize the degree of source contamination. As indicated earlier, organometallics are no worse than any other type of compound, and we have direct evidence of this with our double-beam

MS-30 mass spectrometer (*125*). We normally operate with either perfluorokerosene (PFK) reference or the GC coupled to beam 2, whereas beam 1 is used for solid probe or batch inlet samples including organometallics. There is no evidence for source 1 being contaminated and requiring cleaning at any greater rate than beam 2. The key is to keep source temperatures as low as possible and to minimize the amount of sample. Most troubles arise from the use of too large a sample, resulting not only in greater contamination but in slow pumpout of residual materials between samples, and thus high background, whereas, with care, probe samples can be run at the rate of 8 per hour without background buildup. Background should be checked immediately prior to the running of a sample, and care must be taken that the probe tip is not contaminated. Large samples can also produce ion–molecule reactions, mentioned below.

4. *Ion-Molecule Reactions*

As the ion source pressure rises, ion–molecule reactions become possible, sample ions reacting with sample molecules. In the case of exact mass measurement, reaction can occur with the PFK mass reference (*126*). The observed reactions in the mass spectrum of ruthenium porphyrincarbonyl, yielding ions of the type $[\text{M-CO} + C_nF_{2n}]^+$ ($n = 1$–4), illustrate this problem. Similarly, in the spectrum of $\text{Ni(PF}_3)_4$ ion–molecule reactions result in species such as $\text{Ni}_2(\text{PF}_3)_n^+$ ($n = 2$–5) and $\text{Ni}_2(\text{PF})_2(\text{PF}_3)_m^+$ ($m = 2$–4) and, in the $\text{(CO)}_5\text{CrC(CH}_3\text{)OCH}_3$ system, reactions of the following type are observed (*127*).

$$\text{(CO)}_5\text{CrL}^+ + \text{(CO)}_5\text{CrL} \longrightarrow \text{(CO)}_8\text{Cr}_2\text{L}_2^+ + 2\text{CO} \qquad (4)$$

In the substituted arenechromium tricarbonyl system (*129*), the following ion–molecule reactions are observed:

$$\text{ArCr(CO)}_3 + [\text{ArCr(CO)}_m]^+ \longrightarrow [\text{Ar}_2\text{Cr}_2\text{(CO)}_n]^+ + (m\text{-}n)\text{CO} \qquad (5)$$

In the above systems, it was suggested that the reactions occur at pressures of 5×10^{-6} to 2×10^{-5} torr (*126*, *128*); however, at 10^{-5} torr the mean free path is too long to permit significant ion–molecule reactions. The pressures given are those read from the source pressure ionization gauge. One has to calculate back to determine the actual pressure in the source "cage" (*47*), several orders of magnitude higher.

5. *Relative Volatilities*

Gross volatility differences in the components of a submitted sample may give misleading results. Occluded solvent is often the worst offender, and since the operator of the mass spectrometer usually runs the spectrum when the "total-ion monitor" shows sufficient sample entering the source, a solvent spectrum is obtained. Sample submission forms should indicate solvents that were used so that an alert operator will permit the solvent to be pumped away and then obtain the desired spectrum. Traces of starting materials likewise cause problems if they are more volatile than the desired component. If there is uncertainty, it may be wise to run spectra as a function of time and temperature while the material is evaporated from the probe. The best example of this is Majer's detection and separation of geometrical isomers of metal chelates by fractional sublimation (*129*, *130*). This is clearly shown in Fig. 2 for the iron(II) 8-hydroxyquinoline complex. Ritter and Neuman (*131*) used similar techniques combined with mass chromatograms to identify the components of crude mixtures $(R_2Sn)_n$from the reaction of R_2SnH_2 with $Bu_2{}^+Hg$.

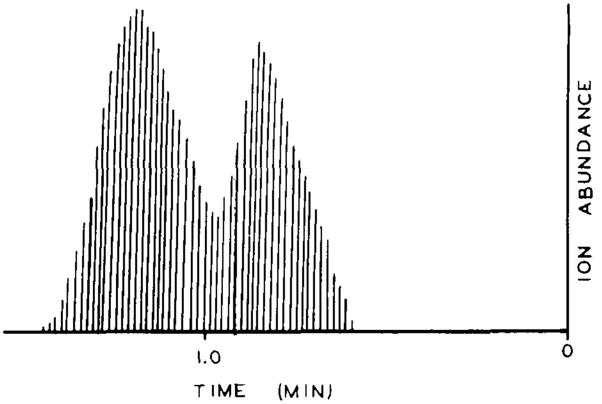


FIG. 2. Integrated ion current curve for iron 8-hydroxyquinolinate on the $FeOX_2{}^+$ peak. [Reproduced by permission from Majer and Reade (*129*)].

6. *Variation in Ionizing Energy of the Electron Beam*

As earlier indicated, most spectra are routinely run at electron beam ionization energies of between 50 and 100 eV. In this range there is little change in the spectrum with changing electron voltage. However, at lower electron energies, pronounced changes occur, as is clearly shown in Fig. 3, which, using the "clastogram" presentation of Kiser (*25*), illustrates the variation of the fractional abundance of each species in the spectrum of $HCo(PF_3)_4$ with electron voltage (*132*). It is thus clearly seen that at 70 eV the parent ion is a small fraction of the total ion current, whereas below 20 eV it becomes a significant fraction of the total positive ionization. Thus, it is often advantageous, if no parent ion is observed,

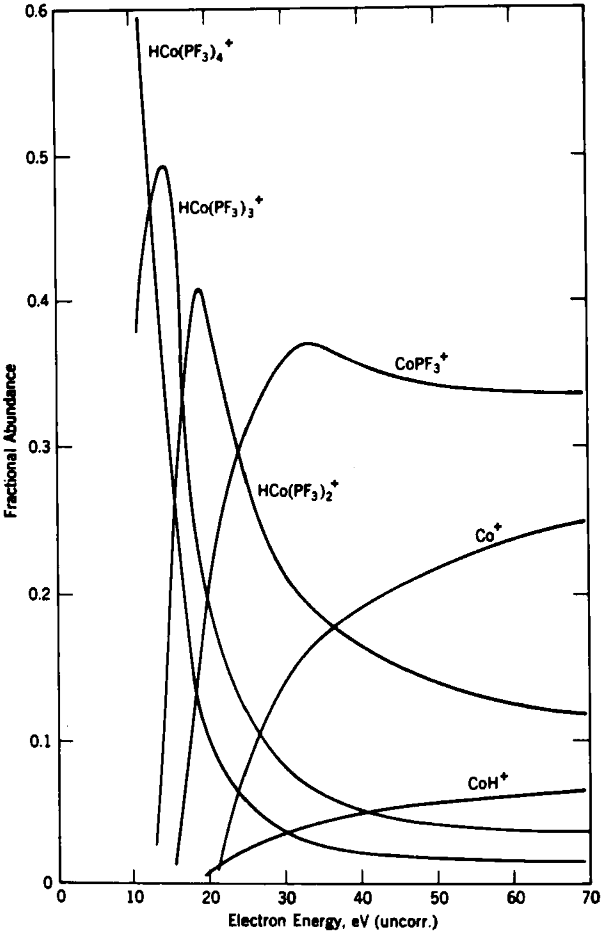


FIG. 3. Clastogram of $HCo(PF_3)_4$. [Reproduced by permission from Kiser (*6*).]

to attempt to run the spectrum at between 10 and 20 eV. It should be remembered that the absolute ion intensity drops drastically at lower electron voltages, so that, although the parent ion may be a large fraction of the total ionization, the latter is itself reduced many orders of magnitude, as shown in the ionization efficiency curves (Fig. 4) for $SnCl_4$ (*133*).

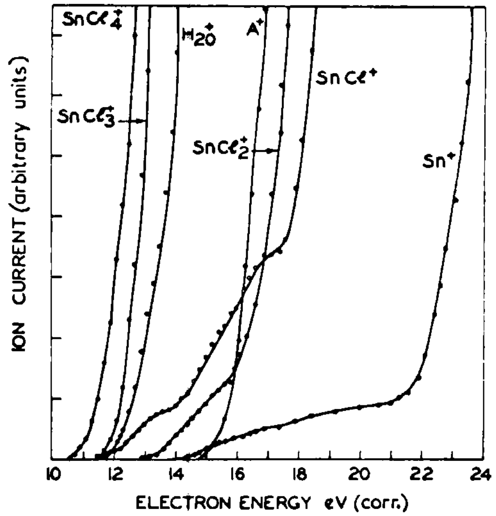


FIG. 4. Ionization efficiency curve's for $SnCl_4$. [Reprinted by permission from A. S. Buchanan, D. J. Knowles, and O. L. Swingler, *J. Phys. Chem.* 73, 4394 (1969); copyright by the American Chemical Society.]

IV. Low- and Medium-Resolution Studies

Most problems in organometallic and inorganic mass spectrometry are solved using resolutions of less than 3000. Compared to organic compounds, the polyisotopic nature of most metals and metalloids simplifies the task of identification of a particular species without resorting to high-resolution exact mass measurement. It is usually assumed that under electron impact (*a*) the decomposition of organometallic complexes is largely controlled by the central metal, (*b*) that free and complexed ligands decompose via different mechanisms, (*c*) that on decomposition of a complex ion, the positive charge usually remains on the metal-containing fragment, and (*d*) that ions with multiple positive charges occur relatively frequently (*13*). There are exceptions; for example, the fragmentation of R_4M species ($M = Si$, Ge, Sn; $R = C_6F_5$ or C_6H_5) shows greater differences on changing R than M (*86*, *87*, *89*) and more of the positive charge is carried by fluorocarbon species (73%) rather than metal-containing species for $(C_6F_5)_4Si$, whereas for the lead compound, 88% of the charge is carried by metal-containing species (*89*). It is such differences as these that make the subject interesting, but they undoubtedly complicate interpretations. Decomposition under electron bombardment falls into three categories as shown for the $(C_6F_5)_3Si^+$ ion:

$$(C_6F_5)_4Si^{+\cdot} \longrightarrow (C_6F_5)_3Si^+ + C_6F_5^{\cdot}$$

$$\longrightarrow (C_6F_5)_2Si^{+\cdot} + C_6F_5^{\cdot} \qquad (6a)$$

$$\longrightarrow C_{17}F_{13}Si^+ + CF_2 \qquad (6b)$$

$$\longrightarrow (C_6F_4)_3^{+\cdot} + SiF_3^{\cdot} \qquad (6c)$$

Equation (6a) illustrates cleavage of metal–ligand bond; Eq. (6b), rupture of a bond and/or rearrangements in the ligand; and Eq. (6c), a rearrangement reaction involving the metal atom in both bond breaking and bond making.

A common mass spectral fragmentation scheme observed for organic compounds involves the loss of a radical from an odd-electron parent ion, followed by loss of even-electron neutral fragments. Even-electron ions are, therefore, observed in high abundance. For organometallics, by contrast, successive loss of neutral ligands such as CO or PF_3 from the parent ion is a very common occurrence. Inorganic compounds also have another common source of odd-electron ions, the metal ion itself, for all even-electron metals. Normally, as one goes down a group in the periodic table, the bare metal ion becomes more common in the spectrum. These and other trends are illustrated for selected examples in the following sections.

A. FRAGMENTATIONS

1. *Halides and Related Compounds*

Among the simplest systems studied by mass spectrometry are metal halides and related compounds. For the simple binary halides, metal–ligand cleavages are the important breakdown mechanism, although for silicon tetrahalides, metastable ion studies show simultaneous as well as consecutive loss of halogen (*134*). Under ideal conditions, Group IV tetrahalides show all ions in the series MX_n^+ (where $n = 0$–4), but parent ions may be weak or nonexistent as shown in Table II for the spectrum of $(GeCl_3)_2CCl_2$ and $GeCl_3CCl_3$ (*135*). Except for $GeCl_4^+$ rearrangement ions, these compounds have undergone simple fragmentation, and mass spectroscopy proved invaluable in their identification among the reaction products of molecular carbon with $GeCl_4$. Similarly the preparations of B_8Cl_8 (*136*) and B_9Cl_9 (*137*) were confirmed by their mass spectra. In both cases simple fragmentation occurs, although the spectra are complicated by the isotopes of boron and chlorine. Both PF_3 and PF_2CN undergo the

TABLE II

MASS SPECTRUM OF $(GeCl_3)_2CCl_2$ AND $GeCl_3CCl_3$

Ion$^+$	$(GeCl_3)_2CCl_2$ (Relative abundance)	$GeCl_3CCl_3$ (Relative abundance)
CGe_2Cl_8	0.02	—
CGe_2Cl_7	0.2	—
CGe_2Cl_6	0.04	—
CGe_2Cl_5	0.05	—
CGe_2Cl_4	0.02	—
$CGeCl_6$		Parent not observed
$CGeCl_5$	1.5	4.7
$CGeCl_4$	41.1	0.3
$GeCl_4$	0.9	Very weak
$CGeCl_3$	6.7	0.4
$GeCl_3$	16.0	5.0
$CGeCl_2$	2.7	0.4
$GeCl_2$	3.5	1.8
CCl_3	54.5	100.0 (plus GCeCl)
$GeCl$	100.0	12.2
CCl_2	32.0	94.3 (plus CGe)
Ge	6.4	0.3
CCl	20.5	12.0

simple central atom–ligand cleavages expected (*138*), but PF_2CN shows cleavage of the cyano ligand as well, with species such as PFC^+, PC^+, C^+, and N^+ appearing in the spectrum.

Molecular beam mass spectrometry has been used to study pentafluorides of Nb, Ta, Mo, Re, Os, Ir, Ru, Rh, Pt, Sb, and Bi (*139*), indicating dimeric, trimeric, and even tetrameric ions (*139*). Simple fragmentations of the type

$$Rh_4F_{20}^+ \longrightarrow Rh_4F_{19}^+ \longrightarrow Rh_4F_{18}^+ \tag{7}$$

and

$$Rh_3F_{15}^+ \longrightarrow Rh_3F_{14}^+ \longrightarrow Rh_3F_{13}^+ \longrightarrow Rh_3F_{12}^+ \longrightarrow Rh_3F_{11}^+ \tag{8}$$

are observed, and the polymeric ions are shown to arise from the neutral vapors rather than from ion–molecule reactions. In further studies it has been shown that only the lighter pentafluorides and interhalogen pentafluorides are not associated, with the simple spectrum expected for a binary pentafluoride (*140*). Dioxygenyl salts of the type $O_2^+MF_6^-$ (M = As, Sb, Bi, Ru, Rh, Au, and Pt) have been studied by mass spectrometry (*141*), and although no parent ion is detected, O_2^+ and MF_n^+ ($n = 0$–6) are observed. For gold, the spectrum more closely resembles that of a pentafluoride with $Au_2F_9^+$ and $Au_3F_{12}^+$ species observed, suggesting the independent existence of AuF_5. Similar studies have been carried out with transition metal oxo- and thiohalides and their fragmentation patterns indicate essentially monomeric species (*142*). The spectra of the lanthanide triiodides have been measured using Knudsen cell techniques and show simple fragmentation (*143*).

The mass spectra of the boron trihalides and mixed trihalides have been studied (*144*), the latter being formed on mixing the simple halides. All species undergo simple fragmentation. The corresponding trimethylamine adducts show both metal–ligand and ligand–ligand cleavages (*145*):

$$X_2B\cdot NMe_3^+ \longrightarrow NMe_3^{+\cdot} + X_2B\cdot \tag{9}$$

$$X_2B\cdot NMe_3^+ \longrightarrow X_2B\cdot NMe_2^{+\cdot} + Me\cdot \tag{10}$$

$$I_2B\cdot NMe_3^+ \longrightarrow BNMe_3^+ + I_2 \tag{11}$$

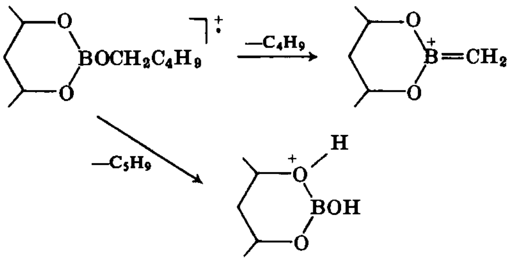
Ion abundances are consistent with increasing B–N and decreasing B–X bond strength as X varies from F to I.

2. *Main Group Organometallic Compounds*

The mass spectra of main group organometallic compounds have been discussed in many of the reviews listed in the Introduction, and here we only summarize some recent examples.

Cragg and Weston (*11*) in their review of the mass spectra of boron compounds have shown the great amount of work being done with cyclic boron compounds. This trend has continued. Straight-chain trialkylborates fragment by C—O cleavage reactions accompanied by hydrogen transfers,

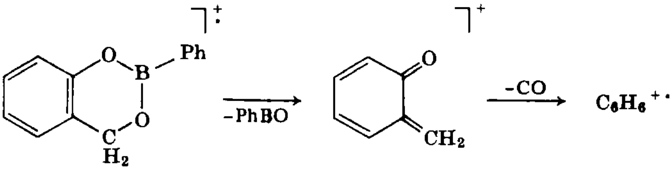
$$(C_7H_{15}O)_3B^{+\cdot} \xrightarrow[-C_7H_{13}\cdot]{} (C_7H_{15}O)_2BO^+H_2 \tag{12}$$



(13)

whereas tri-(*sec*-alkyl)borates tend toward α-cleavage reactions (cleavage of C—C bond between carbons α and β to the oxygen) (*146*).

A B—O bond is broken in the case of phenylboron derivatives of *o*-hydroxybenzyl alcohol (*147*) where the loss of PhBO is observed,



(14)

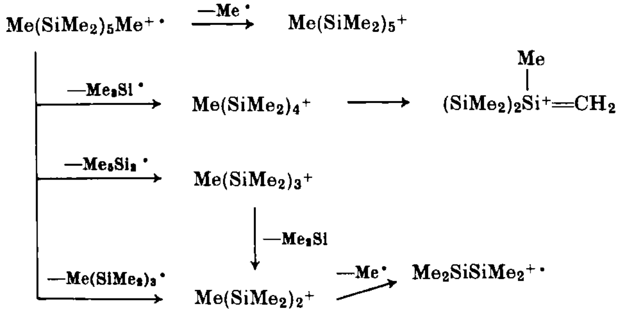
rather than the expected process leading to formation of a tropylium ion (*148–150*). In the case of chelates involving aromatic amines and *N*-oxides with Ph_2B or F_2B (*151*), the base peak is usually a result of loss of either Ph or F, and from the base peak fragment, neutral OBPh or OBF may be eliminated. Boronsulfur heterocycles also exhibit stability under electron bombardment (*152*): triphenylborthiin $(PhBS)_3$ gives an intense parent ion (28.5%)* and doubly charged parent (4%), but no PhBS or $(PhBS)_2$ type ions were observed.

The mass spectra of Group IV derivatives have received much attention, the most recent review being that of Orlov (*8a*). Current areas of interest vary from organopolysilanes (*153*) to detailed studies of the simple tetramethyl derivatives (*154*). For the latter compounds, the high intensity of the R_3M^+ ion is explained on the basis that it is "even-electron," or isoelectronic with the R_3N compounds (N = Group IIIA metal); the increasing intensity of RM^+ ions at the expense of R_3M^+ ions as the central atom gets heavier is explained by the increasing stability of the lower oxidation state.

Mass spectra of disilanes (*155–157*) and, more recently, polysilanes (*153*) up to dodecamethylpentasilane have been investigated; the important fragmentation is shown in Scheme 1. Lageot *et al.* (*158*) have investigated the expulsion of neutral fragments in the mass spectra of germacyclopentenes (III); this process occurs in addition to the simple cleavages of these compounds. Fragmentations of organogermanium hydrides (*159*) are quite straightforward, but their interpretation is

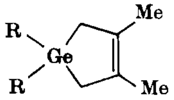
---

* For comparison purposes, mass spectral relative abundances are best described as a percent of the total positive ionization, rather than the traditional percent of base peak height, where the base or largest peak is normalized to 100%. If, in comparing spectra in a series of compounds, the base peak differs very confusing results may be obtained. Percent of the total positive ionization gives a much clearer picture of the nature of the charge-carrying species; for example, knowing that the base peak is 45% of the total positive ionization is more informative than knowing it simply as the largest peak.



SCHEME 1

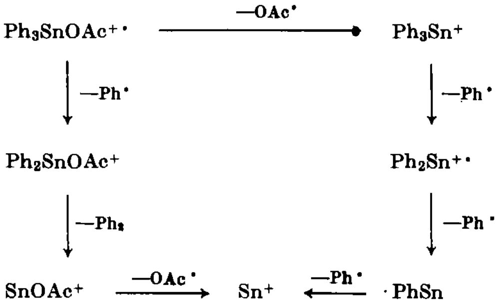
complicated both by the germanium isotope pattern, especially for the digermanes, and by many successive losses of hydrogens. The base peaks



(III)

of diethylmonogermanes and diethyldigermanes occur in the GeC_2H_n ($n = 0$–7) region, rather than the parent ion region. The monogermane also has well-defined envelopes in the regions of GeH_n^+ ($n = 0$–3) and $GeC_4H_n^+$ ($n = 0$–12). In addition the digermane has peaks in the region of $Ge_2H_n^+$ ($n = 0$–4), $Ge_2C_2H_n^+$ ($n = 0$–9), and $GeC_4H_n^+$ ($n = 0$–11).

A recent area of interest has been the mass spectra of organotin pesticides (*160*, *161*), for example, triphenyltin acetate that fragments as follows:



(15)

Relatively few rearrangements are noted in the spectra of these tin pesticide compounds which fragment in a simple manner.

Group V has also been an area of interest, the mass spectrometry of phosphorus compounds having recently been reviewed (*162*). The mass spectra of phosphorus-containing pesticides have attracted interest

(*163–164*), the studies including phosphates (*165*), phosphorothiolates (*163*), phosphorothionates (*165, 166*), phosphorodithionates (*166*), and metabolites of organophosphorus pesticides (*167–170*).

In a recent study (*171*) the Group V acetylides $M(C{\equiv}C{-}CH_3)_3$ ($M = P$, As, Sb) are compared with their Group IV analogs (Table III).

TABLE III

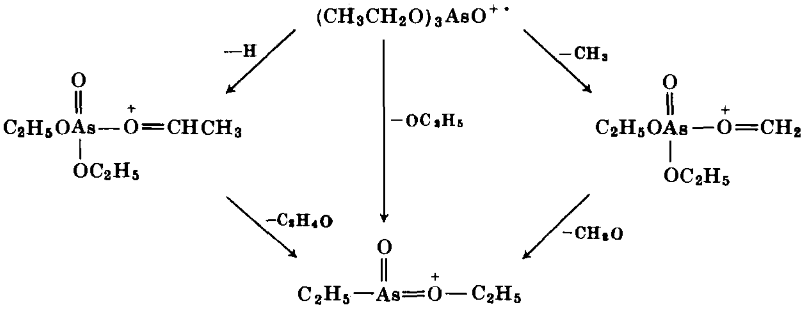
COMPARISON OF THE PARTIAL MASS SPECTRA OF PROPYNYL DERIVATIVES OF GROUPS IV AND V

	Abundances as percent of total positive ionization			
Metal M	Parent ion	$(P{-}15)^+$	$M(C{\equiv}CCH_3)_2^{+\cdot}$	$M(C{\equiv}CCH_3)^+$
Si	12.9	15.1	3.2	15.4[a]
Ge	3.7	1.1	0.3	8.2[a]
Pb	—	—	—	7.3
P	9.5	10.6[a]	0.6	5.9
As	2.9	4.2	2.0	10.5[a]
Sb	1.1	0.2	1.3	21.2[a]

[a] Base peak.

The $M(C{\equiv}C{-}CH_3)^+$ ion is the base peak except for the lead compound (base peak = $Pb^{+\cdot}$) and the phosphine [base peak = $(P{-}CH_3)^+$]. For Group V divalent metal species are of lower abundance than either mono- or trivalent ions. As expected, metal-containing ions carry the bulk of the ion current. Rearrangements were also observed corresponding simply to loss of a neutral metalloid atom.

Organoarsenic and -arsenate compounds have been studied by Froyer and Moller (*172–173*). In the initial stages, $(CH_3CH_2O)_3AsO$ fragments by simple cleavage (6) (Scheme 2), after which the $(RO)_2AsO^+$



SCHEME 2

ion fragments with extensive rearrangement. A study of a series of *O*-phenylenediarsines (*174*) shows stepwise loss of alkyl substituents from the arsenic, but, for halogen- or phenyl-substituted arsenic compounds, rearrangements and migrations analogous to those for phenyl derivatives of Group V are observed (*90, 175–180*).

Perfluoroaromatic derivatives of Group VI (*180–182*) primarily undergo simple fragmentation rather than the rearrangements usually observed for other fluoroaromatic derivatives (*182*). Aliphatic and aromatic selenides have been extensively studied by Rebane (*183–184*). Compounds R_2SeCl_2 usually show no molecular ions, the highest *m/e* corresponding to $(P—X)^+$. The aryl derivatives eliminate the second halogen to give $R_2Se^{+\cdot}$ ions, whereas the dialkyl or alkyl/aryl derivatives show alkyl elimination producing $(RSeX)^{+\cdot}$ ions. Further simple fragmentation then occurs, although some rearrangement species are also observed.

The mass spectra of organomercurials were neglected for some years, the first comprehensive study of these compounds being by Byrant and Kinstle (*185*). They observed that for R_2Hg and $RHgCl$ ($R = \text{alkyl}$) there was a surprising tendency toward charge retention on carbon rather than mercury, although this could be varied with appropriate substituents. Extrusion of a mercury atom is also favored in diaryl derivates (*186*), of which the fragmentation routes are

$$\begin{tikzcd}
Ar—Hg—Ar^{+\bullet} \arrow[r, "-Ar^{\bullet}"] \arrow[dd, "-Hg"'] \arrow[dr, "-ArHg"] & HgAr^{+} \arrow[d, "-Hg"] \\
 & Ar^{+} \\
Ar—Ar^{+\bullet} &
\end{tikzcd} \qquad (16)$$

Exchange of organic groups was also detected, since if pairs of compounds, R_2Hg and R'_2Hg, were introduced simultaneously, then $RHgR'^{+\cdot}$ and $R'R^{+\cdot}$ were observed. Recent concern over environmental matters has led to the mass spectral study of methylmercury compounds from fish (*123*), and also to an interest in fungicidal organomercury compounds (*161, 187*) and the use of the mass spectrometer in their detection and identification. The important ions observed in the mass spectrum of CH_3HgI include CH_3HgI^+, HgI^+, CH_3Hg^+, Hg^+, I^+, and the rearrangement ions $I\text{-}CH_3^{+\cdot}$ and $HI^{+\cdot}$. Organomercury carboxylates also show a rearrangement corresponding to loss of CO_2 from the parent ion.

3. *Transition Metal Complexes*

The mass spectra of metal β-diketonates have been extensively studied (*105–106, 188–192*). The fragmentation of these complexes has been rationalized by Shannon (*193–194*) in terms of the "valence change concept," the modes of dissociation being dependent on the oxidation states normally assumed by the metal concerned. They postulate electron transfers between metal atom and ligand, such that the odd- or even-electron character of the ion is interchangeable, accounting for the ready consecutive loss of two radicals, normally improbable for organic compounds. Thus two "acac" ligands are lost from the $Fe^{III}(acac)_3$ molecular ion, but not from the analogous Al(III) compound, since iron but not aluminum may normally assume a lower oxidation state (*193*). They consider $[M^{III}(acac)_2]^+$ and $[M^{II}(acac)_2]^{+\cdot}$ as canonical contributions to a resonance hybrid, and the latter odd-electron species can eliminate a second ligand radical to become even-electron.

Recent studies have involved some fluorinated monothio-β-diketones with zinc and nickel (*195*) and palladium and platinum (*196*). Both nickel and zinc show valence change of the metal,

$$[M^{II}L_2]^+ \longrightarrow L^+ + M^IL \qquad (17)$$

The number of metal-containing fragments were found to be small for Zn and Pd, but large for Ni and Pt chelates, whereas the $(ML)^+$ ion is very strong for zinc, moderate for platinum, and weak for nickel and palladium chelates. Free metal is observed for the nickel complex only.

Volatile metal chelates are also useful in determining isotope ratios of geological interest, e.g., the Zr/Hf ratio (*197*). This method proved invaluable as a microtechnique for chromium isotope analysis of lunar samples from the Apollo program (*198*).

The mass spectra of metal phthalocyanines and porphyrins have also been studied: Eley *et al.* (*199*) compared the spectra of free ligand and transition metal phthalocyanines. Both the free ligand and the complexes are among the most stable compounds toward dissociation by electron impact, the parent ion being the base peak in all cases, and the doubly charged parent the second most abundant species. Significant amounts of triply charged parent ions are observed for some complexes. The various parent ion species carry from 54 to 90% of the total positive ionization. The perfluorophthalocyanine complex of zinc has an even more stable molecular ion (*200*). The limited ligand fragmentation that does occur involves either halves or quarters of the ligand.

Studies of copper(I) (*102, 210, 202*) and copper(II) carboxylates (*203*) show that the copper(II) derivatives have the general formula $[Cu_2R_4]\cdot 2H_2O$, where $R = CH_3CO_2$, $C_2H_5CO_2$, n-$C_3H_7CO_2$, and n-$C_4H_9CO_2$. The samples dehydrate and the fragmentations are essentially based on Cu_2R_4. Very intense ions are observed for $Cu_2R_2^+$ and Cu_2R^+ ions with higher molecular weight species such as $Cu_3R_2^+$, $Cu_3R_3^+$, $Cu_3R_5^+$, and $Cu_4R_3^+$. Ogura and Fernando reported that the copper(I) derivatives do not show peaks above the parent ion $Cu_2R_2^+$ (*102*), but Edwards and Richards (*201*) described weak peaks for trimers and tetramers. Extensive fragmentation of the bridging ligands is observed. Alkyl carboxylic acid salts of copper(I) fragment via loss of $RCO_2^{\bullet}$ from the molecular ion, whereas aryl carboxylates have a parallel pathway involving loss of CO_2 from the molecular ion and migration of the aryl group to the metal (*202*).

The importance of metal coordination compounds in biological systems has led to the study of polydentate Schiff base complexes of cobalt(II), nickel(II), and copper(II) (*204*, *205*). Dimers have been observed in the spectra of complexes of both tri- and tetradentate ligands [e.g., salicylaldehyde and *N*,*N*-bis(salicylidene)ethylenediamine]. The parent ions form the base peaks, and the spectra are characterized by complex ligand fragmentations. It is for complexes such as these, of potential biological interest, that field desorption mass spectrometry may prove valuable.

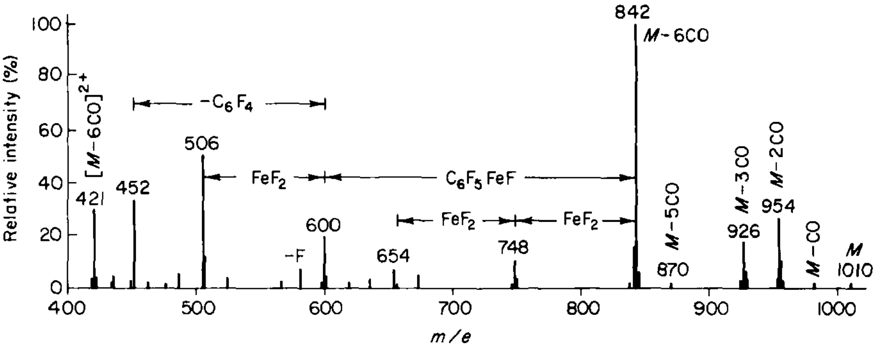


FIG. 5. Mass spectrum of $[(C_6F_5)_2PFe(CO)_3]_2$. [Reproduced by permission from Miller (*90*).]

The fragmentation of metal carbonyl derivatives is characterized by successive loss of carbonyl groups, but in some cases all possible losses of CO are not observed. For $[(C_6F_5)_2PFe(CO)_3]_2$, in addition to the parent ion, there are peaks corresponding to the loss of 1, 2, 3, 5, and 6-carbonyl groups, but for reasons which are not clear, the loss of 4 is not observed (*90*) (Fig. 5).

Innorta *et al.* (*206*), in a study of carbonyl complexes containing organic rings, have rationalized the loss of small stable molecules, rather than radicals, in terms of the activation energies for fragmentation pathways possible from the molecular ion. Thus loss of H_2 after CO has been removed can become common if it results in aromatization of a ring.

In the spectrum of π-tetrahydronaphthalenenonacarbonyltetracobalt, $(P\text{-}n\mathrm{CO})^+$ ions become less intense with increasing n, whereas $[P\text{-}(n\mathrm{CO} + \mathrm{H_2})]^+$ and $[P\text{-}(n\mathrm{CO} + 2\mathrm{H_2})]^+$ predominate for $n \geqslant 4$. The free ligand itself shows loss of atomic hydrogen, and complexed ligand predominantly has ions due to the loss of H_2 or $2H_2$. Unsaturation of the cobalt or loss of CO is not applicable as the driving force, as was suggested for loss of H_2 from ions in the spectrum of π-$C_6H_8Fe(CO)_3$ (*207*). It is, therefore, the influence of π-bond formation on the loss of H_2 that lowers the activation energy sufficiently for this process to compete with CO loss (*208*).

In the spectra of some iron carbonyl derivatives of CF_3-substituted polyphosphines (*209*), cleavage of CO groups and fragmentation of the phosphine are competitive. The main fragments from $(CF_3)_2P_2C_2(CF_3)_2Fe(CO)_4$ include successive loss of all 4 carbonyls, or loss of a fluorine from the ligand. For $(CF_3)_2P_2C_2(CF_3)_2Fe_3(CO)_{10}$, loss of carbonyl is observed, as well as the loss of 4 carbonyls and P_2F. Similarly, P_4F and 4 carbonyls have been split from $(CF_3P)_4Fe_2(CO)_6$.

B. REARRANGEMENTS

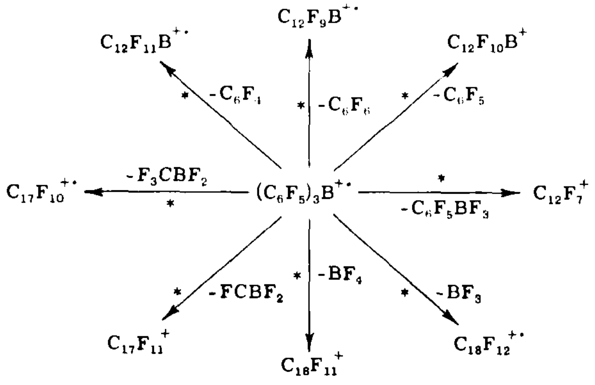
Bombardment with 70-eV electrons is not a gentle process: the molecular ions formed have sufficient activation energy to undergo not just simple cleavage but rearrangements involving both cleavage and bond formation. Organic ligands attached to a metal atom may undergo rearrangement reactions similar to those observed for simple organic molecules. Of far more interest are those reactions that involve the central metal atom itself, either accompanied by the transfer of an atom or group to the central metal in a fragment ion, or the expulsion of the neutral metal atom or a neutral metal-containing species from an ion. Perhaps one of the most interesting of these reactions in organometallic chemistry, as pointed out by Kiser (*6*), involves transfer of fluorine to the central metal in the mass spectra of fluorocarbon-containing organometallics and complexes (*90*). Aided by metastable ion studies one can execute a detailed study of unimolecular gas phase reactions having potential synthetic analogies.

1. M—F Bond Formation

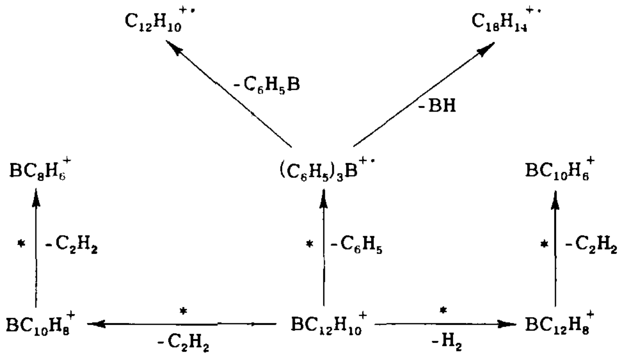
Miller (*90*), King (*209, 210*), and Bruce (*211*) first observed the formation of neutral metal fluoride species and metal fluoride-containing ions in the mass spectra of pentafluorophenyl derivatives of phosphorus, germanium, silicon, and phosphido-bridged iron carbonyls (*90*) and aliphatic and aromatic fluorocarbon derivatives of iron, cobalt (*209–211*), and manganese (*212–213*). Trifluoromethyl derivatives exhibit similar behavior as shown by Cavell and Dobbie (*214–217*). The nature of the exotic ions and transitions observed are clearly illustrated in Fig. 5, where after the loss of 6 carbonyls from $[(C_6F_5)_2PFe(CO)_3]_2$, the following transitions are observed from the base peak (*90*):

$$\begin{tikzcd}
C_{24}F_{20}P_2Fe_2^{+\cdot} \arrow[rr, "-FeF_2"] \arrow[d, "-C_6F_5FeF"] & & C_{24}F_{18}P_2Fe^{+\cdot} \arrow[d, "-FeF_2"] \\
C_{18}F_{14}P_2Fe^{+\cdot} \arrow[d, "-FeF_2"] \arrow[dr, "-C_6F_4"] & & C_{24}F_{16}P_2^{+\cdot} \\
C_{18}F_{12}P_2^{+\cdot} & C_{12}F_{10}P_2Fe^{+\cdot} &
\end{tikzcd} \tag{18}$$

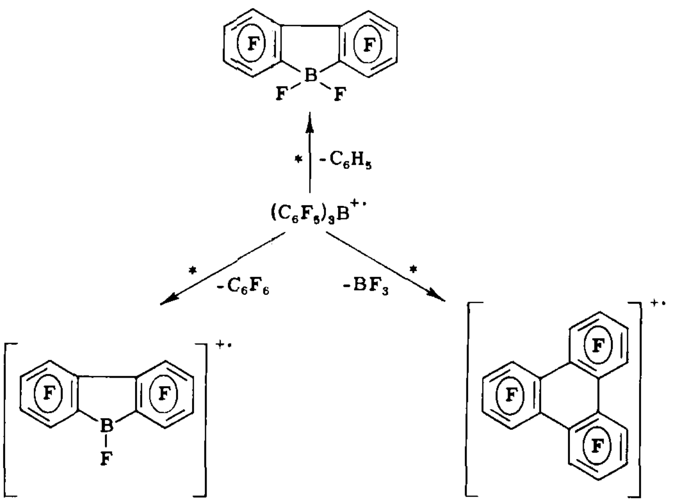
All of these ions are of high abundance and all are odd-electron species. Further work has been carried out in the authors' laboratory on fluoroaromatic derivatives of Groups III (*217–218*), IV (*88, 89, 157, 181, 182, 219*), V (*176–178*), and VI (*180–182*). McGlinchey has recently studied chromium derivatives (*220*) whereas Clark and Rake (*211*) have studied in detail the system $Ph_{3-n}(C_6F_5)_nMMn(CO)_5$ ($n = 0$–3; M = Si, Ge, Sn); species corresponding to the loss of F_3SiMnF and MnF_3 from $(C_6F_5)_3$-$SiMn^{+\cdot}$ were observed. Thus in all of these systems, extensive fluorine transfers occur. Scheme 3 illustrates the complexities of the spectra for $(C_6F_5)_3B$, whereas the analogous $(C_6H_5)_3B$ shows little proton migration (Scheme 4) corresponding to the B—F bond formation (*217*). Postulated structures for some of the ions concerned are shown in Scheme 5, in particular the polyphenylenes and fused-ring systems.



SCHEME 3



Scheme 4

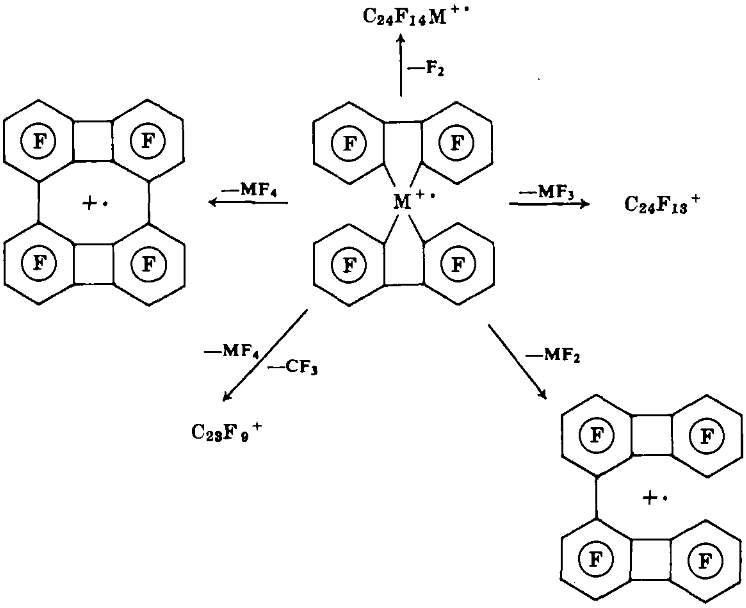


Scheme 5

In studies of the mechanism of fluorine transfer from a fluoroaromatic ring to the central atom, no such migrations are observed if the central atom is carbon (*89*), nitrogen (*222*), oxygen (*180*), or sulfur (*180*), whereas selenium fluorides are formed to only a slight extent (*180*). Although electronegativity arguments cannot be ruled out, it would appear that the transfer requires vacant orbitals on the central atom, such orbitals being absent for the C, N, and O derivatives, whereas for sulfur, sulfur–fluorine bond formation may not be particularly favorable energetically. Of the first-row elements, pentafluorophenyl derivatives of trigonal boron, which is both electropositive and electron deficient, exhibit extensive loss of BF_3, BF_2, and BF species in their mass spectra (*217*, *223*).

Cavell and Dobbie (*214–216*) have suggested that halogen transfer rearrangements in trifluoromethylphosphines arise from interactions of nonbonding fluorine p orbitals with vacant d orbitals on phosphorus. Such an explanation is consistent with observations for the Groups IV and V pentafluorophenyl derivatives, exclusive of carbon and nitrogen, and similarly fits the behavior of boron with its vacant p orbital.

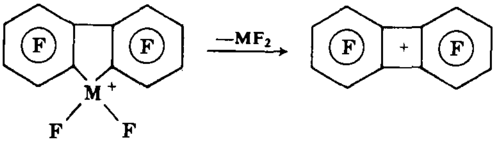
The involvement of d orbitals can also explain the existence of fluorine transfer to transition metals (*90*, *209–213*, *220–221*, *224–227*). Hawthorne *et al.* (*212*) have suggested that when there are unsaturated σ-bonded organic ligands the rearrangement ion can be rationalized by assuming that the ligand becomes "π"-bonded to the metal during the fragmentation. They based this suggestion on fluorine migrations to the metal atom occurring from all the *o*-, *m*-, and *p*-substituted monofluorophenyl manganese pentacarbonyls, although *ortho* migrations are most favored. The well-established scrambling of aromatic substituents under electron bombardment could also account for their observations, however.



SCHEME 6

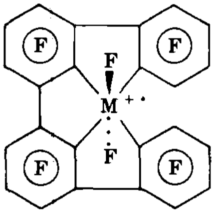
It is difficult to conceive of these σ–π type transfers in compounds such as $(C_{12}F_8)_2Si$, as shown in Scheme 6. These fused-ring compounds are analogous to the intermediates proposed for the boron compounds (Scheme 5) and for the mass spectra of diarylphosphinic acids in which

Haake *et al.* (*228*) postulate that the structures of both the $[(C_6H_5)_2PO]^+$ and $[(C_6H_5)_2P]^+$ ions involve cyclized systems with four-coordinate phosphorus. Rake and Miller (*176–177*) have suggested that the loss of MF_2 from $[(C_6F_5)_2M)^+$ (M = P, As, Sb) occurred via similar structures, as shown for ions (IV) and (V), also consistent with the structures proposed by Williams *et al.* (*175*), Bowie and Nussey (*179*), and Chow and McAuliffe (*229*), all involving expansion of the coordination shell of the central metal.



(IV) (V)

Therefore by starting with heterocyclic ring systems analogous to structure IV, e.g., $(C_6H_5)_2Ge(C_{12}F_8)$, it was hoped analogous transitions might be observed (*182*), but this compound shows loss of HF or GeF, but not $(C_6H_5)_2Ge$. It was thus postulated that expansion of the coordination shell of the central atom from 4 to 6 in systems such as Scheme 6 was the only mechanism that could explain all observations, a species such as structure VI being a possible intermediate. Such an ion could then lose MF_2 or undergo further bond breaking and reforming rearrangements to allow the elimination of MF_3 or MF_4 as shown in Scheme 6.



(VI)

When looking at the $(C_{12}F_8S)_2M$ species, it can again be postulated that in the parent ion (also stable and highly abundant as for Structure VI) the metal expands its coordination number to six, resulting in elimination of MF_2, MF_3, and MF_4.

Although by no means conclusive, the work on cyclic fluoroaromatic organometallic systems suggests that various fused-ring ions, postulated as intermediates in [MF] elimination from pentafluorophenylorganometallics, are entirely plausible. Similarly, if valence shell expansion were not involved, systems such as $(C_{12}F_8)_2M$ would also split out the metal atom alone to yield the very stable, previously isolated perfluorotetraphenylene ion $[(C_6F_4)_4]^+$. This is not observed, the metal being eliminated only in company with fluorines. Thus, although $(C_6F_5)_4Si$ eliminates SiF_4 to give $(C_6F_4)_4^{+\cdot}$, compound $(C_{12}F_8)_2Si$ eliminates SiF_4 to give $(C_6F_3)_4^{+\cdot}$.

As in all mass spectrometric systems, the postulated ion structures cannot be directly verified, but recent advances in ion kinetic energy spectroscopy (see Section VI) allow one to prove that two ions of the same mass from different sources have either identical or differing structures. Ionic structures tend to be drawn based on common sense and chemical intuition.

2. *Rearrangements in B—N and B—O Heterocycles*

Borazines have been shown to undergo some remarkable rearrangements. Lanthier (*217*) and Wilson (*230*) observed ions corresponding to the loss of ammonia from various fragment ions. This was more strikingly demonstrated for B-trispentafluorophenyl borazine (*217*, *218*):

$$\begin{tikzcd}
(C_6F_5BNH)_3^{+\cdot} \arrow[r, "-C_6F_5"] & B_3N_3H_3C_{12}F_{10}^{+} \arrow[r, "-NH_3"] \arrow[d, "-C_6F_4"] & B_3N_2C_{12}F_{10}^{+} \\
 & FB_3N_3H_3C_6F_5^{+} \arrow[r, "-NH_3"] \arrow[d, "-C_6F_4"] & FB_3N_2C_6F_5^{+} \\
 & F_2B_3N_3H_3^{+} \arrow[r, "-NH_3"] & F_2B_3N_2^{+}
\end{tikzcd} \qquad (19)$$

After the first loss of a $C_6F_5^{\cdot}$ group, neutral NH_3 may be lost, or, after loss of one or two C_6F_4 groups (presumably resulting in the formation of a B—F bond), ammonia may also be ejected. A drastic rearrangement is necessary for a single nitrogen to remove all three hydrogen atoms.

The rearrangements involved in fragmentation of $(C_6H_5)_2C_6F_5B_3O_3$ are less drastic, since there is only one example each of H—B and F—B bond formation:

$$\begin{tikzcd}
(C_6H_5)_2C_6F_5B_3O_3^{+\cdot} \arrow[r, "-C_6F_4"] \arrow[d, "-C_6F_5BO"] \arrow[dr, "-C_6H_5BO"] & (C_6H_5)_2FB_3O_3^{+\cdot} \\
(C_6H_5)(C_6F_5)B_2O_2^{+\cdot} \arrow[d, "-BO_2"] & (C_6H_5)_2B_2O_2^{+\cdot} \arrow[d, "-HBO_2"] \\
C_6H_5BC_6F_5^{+} & C_{12}H_9B^{+\cdot}
\end{tikzcd} \qquad (20)$$

This is also an example of a ligand-transfer rearrangement—two phenyls ending up on one boron. Such ligand transfers are very common, for example, the spectrum of $Ph_2PCH{=}CHPPh_2$ shows an abundant ion corresponding to $Ph_3P^{+\cdot}$ (*229*).

3. *Other Rearrangements*

The mass spectra of π-cyclopentadienyl metal compounds usually give abundant parent ions and show varying degrees of ring fragmentation. Despite this, however, processes are observed corresponding to the extrusion of the metal ion (*231*) or neutral metal atom (*232*), e.g.,

$$(C_5H_5)_2Fe^{+\cdot} \longrightarrow Fe^{+\cdot} + C_{10}H_{10} \qquad (21)$$

$$C_5H_5FeC_5H_4{}^{+} \longrightarrow C_{10}H_9{}^{+} + Fe \qquad (22)$$

Compound II mentioned in Section III, A, fragments with the loss of CrS_2 from the parent ion, leaving $(C_5H_5)_2Cr^{+\cdot}$ (*91*). In some substituted ferrocenes, transfer of a substituent to the iron has been noted:

$$(C_5H_5FeC_5H_4C(O)R)^{+\cdot} \longrightarrow C_5H_5FeR^{+\cdot} \quad (R = C_6H_5,\ OH,\ OCH_3,\ NHCN_3) \qquad (23)$$

Similar arrangements occur with alkylhydroxy side chains, the OH group migrating to the metal (*233*). Müller (*13*) has shown that migration of electronegative groups is favored if stable ions such as the tropylium ion can be formed:

$$CrC_7H_7CN^{+} \xrightarrow{-CrCN} C_7H_7{}^{+\cdot} \qquad (24)$$

$$CrC_6H_5CH_2OH^{+} \xrightarrow{-CrOH} C_7H_7{}^{+\cdot} \qquad (25)$$

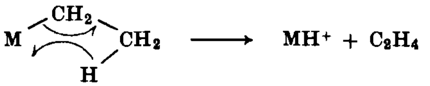
Migrations of oxygen to the metal from nitroso derivatives have been observed (*234*), e.g.,

$$C_5H_5V(NO)_2CO^{+} \xrightarrow{-NO,\ -CO} C_5H_5VNO^{+} \longrightarrow VO^{+} + (C_5H_5N) \qquad (26)$$

Rearrangements involving hydrogen transfer, either within the ligand or to the metal, have been discussed extensively by Müller (*13*) and Chambers *et al.* (*5*). These include main group elements for which alkene elimination from even-electron alkyl-containing ions,

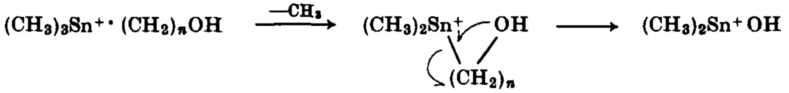
$$Et_3M^{+} \xrightarrow{-C_2H_4} Et_2MH^{+} \xrightarrow{-C_2H_4} EtMH_2{}^{+} \xrightarrow{-C_2H_4} MH_3{}^{+} \qquad (27)$$

proceeds via a β-elimination,*



$$M(CH_2)_2H \longrightarrow MH^+ + C_2H_4 \qquad (28)$$

Several recent studies have shown the ease of oxygen migration to tin, OH groups from hydroxylic ligands (*235*) [Eq. (29)] as well as oxygen from nitro groups becoming bonded to tin (*79*):



$$(CH_3)_3Sn^{+\cdot}(CH_2)_nOH \xrightarrow{-CH_3} (CH_3)_2Sn^+(CH_2)_nOH \longrightarrow (CH_3)_2Sn^+OH \qquad (29)$$

$$Sn^+O_2^\cdot + NO^\cdot \longleftarrow Sn^+NO_3 \longrightarrow Sn^+O^\cdot + NO_2 \qquad (30)$$

Glockling *et al.* (*236*) have recently investigated platinum alkyl and aryl complexes in which organic groups are transferred to and from phosphorus and platinum. The $(C_6H_5)_3P^{+\cdot}$ ion is detected in the spectrum of $Pt(C_6H_5)_2[((C_6H_5)_2P)_2CH_2]$, and, by labeling the phenyl group on platinum with fluorine (m-C_6H_4F), it is shown by formation of both $(C_6H_5)_3P^{+\cdot}$ and $(C_6H_5)_2PC_6H_4F^{+\cdot}$ that phenyl migration occurs from Pt to P. The apparent insertion of C_6H_4, arising from a $P(C_6H_5)$ group, into Pt—$C_6H_4F^+$ is also observed.

C. ISOTOPE ABUNDANCES

In inorganic and organometallic mass spectroscopy, one encounters the presence of polyisotopic atoms in most molecules. Although, as a result, the spectra appear to be somewhat complicated, the presence of isotope clusters is usually of great advantage in providing positive identification of high molecular weight species without exact mass verification. A good example is compound I (Section III, A): the envelope of the molecular ion cluster, centered about m/e 1010, demands the presence of two iron atoms. If, for example, the species contained only one iron but two more carbonyls (a chemically implausible species), although the nominal molecular weight would be unchanged [$-58 + (2 \times 28)$], the pattern would be considerably different (Table IV). For systems such as B_8Cl_8 (*136*) (Fig. 6) and B_9Cl_9 (*137*), the confirmation by isotopic species is as definitive as an exact mass measurement, perhaps more so, because exact mass measurement can be made

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* The mass spectrometric convention is that a double-barbed arrow (→) implies transfer of two electrons, whereas a single barb (⇀) indicates a one-electron transfer.

TABLE IV

OBSERVED AND CALCULATED ISOTOPIC PATTERN FOR THE PARENT ION CLUSTER OF $[(C_6F_5)_2PFe(CO)_3]_2$

m/e	Observed intensity[a]	Calculated intensities[b]	
		$C_{24}F_{20}P_2Fe_2(CO)_6$	$C_{24}F_{20}P_2Fe(CO)_8$
1008	14.0	12.6	6.3
1009	6.2	4.6	2.3
1010	100.0	100.0	100.0
1011	40.0	38.5	38.5
1012	10.0	9.1	9.1
1013	3.8	1.6	1.6
1914	1.0	0.2	0.2

[a] Miller (*237*).

[b] Calculated using computer program BMASROS (*182*).

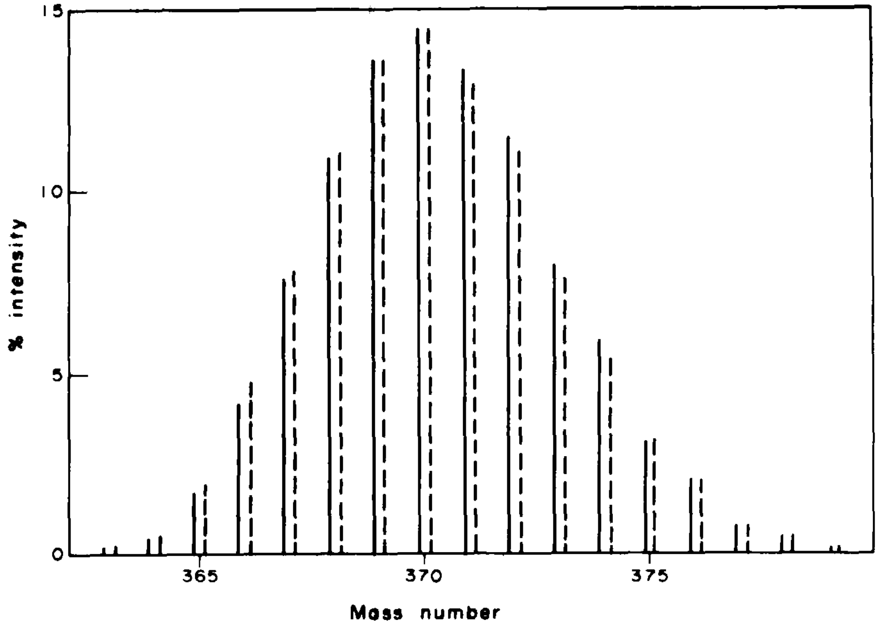

FIG. 6. Comparison of observed (solid line) and theoretical (broken line) isotopic intensities for the molecular ion of B_8Cl_8. [Reproduced by permission from Lanthier (*136*).]

difficult by many species of the same nominal mass and by the absence of good mass references at high *m/e* values.

A complication is introduced for systems that readily lose protons, or have two different coincident species overlapping in the same *m/e* region. In this case, deconvolution of the overlapping spectra becomes necessary. Once begun, however, deconvolution must be carried to completion. As shown in Table V, for $B_3N_3H_6$ serious errors can occur if only P^+ and $(P—H)^+$ contributions are considered (*238*) rather than all contributing species (*239*). Note that the $(P—H)^+$ contribution drops from 70.6 to 57.3% on consideration of all possible overlapping species.

TABLE V

CONTRIBUTIONS TO THE PARENT ION CLUSTER IN THE MASS SPECTRUM OF BORAZINE

	Relative intensity		
m/e	P + (P—H)[a]	P + (P—*n*H) *n* = 1–6[b]	Observed[c]
75	0.0	4.1	4.1
76	0.0	9.3	9.3
77	1.1	13.3	13.3
78	14.0	23.2	23.2
79	61.5	64.8	64.8
80	100.0	100.0	100.0
81	32.9	35.5	35.5
82	0.4	0.4	0.0

[a] Melcher *et al.* (*238*): P = 29.4%; P—H = 70.6%.

[b] Computer fit of the observed data shows the following relative contributions: P = 26.5%, P—H = 57.3%, P—2H = 3.2%, P—3H = 4.8%, P—4H = 5.3%, P—5H = 2.4%, P—6H = 0.4% (*239*).

[c] Melcher *et al.* (*238*).

Although isotopic patterns and deconvolutions may be calculated manually (*6*), to achieve full potential a computer is virtually a necessity. Manual calculations often omit the 1.1% contribution for ^{13}C; for molecules with large ligands, thirty carbons are not unusual, and these would give a 33% contribution to the *m/e* value, greater than that from the nominal mass by one mass unit.

Various computer programs are mentioned in the literature for calculating isotopic patterns (*182*, *240–242*) and the least-squares deconvolution of overlapping species, i.e., the calculation of monoisotopic mass spectra. McLaughlin *et al.* (*241*, *243*) have used their programs to generate monoisotopic mass spectra of complex boranes and to establish the existence of heptaboranes.

D. NEGATIVE IONS

Although negative-ion mass spectra are easily obtained in most mass spectrometers by relatively simple reversal of magnetic and electric field polarities, frequent absence of molecular ions and low negative-ion intensities [about 10^{-3} that of positive ionization (*244*)] have meant, until recently, few negative-ion studies.

A series of papers has appeared on the negative-ion spectra of binary fluorides of boron (*245*, *246*), Group IVA (*247*, *248*), phosphorus (*245*), and Group VIA (*249*). The Group III and IV fluorides, as well as showing fragment negative ions, showed species such as BF_4^-, SiF_5^- and GeF_5^-, presumably the result of ion–molecule reactions. Pignataro's (*244*, *250–254*) and Kiser's (*6*, *255*, *256*) groups have been active in the applications of negative-ion mass spectroscopy to organometallic metal carbonyl systems. They find that in general, if a positive ion is abundant, the corresponding negative ion is not, and vice versa. In contrast to the general rule that relatively few ions are observed in the negative-ion spectra, they found the negative-ion spectrum of $W(CO)_5PPh_3$ to show more peaks than its positive-ion spectrum. Thus positive- and negative-ion spectra are highly complementary.

Further negative-ion mass spectral studies include Cohen's work (*257*, *258*) on organomercurials, Pant and Sacher's (*258*) on tetrakis-(3,3,3-trifluoropropynyl) silane, Onak's *et al.* (*259*) on some closocarboranes as shown in (15), whereas Fraser *et al.* (*260*) have looked at the negative-ion spectra of some fluorinated β-diketonates of various metals. Molecular ions and ligand ions predominate in these latter spectra. Thus, it would appear that negative-ion mass spectrometry is an area offering great potential growth, provided more mass spectrometry laboratories would offer negative-ion spectra as a routine service. In the future the atmospheric pressure ion source discussed earlier (*66*, *67*) may prove to be an excellent source of negative ions:

$$\begin{tikzcd}
C_2B_4H_6 \arrow[r, "e^-"] & C_2B_4H_6^{\overline{\cdot}} \arrow[r, "-{[BH_3 + H^\cdot]}"] \arrow[d, "-H^\cdot"'] & C_2B_3H_2^- \\
& C_2B_4H_5^- \arrow[ur, "-BH_3"'] &
\end{tikzcd} \tag{31}$$

E. SYNTHETIC MODELS

Mass spectrometry can serve as a model for chemical synthesis since pyrolysis or thermolysis of compounds often leads to products analogous to the rearrangement ions observed. One of us (*90*) had suggested on the basis of mass spectral rearrangements that pyrolysis of the $(C_6F_5)_4M$ compounds of Group IV could serve as a synthetic route to the unknown perfluoro di-, tri-, and tetraphenylenes. These compounds were in fact synthesized (*261*, *262*) by the decomposition of unstable C_6F_5 derivatives of titanium. Clinton and Kochi (*263*) used selectivities in the mass spectral cracking patterns of tetraalkyllead compounds as models for the selective cleavages of cation radicals in solution. Bryant and Kinstle (*185*) have observed loss of methylene ($:CH_2$) from the molecular ion of 2-hydroxycyclooctyl mercuric chloride and suggest that this compound might be a useful carbene source under thermal conditions.

Orlov (*8a*) has compared the dissociative ionization and thermal decomposition of a series of Group IV compounds and discusses the use of the mass spectrometer to study the unstable or "nonexistent" compounds that are presumably thermolysis intermediates. These include bivalent compounds of Group IV such as silicon(II) derivatives and compounds with multiple bonds. Not only are ions observed important in such correlations, but the mass of the neutral fragment, as confirmed by the decomposition of metastable ions, is of equal importance.

V. High-Resolution Studies

Whereas the exact measurement of mass is a necessity for the unambiguous confirmation of the empirical formulas of organic ions, isotopic patterns can often serve the same purpose in inorganic and organometallic chemistry (Section IV, C). Most exact-mass measurements have been made manually using a peak-matching accessory, which permits the accelerating voltage to be changed, alternately focusing an unknown and reference peak at the exit slit. The two peaks are displayed on an oscilloscope and adjusted for superposition. This technique, although accurate to about 1 ppm is slow and tedious and requires considerable quantities of sample. More recently, on-line computers have been used to determine exact mass "on the fly" with scan rates of 10 sec per mass decade, or faster, using a continuous interpolation beween internal reference peaks. Unfortunately, most of the on-line data acquisition systems are based on minicomputers with restricted core capacity. Although they may be advertised as capable of handling up to ten elements simultaneously when calculating "element maps," each isotope counts as one element. Thus heteronuclear metal clusters or elements such as tin or mercury can cause confusion. A second problem for the computer is a suitable mass marker with high molecular weight; PFK, most commonly used, is good only to about *m/e* 800. Various reference compounds have been prepared for special purposes, the highest having masses up to 3628 (*264*); others of lower mass are available commercially (*265*). Hexakis(pentafluorophenyl)benzene, itself a product of an organometallic reaction (*226*), is a useful reference. Most reference compounds have been fluorocarbon-containing compounds since (*a*) monoisotopic fluorine results in simple spectra, (*b*) the molecular weights increase rapidly while volatility remains high, and (*c*) the fluorine mass defect permits resolution from hydrocarbon compounds. This latter point may well be a disadvantage for organometallics that also display a mass defect.*

An alternative to observing sample and reference together at high resolution involves the use of a double-beam mass spectrometer such as the AEI MS-30. If closely spaced mass multiplets need not be resolved, one can determine the exact mass of each peak in the spectrum at resolutions of ~1500, the computer acquiring data from the independent sample and reference beams simultaneously (*226*). Thus, source conditions can be optimized for compound and reference at the higher sensitivities available at lower resolutions, the mass measuring accuracy still being in the order of 10 ppm. This is possible, since if mass doublets are not involved, the centroid of a peak is as well defined at resolution 1500 as at 10,000.

In Table VI we illustrate the mass-measuring accuracy attainable even for polyisotopic species such as decaboranes (*267*) showing resolution of mass doublets, and uranium(IV) *N,N′*-ethylenebis(salicylideneimiminato) (Salen) complexes (*96*) at higher molecular weights. In this latter case the parent ion at *m/e* 702 was not determined due to lack of a suitable reference. The values recorded for the iron(II) dimethylglyoxime clathrochelates with boron compounds are examples of less accurate mass measurement, and for which the same information might have been obtained by isotope abundance measurements (*268*). The corresponding cobalt compounds (*268a*) were determined to even lesser precision.

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* The mass defect is the deviation of exact monoisotopic masses from integral whole numbers. Hydrocarbons have a positive mass defect ($^{12}C = 12.0000$ and $^{1}H = 1.0078$) resulting in exact masses slightly greater than the integral value, whereas the elements in the center of the periodic table (from oxygen to bismuth) usually have negative mass defects resulting in compounds with exact masses somewhat less than the nearest integral value.

TABLE VI

SOME EXAMPLES OF EXACT-MASS MEASUREMENT

Ion$^+$	Observed *m/e*	Calculated *m/e*	Error (amu)	Error (ppm)
$^{10}B_2{}^{11}B_8{}^1H_9{}^{35}Cl$	152.1396	152.1396	0.0000	0.0
$^{11}B_{10}{}^1H_7{}^{35}Cl$	152.1184	152.1167	−0.0017	−11.2
$^{10}B_3{}^{11}B_7{}^1H_9{}^{127}I$	243.0784	243.0788	0.0004	1.6
$^{10}B{}^{11}B_9{}^1H_7{}^{127}I$	243.0551	243.0559	0.0008	3.3
U(Salen)acac (i.e., M-acac)	603.2000	603.1996	0.0007	0.7
$[Fe(DMG)_3(BF)_2]$	458.079	458.080	0.001	2.2
$[Fe(DMG)_3(BOH)_2]$	454.087	454.081	−0.006	−13.2
$[Fe(DMG)_3(BOC_4H_9)_2]$	566.212	566.155	−0.057	−100.7
$^{59}Co{}^{12}C_8{}^1H_{12}{}^{14}N_4{}^{16}O_4{}^{11}B_2{}^{19}F_2$	347.04	347.03	−0.01	−28.8
$^{59}Co{}^{12}C_{12}{}^1H_{18}{}^{14}N_6{}^{16}O_6{}^{11}B_2{}^{19}F_2$	461.08	461.08	0.00	0.0

Haegele *et al.* (*269*) have used exact isotope masses and isotope abundances together in determining the detailed fragmentation patterns of square planar rhodium(I) β-diketonate complexes. They found that some species postulated by other workers were in error. High resolution is needed to distinguish the 28 mass units for loss of CO (27.9949) from C_2H_4 (28.0313) (*269*) or the 69 mass units for PF_2 (68.9906) from CF_3 (68.9952) (*90*).

VI. Metastable-Ion Techniques

To the novice, the rearrangements discussed in Section IV, B may appear to be alchemical figments (or fragments) of the imagination. However, the modern magnetic-sector mass spectrometer provides a method for the verification of these transitions in the form of "metastable ions," and all of the exotic transitions discussed in Section IV, B were so verified as being due to unimolecular dissociation and not source pyrolysis products. "Metastable-ion peaks" is perhaps a misnomer, since the low-intensity broad diffuse peaks actually observed are normal ions arising from the decomposition of metastable ions in field-free regions of the mass spectrometer, but the term metastable or metastable ion is often attributed to them. Metastable ions have been the subject of a comprehensive monograph (*270*), but applications to organometallics have not been included.

"Normal" metastable ions are formed between the source and magnet of single-focusing sector instruments. In double-focusing instruments of Nier-Johnson geometry, these arise in the second field-free region between the electric and magnetic sectors, where a precursor ion m_1 decomposes to give a daughter ion m_2, now carrying only a fraction m_2/m_1 of its original energy. These are brought to a focus by the magnet at an apparent mass $m^* = m_2{}^2/m_1$ (see Ref. *77* for sample calculation). Normally then, decomposition pathways are verified by measuring the position of m^* and by trial-and-error fit of m_1 and m_2 (almost invariably abundant fragments). Since m^* appears at a lower apparent mass then either m_1 or m_2, transitions between high m/e fragments are much easier to assign, as the choices for m_1 and m_2 are limited (only those peaks appearing above m^*); metastable ions appearing at lower m/e values may be found to have more than one set of precursor-daughter couples satisfying the measured m^*. The importance of normal metastable ions has long been recognized (*77*, *270*, *271*), and most of the rearrangements discussed have been studied with the aid of normal metastables.

More recently, several metastable "defocusing" techniques have been introduced, which gives enhanced metastable-ion sensitivity by removing the normal ions, as well as removing much, if not all, of the ambiguity involving trial-and-error fits of m_1 and m_2. The first of these, the Barber and Elliott technique and its refinements (*272–274*) permits metastable ions formed in the first field-free region between the source and electrostatic analyzer (ESA) to be focused on the collector. After tuning the magnet to a particular ion, the accelerating voltage is increased while the ESA voltage is held constant, and the collector output is recorded as a function of accelerating voltage. A discussion of the ion optics of these techniques may be found in Cooks *et al.* (*270*). By this means the precursors to the ion tuned in by the magnet are observed, i.e., $m_2/m_1 = V_0/V_1$, where m_1 and m_2 are the masses of the precursor and daughter ions and V_0 and V_1 are the initial accelerating voltage and that required to tune the precursor ion to the energy of the ESA. A later development of this technique, referred to as "ion kinetic energy (IKE) spectroscopy" by Beynon (*77*, *270*, *275*, *276*), involves an ESA voltage scan with the accelerating voltage held constant. Now all the first drift-region metastables are recorded at the total-ion monitor between the ESA and magnet. Interpretation of these results requires trial fits to all possible transitions.

The most recent metastable defocusing technique, which is referred to as "mass-analyzed ion kinetic spectroscopy" (MIKES) by Beynon (*77*, *270*, *277*) and as "direct analysis of daughter ions" (DADI) by Maurer (*278*) requires the interchange of the source and collector positions in a double-focusing mass spectrometer of Nier–Johnson geometry. With this configuration, if the magnet is tuned to a particular ion and the ESA voltage scanned while keeping the accelerating voltage constant, the collector output as a function of ESA voltage gives all the daughter ions formed in the region between the magnet and ESA. To obtain MIKES involves either extensive mechanical modification of conventional commercial instruments (*277*, *279*), i.e., physically interchanging the source and collector ends of the instrument or the purchase of a machine constructed with reverse geometry (*278*). Such reversed geometry instruments have the disadvantage, for a normal, mass spectrometry service laboratory of suppressing "normal" metastables. If the nonexpert does not see normal metastables, he has nothing to entice him to study further metastable ions.

We have observed that the AEI MS-30 mass spectrometer has the potential for all of the above methods included in its design and have recorded MIKE spectra (*280*) by scanning the beam-2 deflector plates, which are located between the magnet and the beam-2 collector, in an instrument of otherwise conventional Nier–Johnson geometry. Normal metastables are observed in good intensity in beam 1. An extension of the MIKES or DADI technique permits direct observations of "metastable ions arising from metastable ions in ion energy spectra" (MAMIES) (*281*) for which it was possible to observe in the spectrum of *N*-trimethyl borazole, the following consecutive transitions from m/e 122: 122 → 81 → 65; 122 → 81 → 54; and 122 → 81 → 40.

Results of a low-resolution MIKES study of $C_6F_5Si(CH_3)_3$ (*280*) are shown in Fig. 7, for transitions from the parent ion, the base peak, $C_6F_5Si(CH_3)_2^+$, and from the rearrangement ion $(CH_3)_2SiF^+$. Only the more intense peaks are also observed as normal metastable ions ($m^* = 69.4$ for the transition $C_6F_5Si(CH_3)_2^+ \rightarrow C_6F_2CH_3^+ + CH_3SiF_3$).

Various other techniques are available for the observation of normal metastable ions in the absence of the much more intense normal ions, and these can be of use for photographic instruments of Mattauch–Herzog geometry (*282*, *283*), for instruments with a Daly detector (*284*), and for instruments able to observe MIKE spectra (*285*). Metastable ions have also been used to establish the existence of unobserved parent ions (*286*). The development of high-resolution MIKE spectrometers, studies of kinetic energy release, and ion–molecule reactions are all areas of development of metastable-ion studies with great practical application to inorganic and organometallic chemistry. Cooks *et al.* (*287*) have shown that one can detect charge-stripping transitions both from the ground and excited states for $NO^+ \rightarrow NO^{2+}$, but to date high-resolution MIKES have not been applied to organometallic compounds. Now that negative-ion studies on organometallics are becoming common, another area ripe

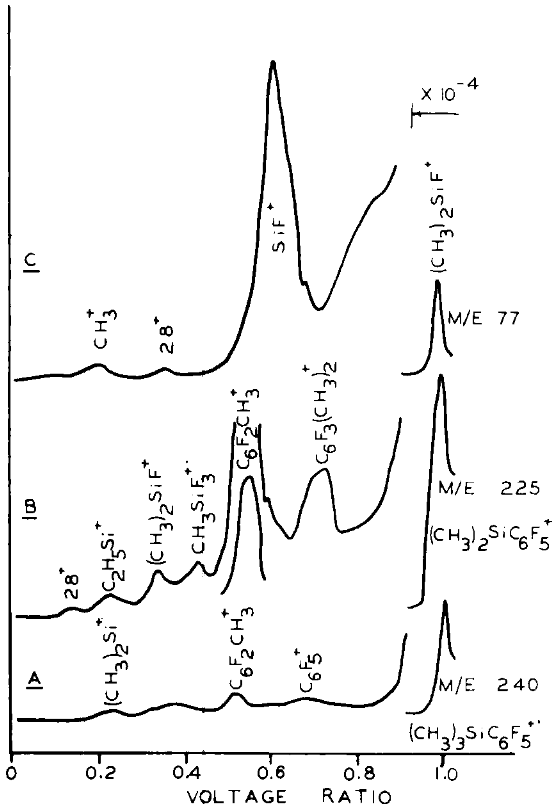

FIG. 7. Mass-analyzed ion kinetic energy (MIKE) spectra of $C_6F_5Si(CH_3)_3$. [Reproduced with permission from J. M. Miller, J. Ross, J. Rustenberg, and G. L. Wilson, *Anal. Chem.* **45**, 627 (1973); copyright by the American Chemical Society.]

for development will be the applications of both normal metastables and MIKES techniques to these negative-ion spectra.

VII. Coupled Gas Chromatography and Mass Spectrometry Applied to Inorganic and Organometallic Compounds

Application of the integrated GC/MS system to problems in organometallic chemistry currently falls far short of potential. Interestingly, one of the major applications of GC/MS in organometallic systems has been made with compounds of biochemical interest. The widespread use of trimethylsilyl derivatives for GC (*288*, *289*) was extended to MS (*290*) and GC/MS spectrometry (*291*, *292*). Similarly, the use of GC for the detection and analysis of organomercury compounds in environmental samples is widespread (*293*), and concern over possible decomposition has led to GC/MS studies of such systems (*123*, *124*, *161*, *293*, *294*).

The following examples (*217*, *295*) illustrate the routine use of GC/MS in the solution of day-to-day laboratory problems, solving in an hour or 2, problems that may either be ignored and bypassed or that would require more difficult and time-consuming methods to solve. It is possible to check the purity of starting materials and products and to identify unwanted components, which often is a great aid in their elimination during synthesis or in deciding on purification techniques. The monitoring of exploratory syntheses by GC/MS permits a rapid identification of GC peaks so that GC alone may be used as an aid, as the synthetic procedure is refined for optimal yield, purity, etc. Similarly, the products of unexpected reactions, as may occur between solute and solvent in an NMR tube, may be monitored rapidly with minimal sample consumption (1 μl); air- and moisture-sensitive compounds are readily handled using microsyringes.

Recently, using as a starting material a commercial sample of borazine, $B_3N_3H_6$, purported to be "pure," inexplicable products were detected by GC/MS, suggesting impure starting materials. The borazine was thus subjected to GC/MS analysis. Although the first and largest GC peak corresponds to $B_3N_3H_6$, the impurities predominate. A peak of about equal intensity was readily identified as chlorobenzene (*m*/*e* 112:114 in a 3:1 ratio), a solvent used in one preparation of $B_3N_3H_6$ (although the manufacturers initially suggested that chlorobenzene had not been used, later correspondence admitted its probable presence), and trimethylamine, another possible precursor in the synthesis was also found. Other peaks corresponded to the formula $B_5N_5H_8$ (cluster at *m*/*e* 133, 132, 131, etc.), a previously identified material (*296*), i.e., the BN naphthalene analog, the biphenyl analog (*296*) $(B_3N_3H_5)_2$ (cluster at *m*/*e* 160, 159, 158, 157, etc.), and two higher polymers, although no mass spectra have been previously reported for either species, $B_6N_7H_{11}$ (*m*/*e* 175, 174, 173, etc.) and $B_7N_7H_{10}$ (*m*/*e* 185, 184, 183, etc.) the latter being the anthracene analog. In a matter of minutes, the nature of the impurities were determined and the presence of unexpected, but interesting species revealed. Analysis via the GC/MS system, therefore, may offer a saving in time where the purity of starting materials is suspect, as well as potentially revealing new and interesting compounds previously discarded as unwanted impurities.

Another example involves a sample of $(C_6F_5)_2Si(CH_3)_2$ which was 99%+ pure by GC and "pure" by the criterion of ^{1}H NMR spectra, but which showed peaks in the mass spectrum to high mass of the expected parent at *m/e* 392. It was therefore subjected to a GC/MS analysis, and the compounds detected are shown in Table VII. Peaks 6 and 7 correspond to two different isomers.

During a proton NMR examination of a CCl_4 solution of $Me_3N_3B_3F_3$, an extraneous peak was observed in the spectrum, although the borazine was known to be analytically and mass spectrometrically pure. One microliter of the solution was subjected to GC/MS analysis. Peaks identified as trimethylsilane (TMS) and CCl_4 were obtained followed by the expected $Me_3N_3B_3F_3$ (*m/e* 177, 176, etc.). An additional component eluted after 15 min was readily identified by its mass spectrum as $Me_3N_3B_3F_2Cl$, undoubtedly the extraneous NMR peak. It appears therefore that B-trifluoro-*N*-trimethyl borazine undergoes halogen exchange with CCl_4, another example of an "inert" NMR solvent acting as a good chlorinating agent for metal–halogen or metal–hydrogen bonds. The rapid identification of the impurity (~10%) permitted the NMR investigation to proceed, as well as suggesting possible synthetic routes to mixed fluorochloro-substituted borazines.

TABLE VII

COMBINED GAS CHROMATOGRAPHY/MASS SPECTROMETRY RESULTS FOR $(C_6F_5)_2Si(CH_3)_2$[a]

Peak No.	Retention time (min)	Quantity	Parent ion (*m/e*)	Identification
1	4.0	Trace	240	$C_6F_5Si(CH_3)_3$
2	8.0	Trace	281	?
3	17.5	99%+	392	$(C_6H_5)_2Si(CH_3)_2$
4	21.0	0.2%	440/438/436	$C_{12}F_7HBr_2$
5	22.0	0.2%	450	$(C_6F_5)_2Si_2(CH_3)_4$
6	23.0	0.3%	454/452	$(C_6F_5)(C_6F_4Br)Si(CH_3)_2$
7	23.7	0.2%	454/452	$(C_6F_5)(C_6F_4Br)Si(CH_3)_2$
8	25.0	Trace	416/414/412/410/408	C_6HFBr_4
9	27.0	Trace	482	$(C_6F_5)_2Si_2O_2(CH_3)_4$

[a] Conditions: 175°C; 25 ml/min He; 5 ft × 0.25 in. 3% SE-30.

Sowinski and Suffet (*297*) have used GC/MS to detect boron hydrides at trace levels, whereas Blum and Richter (*298*) have used capillary columns in the combined GC/MS of a series of phenylboronate derivatives. There have also been recent applications of GC/MS to the TMS derivatives of inorganic anions (*299*). The TMS derivatives of ammonium arsenates, phosphates, vanadates, borates, carbonates, oxalates, and sulfates gave satisfactory GC separation and satisfactory mass spectra, but the corresponding sodium or potassium salts gave unsatisfactory results. Coupled GC/MS has also been satisfactorily applied to the separation of β-diketonates of Ni(II), Pt(II), and Pd(II) (*300*) and to the determination of chromium and beryllium at the picogram level (*301*).

The ready availability of GC/MS instrumentation as well as the speed, specificity, and small sample requirements are likely to result in a great increase in the applications of this technique to inorganic and organometallic chemistry.

VIII. Conclusion

We hope to have given some insight into the present usefulness of mass spectrometry to the inorganic and organometallic chemist, but more important, we would hope to have stimulated thought toward future applications. The possibilities for the chemist implicit in the development of new ion sources, in metastable-ion and ion kinetic energy studies, and in the interfacing of such powerful separation techniques as GC and HPLC, would suggest that mass spectrometry will continue to be of growing interest in the future.

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39. The standard instrument of this type has been the AEI MS 9/MS 902 now superseded by the MS-50, MS-30 and the new MS-1073, others include the Hitachi RMU-7, Dupont 21-491 and 492, and VG instruments.

40. Varian MAT CH-5 DF and 311 and the new 112, and a Nuclide instrument.

41. The long time standard, now discontinued, Mattach-Herzog instrument was the CEC (Dupont) 21-110, while JEOL, Varian MAT and AEI still build instruments of this geometry.

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