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Ion Cyclotron Resonance Study of Ion-Molecule Reactions of Volatile Organometallic Compounds

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The powerful capability of ion cyclotron resonance (icr) spectroscopy for the study of gas-phase ion-molecule reactions has been applied only to a limited extent to organometallic compounds: Foster and Beauchamp have reported a number of cationic reactions of $Fe(CO)_5$, including formation of several product ions containing two iron atoms;[1] Bach, Gauglhofer, and Kevan have reported reactive formation of gaseous mercurinium ions;[2a] and several ions presumed to have Hg-Hg bonds have been reported.[2b] In addition to sample-handling problems, progress in this area is impeded by the rapid degradation of spectrometer performance and resolution at masses above about 200. We report in this note the observation by icr techniques of several binuclear metal-organic ions. The investigation of such heavy ions has involved use of icr techniques especially appropriate for high masses, and we describe here the unusual features of the instrumental methods.

Ion Cyclotron Resonance Technique

Detection of ions up to a mass of 200-250 is achieved in a satisfactory manner using the standard marginal oscillator supplied with the Varian ICR-9 spectrometer with capacitive tuning.[3] However, marginal oscillator performance falls off rapidly at operating frequencies substantially below 100 kHz, and it is often preferable to detect heavier ions by the total ion current (TIC) detection mode described by Goode, *et al.*[4] In this detection mode, the total ion current reaching the collector end of the cell is monitored by an electrometer, while the double-resonance oscillator is frequency swept through the cyclotron frequencies of the ions of interest. When the cyclotron frequency of a particular ion is passed, a dip in the total ion current is observed whose amplitude corresponds to the flux of ions of the indicated m/e value.

This detection mode has several important advantages over marginal oscillator detection. (1) There is no variation in sensitivity for detection of different ion masses. (2) The advantages of sweeping frequency at constant magnetic field (offering unchanging conditions in the cell) are conveniently realized. (3) A scan of the entire spectrum from the lowest mass of interest up to masses above 1000 is conveniently made, with the resolution of each peak equal to the theoretical maximum resolution for the icr cell conditions being used and without any additions or modification to the commercial spectrometer.

The difficulty experienced in the TIC method with drifting base lines and low sensitivity can be alleviated by the use of phase-sensitive detection. We have found a modulated TIC detection mode to be highly satisfactory. In this technique, shown schematically in Figure 1, the ejecting radiofrequency field is switched on and off by a low-frequency square-wave modulation, and the electrometer output is synchronously detected using a Princeton Applied Research Model 126 lock-in amplifier. The long response time of the electrometer necessitates modulation frequencies not much above 0.3 Hz, and the filtering time constant and frequency sweep speed are accordingly slow. With this limitation, the modulated detection mode offers a very convenient means of detection of high-mass ions. A typical spectrum is reproduced in Figure 2. It is found that spurious TIC peaks often appear at frequencies around 10-25 kHz, arising from the resonant trapping ejection effect described by Armstrong and Beauchamp.[5] Since the frequency at which these peaks appear is independent of magnetic field, but dependent on trapping voltage, they are easily identified by taking the spectrum at two different magnetic fields and disregarding those peaks which do not change position.

In a modulated TIC mode of operation, double-resonance verification of reaction pathways is very convenient, since (in contrast to the continuous TIC mode of operation) the output signal is directly proportional to the ion current of ions at the observed mass. Accordingly, irradiation of a reactant ion produces a dip in product ion signal which can be interpreted in exactly the same way as double-resonance signals with marginal oscillator detection.[6]

Experimental Part

The TIC single- and double-resonance techniques were used to obtain the tetraethyllead results reported. Single-resonance spectra for metal carbonyls were obtained by TIC and repeated in the mass range up to about 350 AMU maximum by marginal oscillator detection. The metal carbonyl reactions were confirmed using ion-ejection double resonance[7] with marginal oscillator detection.

Cell conditions and operating parameters for observing positive ions in the "flat" icr cell[3] and negative ions in the "square" icr cell[8] have been described, and the present work followed similar lines. Pressures were in the range 10^{-6}-10^{-5} Torr. Tetraethyllead was obtained by courtesy of the Standard Oil Co. and was distilled and deaerated by freeze-pump-thaw cycles before use. Chromium hexacarbonyl was obtained from Alfa Inorganics and used without purification. Iron pentacarbonyl was obtained from Alfa Inorganics and used without purification other than decanting from a partially frozen sample. Nickel carbonyl was obtained from Alfa Inorganics and was used after pumping the air and CO off the frozen sample.

Observations. The high-mass ions appearing in the spectra of several metal-containing molecules have been examined, and condensation reactions are found to be common. We describe here representative results.

Tetraethyllead. The positive-ion spectrum of tetraethyllead[9] is shown in Figure 2. The principal primary ion is $Pb(C_2H_5)_3^+$, with a small amount of parent cation. Small peaks possibly corresponding to $Pb(C_2H_5)_3CH_2^+$ and $Pb(C_2H_5)_4CH_3^+$ are seen. The

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[1] M. S. Foster and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 93, 4924 (1971).

[2] (a) R. D. Bach, J. Gauglhofer, and L. Kevan, *J. Amer. Chem. Soc.*, 94, 6860 (1972); (b) S. C. Cohen, *J. Chem. Soc. A*, 1571 (1971).

[3] For recent review, see J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, 4, 114 (1971); G. A. Gray, *Advan. Chem. Phys.*, 19, 141 (1971); J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, 22, 527 (1971).

[4] G. C. Goode, *et al.*, *Int. J. Mass Spectrom. Ion Phys.*, 5, 393 (1970).

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[7] R. C. Dunbar, *J. Amer. Chem. Soc.*, 93, 4354 (1971).

[8] R. C. Dunbar, *J. Amer. Chem. Soc.*, 90, 5676 (1968).

[9] See M. R. Ghati and K. N. Bhide, *Indian J. Chem.*, 2, 243 (1964), for low-pressure mass spectra.

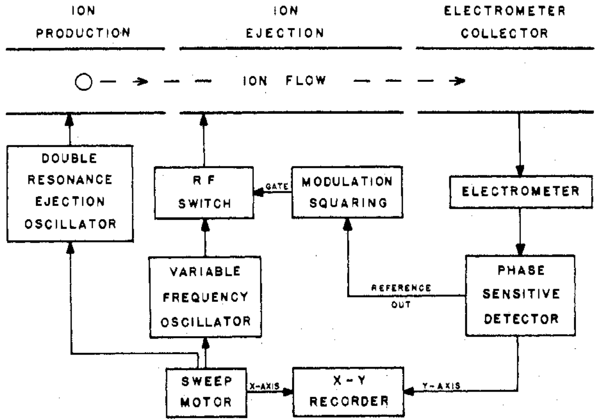


Figure 1. Block representation of the modulated TIC detection mode for high-mass ions. The only units not provided in the commercial spectrometer are the modulation-squaring circuit and the low-frequency phase-sensitive detector.

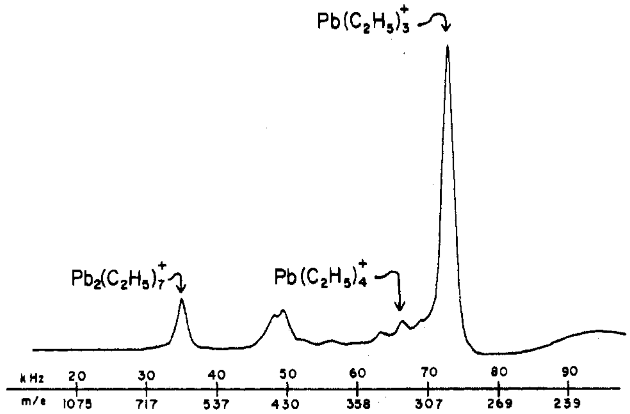


Figure 2. Spectrum of the tetraethyllead system obtained by the modulated TIC method, showing the prominent $Pb(C_2H_5)_3^+$ and $Pb_2(C_2H_5)_7^+$ ions. TIC double resonance confirms that these two ions are reactively coupled.

peaks at about *m/e* 430 are unexplained and possibly are due to an impurity in the sample. Careful examination with an expanded scale of the peak near *m/e* 618 verified the $Pb_2Et_7^+$ assignment within ±2 mass units. The only major reaction observed was the dimerization

$$Pb(C_2H_5)_3^+ + Pb(C_2H_5)_4 \rightarrow Pb_2(C_2H_5)_7^+ \qquad (1)$$

This reaction was confirmed by the modulated TIC double-resonance technique described.

Nickel Tetracarbonyl. Although other primary ions of low intensity might be anticipated at sufficient spectrometer sensitivity,[10] the only primary ion observed in these experiments was $Ni(CO)_3^-$, which was produced at all electron energies from 2 to 30 eV. A very large product peak was observed near mass 285, presumably $Ni_2(CO)_6^-$, and no other peaks were observed with any detection technique. Ejection of $Ni(CO)_3^-$ from the source region totally suppressed the $Ni_2(CO)_6^-$ signal, confirming the reaction

$$Ni(CO)_3^- \xrightarrow{Ni(CO)_4} Ni_2(CO)_6^- + CO \qquad (2)$$

Iron Pentacarbonyl. As expected,[10] the most abundant primary ion at all electron energies was $Fe(CO)_4^-$, which was produced in highest quantity at the lowest accessible electron energy (~1 eV). A small peak was observed for $Fe(CO)_3^-$ with electron energies in the range 1.5-2.3 eV.

The only product ion observed was $Fe_2(CO)_6^-$, which was produced in abundance at electron energies from about 1.8 to 2.4 eV. This product ion signal was totally suppressed by ejection of $Fe(CO)_3^-$ in the source. The double-resonance result and the correspondence of electron energy dependence between $Fe(CO)_3^-$ and $Fe_2(CO)_6^-$ confirm that the only major reaction producing this product is

$$Fe(CO)_3^- \xrightarrow{Fe(CO)_5} Fe_2(CO)_6^- + 2CO \qquad (3)$$

The $Fe(CO)_4^-$ ion does not appear to undergo any significant condensation reaction.

Chromium Hexacarbonyl. $Cr(CO)_5^-$ is the most abundant primary ion at all electron energies, with the largest quantity appearing at the lowest energy.[10] $Cr(CO)_4^-$ was readily observed at electron energies near 4.5 eV, and $Cr(CO)_3^-$ was found near 5.5 eV.

A major peak for the $Cr_2(CO)_8^-$ product was observed using approximately 4.5-eV excitation electron energy. Source-ejection double resonance confirmed that this ion is formed in the reaction

$$Cr(CO)_4^- \xrightarrow{Cr(CO)_6} Cr_2(CO)_8^- + 2CO \qquad (4)$$

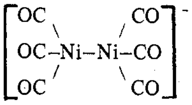
A small $Cr_2(CO)_6^-$ peak was obtained near 5.5-eV electron energy. Double resonance confirmed the reaction

$$Cr(CO)_3^- \xrightarrow{Cr(CO)_6} Cr_2(CO)_6^- + 3CO \qquad (5)$$

Discussion

The tendency of gas-phase organometallic ions of the type described here to "condense" with neutral molecules is important from the viewpoint of synthesis in organometallic chemistry. While ionic gas-phase atomic aggregates (small molecules) such as He_2^+, $ArXe^+$, etc. are well established, reactions 1-5 have not been recognized previously. It is often postulated that observation of an ion as a reaction product under mild icr conditions is more indicative of relatively high stability than is its observation as a product of energetic electron or ion impact. Furthermore, although dimerization and oligomerization of some metal carbonyls is known to occur in solution, the mechanism by which the condensation reactions occur is unknown.

Clearly structural work is essential in order to establish the nature of the products in (1)-(5). Based on known organometallic chemistry it is possible to suggest reasonable metal-metal bond structures[11-13] for each product, although precedent for some is rather limited. For example, $Pb_2(C_2H_5)_7^+$ can be formulated to contain a three-center, two-electron M-C-M bridge bond as in $Al_2(C_2H_5)_6$. The metal carbonyl anions probably display structures consistent with established bonding schemes in polynuclear metal carbonyls.[14] This is particularly likely for $Ni_2(CO)_6^-$, I, since the 18-electron metal-metal bonded $Ni_2(CO)_6^{2-}$ is known.[12] For species such as $Fe_2(CO)_6^-$, $Cr_2(CO)_8^-$, and $Cr_2(CO)_6^-$, bonding representations require multiple metal-metal bond formation.[13] In all reasonable structures the dinuclear anion must be paramagnetic, one electron short of the 16- or 18-elec-



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[10] S. Pignataro, *et al.*, *Z. Phys. Chem.* (*Frankfurt am Main*), 47, 106 (1969).

[11] G. E. Coates and K. Wade, "Organometallic Compounds," Vol. 1, Methuen, London, 1967, p 501.

[12] J. Wender and P. Pino, "Organic Synthesis *via* Metal Carbonyls," Interscience, New York, N. Y., 1968, p 69.

[13] A description of the bonding scheme for these compounds can be formulated in the following manner. For $Cr_2(CO)_8^-$ we assume that a basic square-pyramidal hybridization occurs about each metal ion, producing five filled σ (dsp^3) orbitals. This utilizes two of the 13 metal-based electrons. Two d orbitals (d_{xz}, d_{yz}) and four electrons are involved in metal-metal π bonding. The remaining seven electrons are assigned to the two remaining nonbonding d orbitals on each metal atom. The net result is a Cr≡Cr triple bond. For $Cr_2(CO)_6^-$ an even higher order of metal-metal bonding may be implied.

tron rule.[14] The gas-phase results lead one to expect the synthesis of new stable dianions of formulas $Fe_2(CO)_6^{2-}$, $Cr_2(CO)_8^{2-}$, and $Cr_2(CO)_6^{2-}$.

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Registry No. Tetraethyllead, 78-00-2; nickel tetracarbonyl, 13463-39-3; iron pentacarbonyl, 13463-40-6; chromium hexacarbonyl, 13007-92-6.

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Sulfur-Sulfur Bond Cleavage Promoted by Palladium(0) and Platinum(0) Triphenylphosphine Complexes

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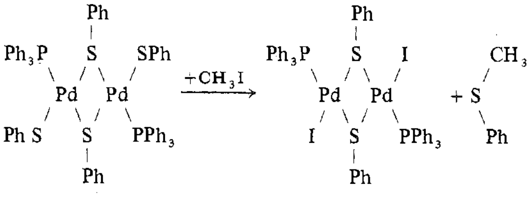
One of the more common features of transition metal complexes containing the coordinated SR^- group is their tendency to form polymeric units.[1] This tendency is greatly reduced as the electron-withdrawing properties of R increase. Thus, for $R = C_6F_5$ only monomeric species have been isolated.[2] However, generally the occurrence of monomers depends on the metal and also on the coordinated ligands, as shown in the cleavage of sulfur-sulfur bonds by $[Ni(L_\pi)_4]$ ($L_\pi = P(OR)_3$, CO), where both monomeric and polymeric derivatives are obtained.[3,4]

With the aim of verifying whether this behavior is common to zerovalent platinum triad metal complexes, we have examined the reaction of organic disulfides with complexes of the type $[M(PPh_3)_4]$ (M = Pt, Pd).

Results and Discussion

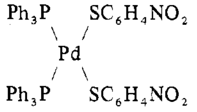
Oxidative addition of organic disulfides RSSR [$R = C_6H_5$, *o*- and *m*-$O_2NC_6H_4$, *t*-Bu, CN] to complexes of the type $[M(PPh_3)_4]$ (M = Pd, Pt) gives a variety of new compounds, the nature of which depends on both the reacting metal and the disulfide.

Reactions with $[Pd(PPh_3)_4]$. $[Pd(PPh_3)_4]$ reacts in benzene solution with $C_6H_5S\text{-}SC_6H_5$ under nitrogen to give a red compound formulated as a dimer having both terminal and bridging sulfide groups (I). This structure has been inferred on the basis of molecular weight measurements (mol wt in C_6H_6: calcd, 1174; found, 1130), elemental analysis, and reactivity with CH_3I to give II. $PhSCH_3$ was detected by glc using a Chromosorb column. Its formation probably occurs *via* an electrophilic attack of the positive end of $H_3C^+\cdots I^-$ on the sulfur atom of the terminal $-SC_6H_5$ group. Nucleophilic substitution of SR^- by I^- can be ruled out since no reaction occurs between I and iodide ion.



I II

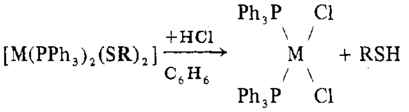
Monomeric compounds of type III are obtained in the reaction of $[Pd(PPh_3)_4]$ with electronegatively substituted aryl disulfides such as *o*- or *m*-nitrophenyl disulfide.



III

Reactions with $[Pt(PPh_3)_4]$. By treatment of $[Pt(PPh_3)_4]$ with electronegatively substituted or unsubstituted aryl disulfide only monomeric complexes are readily obtained. This accords with the smaller tendency of platinum relative to palladium to form polymeric units and with a decreased stability of such species owing to lower electron density on the sulfur atom in the electronegatively substituted aryl groups.

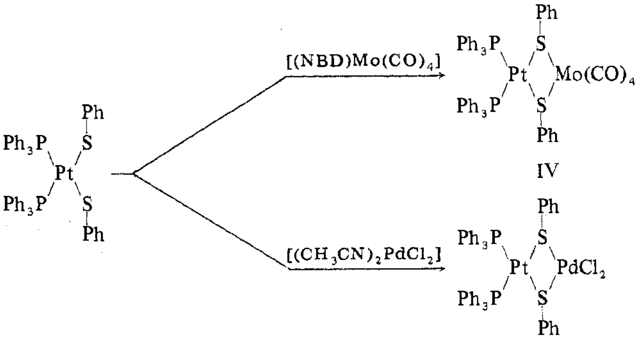
The complexes $[M(PPh_3)_2(SR)_2]$ (M = Pd, Pt), characterized by molecular weight measurements and by elemental analysis, react with hydrogen chloride according to the equation



$$[M(PPh_3)_2(SR)_2] \xrightarrow[C_6H_6]{+HCl} M(Ph_3P)_2Cl_2 + RSH$$

(M = Pd, $R = C_6H_4NO_2$, trans isomer ν(Pd-Cl) 360 cm^{-1}, Nujol mull; M = Pt, $R = C_6H_5$ and $C_6H_4NO_2$, cis isomer ν(Pt-Cl) 330 and 293 cm^{-1}, Nujol mull). The four-coordinate planar complexes $[M(PPh_3)_2Cl_2]$ were identified by comparison with authentic samples.[5,6]

The complex $[Pt(PPh_3)_2(SPh)_2]$ reacts also with transition metal compounds having labile groups such as norbornadiene or CH_3CN to give hetero dinuclear complexes according to



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