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# Mass Spectrometric Study of $\eta$-$C_5H_5Fe(CO)_2$ $EMe_3$ Complexes (E = Si, Ge, Sn and Pb)

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*The complexes $\eta$-$C_5H_5Fe(CO)_2EMe_3$ (E = Si, Ge, Sn and Pb)and $\eta$-$C_5H_5Fe(CO)_2X$ (X = Cl, $CH_3$, I, $SnCl_3$) have been studied by mass spectrometry. Ionization energy data show an easier ionization going down along the IV group, except for the carbon derivative whose I.P. is lower than that of the silicon derivative. Values of D(Fe–E) increase from Si to Sn and decrease from Sn and Pb. The results do not permit to establish the role of the possible $\pi$ back bonding between Fe and E. The 50 eV mass spectra are briefly discussed in terms of competitive fragmentations of the molecular ions.*

## Introduction

In the last few years transition metal complexes with a direct bond between the transition metal and a IV group element have been extensively studied. The possibility of multiple bonding between the transition metal atom and the silicon, germanium or tin atom, involving unoccupied *d* orbitals of the IV group atom, has stimulated several investigations based on solid state structure determination, i.r. and Raman spectroscopy, PES, mass spectrometry, *etc.*[1–18] However, a definite evidence of a $\pi$ character of the metal–metal bond has not been reached, and on the ground of different experimental approaches different conclusions are reported even for the same compounds.

We report a mass spectrometric investigation on $\eta$-$C_5H_5Fe(CO)_2EMe_3$ (E = Si (I), Ge (II), Sn (III) and Pb (IV)) compounds, so extending the previous study to the lead derivative; related compounds of the type $\eta$-$C_5H_5Fe(CO)_2X$ (X = $CH_3$ (V), Cl (VI), I (VII), $SnCl_3$ (VIII)) have also been studied.

## Experimental

The measurements were made with an Atlas $CH_4$, mass spectrometer. The samples were introduced in the ion source via a direct inlet at the lowest possible temperature in the probe (20° C) and in the ion source (150° C). No pyrolysis effect was apparent. The ionization potentials were measured by Honig's[19] method and the appearance potentials by the extrapolated voltage difference method[20]. Xenon was used as standard. Reproducibility was better than 0.1 eV.

The samples were synthesized and purified by published methods[21].

## Results and Discussion

The ionization energies of $\eta$-$C_5H_5Fe(CO)_2EMe_3$ reported in Table I show a somewhat irregular pattern, the I.P. of the germanium derivative being slightly lower than that of the tin derivative; however, as a general trend, an increasing ease of ionization going down along the IV group is apparent. These results are in agreement with the rather few data relative to the ionization energies of related complexes[7,10], so that it is apparent that similar factors influence the I.P. values along a series, while molecular structure and central metal have a strong effect on the absolute values of the ionization energies and possibly on their range of variation.

It has been long before suggested[22], and more recently confirmed by PES[23] data, that in transition metal complexes the orbital involved in the first ionization process has a predominant character of central metal *d* orbital; however, for compounds containing a IV group element the M–E $\sigma$ bonding level is likely to be close in energy to the central metal *d* level[7,8]. It follows that the variation of ionization energy along the series does not necessarily reflect the direct influence of the substituent on the *d* orbitals of the central metal, which might participate in $\pi$ back-bonding between Fe and E; in fact, the M–E $\sigma$ bonding level might become directly involved in the ionization process on going down along the group. The present data do not suffice to establish the nature of the last occupied molecular orbital and, on the other side, preliminary PES data do not clarify this point because, for E = Ge and Sn, the lower energy bands are poorly resolved. However, looking at the appearance potential data for the $(P–Me)^+$ ions, a very different situation for the silicon derivative (I) with respect to the other compounds is

TABLE I. Energetic Data (e.V.) of $\eta$-$C_5H_5Fe(CO)_2X$.

| X | $P^+$ | $(P-Me)^+$ | $EMe_3^+$ | D(Fe–E) | $D(Fe-E)^+$ | $D(E-X)^+$ | $D(E-Me)^{+\,a}$ ($EMe_4$) | D(E–Me) ($E-Me_4$) |
|---|---|---|---|---|---|---|---|---|
| $SiMe_3$ | $8.1_3$ | $10.4_1$ | $8.9_8$ | $1.7_4$ | $0.8_5$ | $2.2_8$ | $0.6_8$ | $3.2_9$ |
| $GeMe_3$ | $7.6_9$ | $8.3_2$ | $8.8_4$ | $1.7_9$ | $1.1_5$ | $0.6_8$ | $0.7_9$ | $3.0_0$ |
| $SnMe_3$ | $7.7_3$ | $8.0_4$ | $9.4_0$ | $2.6_0$ | $1.6_7$ | $0.3_1$ | $0.8_2$ | $2.7_8$ |
| $PbMe_3$ | $7.5_3$ | $7.9_0$ | $8.4_4$ | $1.7_9$ | $0.8_9$ | $0.3_7$ | $0.5_1$ | $2.1_2$ |
| $SnCl_3$ | $8.7_0$ | | | | | | | |
| Me | $7.7_9$ | | | | | | | |
| Cl | $7.8_5$ | | | | | | | |
| I | $7.6_0$ | | | | | | | |

[a] From ref. 26.

apparent. The data of Table I show that the $D(Si-CH_3)^+$ value is markedly higher than those of the other $D(E-CH_3)^+$; comparing the $D(E-CH_3)^+$ values now obtained with those of the $EMe_4$, it is found that (a) for the silicon derivative $D(E-CH_3)^+$ is much higher in the complex than in $SiMe_4$, and is not far (1 eV lower) from the $D(Si-CH_3)$ of tetramethylsilane; (b) for the other complexes $D(E-CH_3)^+$ is always sligthly lower than the corresponding value of the tetramethyl derivative. These results suggest that the Si atom is not involved in the ionization process ($D(Si-CH_3)$ is scarcely affected by the ionization), while for the other complexes the weakening of the $D(E-CH_3)$ by ionization suggests a strong character of E element for the last occupied molecular orbital. According to this interpretation only for the silicon derivative is an ionization from the iron *d* orbitals likely, and the ionization potential data cannot be safely used to obtain information on the possibility of $\pi$ back bonding between the central metal and the $EMe_3$ groups. It is noteworthy that in $\eta$-$C_5H_5Fe(CO)_2CH_3$, where back bonding can be excluded for the lack on the carbon atom of empty orbitals to interact with the iron atom *d* orbital, the I.P. is lower than that of the silicon derivative (if the methyl group is substituted by a t-butyl group the molecular I.P. should be even lower). This order of *d* electron binding energy, unexpected on the basis of most electronegativity scales, has been found for other series and was explained in terms of stabilization of the *d* orbitals of the central metal as a consequence of the $\pi$ bond[9,11,24]. This interpretation has been recently questioned on the basis of PES spectra of some manganese carbonyl complexes[7]. However, to explain the experimental results of the PES spectra[7] and of the bond lengths[15,16] the authors are forced to admit that the silyl group is a slightly better $\sigma$ acceptor than the germyl, and this is a much better $\sigma$ acceptor than methyl; such an order is difficult to justify, and requires further investigation. The rather high I.P. value of $\eta$-$C_5H_5Fe(CO)_2SnCl_3$ is in agreement with the strong $\pi$ acceptor ability of the $SnCl_3$ group, taking also into account the stronger electron withdrawing ability of the Cl compared to $SnCl_3$[3,25] and the lower I.P. of $\eta$-$C_5H_5Fe(CO)_2Cl$.

Appearance potential measurements of the ions $EMe_3^+$ allow the estimation of the bond dissociation energy both in the neutral molecule and in the molecular ion, provided that these ions originate from the process:

$$C_5H_5Fe(CO)_2EMe_3^+ \rightarrow EMe_3^+ + C_5H_5Fe(CO)_2 \quad (1)$$

Other possible sources of $EMe_3^+$ ions are the fragment ions $C_5H_5FeCOEMe_3^+$ and $C_5H_5FeEMe_3^+$; there are however indications that the main source of $EMe_3^+$ is the process (1): (i) the measured appearance potentials of $C_5H_5FeEMe_3^+$ (E = Si or Ge) are higher than the A.P.'s of the corresponding $EMe_3^+$; (ii) the A.P.'s of $C_5H_5FeCOEMe_3^+$ (E = Si or Ge) are slightly lower than those of $EMe_3^+$; if the $EMe_3^+$ ions derive from $C_5H_5FeCOEMe_3^+$, it would imply very low bond dissociation energies (in the range 30–60 kj/mol), which are unlikely when compared with other literature values; (iii) for the tin derivative a metastable ion corresponding to reaction (1) has been found.

The calculated D(Fe–E) and $D(Fe-E)^+$ are reported in Table I; literature values[26] have been used for the ionization potentials of the radicals $EMe_3$. Both bond dissociation energies increase from Si to Sn and decrease from Sn to Pb; this could be connected with the general greater stability of tin derivatives.

Only few and scattered data are available in the literature regarding related bond energies, so that any attempt to interprete these data may be speculative. From the available data[12,13,10] the following points emerge: (1) the bond dissociation energy between a transition metal and a IV group element increases on going from the first transition series to the second and third one; (2) different trends are found when comparing complexes with different central metals; trends as the present ones have been observed for $\eta$-$C_5H_5(CO)_3MEMe_3$ (M = Cr, Mo and W) and $Me_3ERe(CO)_5$; instead, the D(Mn–E) for $Me_3EMn(CO)_5$ is almost constant while a definite decrease can be noticed

for the $D(Mn–E)^+$ in the order Si > Ge > Sn; also for $Me_3ECo(CO)_4$, D(Ge–Co) > D(Sn–Co).

Other data clearly are needed to ascertain the influence of the central metal and of the molecular structure on the bond energies;a knowledge of these factors could give information on the relevance of $\pi$ back bonding between the central metal and the IV group elements. The extent of this $\pi$ bond should depend markedly on the nature of the ligands surrounding the central metal, a strong $\pi$ interaction being possible only when the other ligands do not compete effectively with the $EMe_3$ group for this back bonding.

The 50 eV mass spectra, presented in Table II, show the usual features of the spectra of related compounds; few points deserve some comments: (a) The Fe–E bond is cleaved even in the molecular ion while in $\eta$-$C_5H_5Fe(CO)_2GeCl_2X$[27] there is evidence that this bond is cleaved only after the loss of the two CO groups. In this fragmentation the positive charge remains on the E containing fragment, except compound (VIII), in which the increased I.P. of the $Cl_3Sn$ radical drastically lowers the probability of formation of the corresponding ion. A similar effect should hold also for the $\eta$-$C_5H_5Fe(CO)_2GeCl_2X$ compounds, where the positive charge is always found in the iron containing fragment. (b) $(C_5H_5E)^+$ ions are well represented; this ion can arise from different precusors; however, for compound III it should be formed from the molecular ion, since its A.P. is very low (8.18 eV); this confirms the hypothesis[27] of a low activation energy (0.45 eV for III) for its formation. (c) Other fragmentation reactions involving group migration are evident only for VIII, where the ion $C_5H_5Fe(CO)_2Cl^+$ was found, which, as shown by the observed metastable ion, originates from the molecular ion.

These mass spectra indicate very clearly that the activation energies of the competing reactions and the ionic fragment intensities are tightly linked, as previously pointed out in organic compounds[28].

The more important competitive fragmentations of the molecular ion are

$$P^+ \rightarrow (P–CH_3)^+ \quad (a)$$
$$P^+ \rightarrow (P–CO)^+ \quad (b)$$
$$P^+ \rightarrow (EMe_3)^+ \quad (c)$$

Going down along the IV group, the relative intensity of $(P–CH_3)^+$ increases while that of $(P–CO)^+$ decreases: for the ions $(EMe_3)^+$ the lowest relative intensity is found for E = Sn. The trend of the relative abundancies of the ions $(EMe_3)^+$ is strictly correlated with the approximate activation energies (A.P. $(EMe_3)^+$–I.P.) for their formation.* The fragmentation reactions (a) and (b) strongly compete each other; the activation energy for (b) should not be very sensitive to the variation of E, while that for (a) decreases markedly from Si to Pb. As a consequence, in I and II the loss of a CO group is the lowest activation energy process, while in III and IV the lowest activation energy process is the methyl loss. Accordingly, the relative abundance of $(P–CH_3)^+$ increases, and that for $(P–CO)^+$ decreases from Si to Pb**.

TABLE II. Ion Abundances, $\eta$-$C_5H_5Fe(CO)_2EMe_3$, at 50 eV.

| Ion/E | Si | Ge | Sn | Pb |
|---|---|---|---|---|
| P | 20 | 18 | 12 | 1 |
| P–Me | 3 | 29 | 61 | 100 |
| P–3Me | – | – | – | 21 |
| P–CO | 21 | 17 | <0.1 | – |
| P–(CO + Me) | 8.5 | 7 | 5 | |
| P–2CO | 43 | 18 | 2 | – |
| P–(2CO + Me) | 22 | 53 | 37 | 11 |
| P–(2CO + 2Me) | – | – | – | 33 |
| P–(2CO + 3Me) | – | – | – | 10 |
| $EMe_3$ | 100 | 100 | 17 | 76 |
| $EC_5H_5$ | 18 | 62 | 100 | 100 |
| $EMe_2$ | – | – | – | 15 |
| EMe | – | – | 13 | – |

* The correlation between $\frac{I(EMe_3)^+}{I_{tot}}$ and the activation energy ($I_{(EMe_3)})^+$ is the sum of the intensity of the ions $(EMe_3)^+$ and $(EMe_n)^+$, $I_{tot}$ is the total ionization current) is linear; the significance of this linearity, in view of the competition of the three above fragmentations, is questionable.

** The relative abundance of ions obtained by CO losses is further lowered by the possible secondary methyl loss.

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