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MASS SPECTROMETRIC STUDY OF COMPOUNDS CONTAINING TRANSITION METAL TO MAIN GROUP IV ELEMENT BONDS: BOND DISSOCIATION ENERGY DATA FOR SOME (Fe—M) BONDS

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Summary

Ionisation and appearance potential data from compounds containing Mn, Fe, and Co to Si or Sn bonds have been measured. Neutral and ionic bond dissociation energies have been calculated and compared with respect to the effect of the metals and ligands. Trends in metal—metal bond dissociation energies from $Cp(CO)_2FeSnX_3$ (X = Me, Ph, Cl) are discussed with regard to results from X-ray diffraction and Mössbaur spectroscopic experiments.

Introduction

A number of papers have appeared [1—6] in which metal—metal bond dissociation energies $D(M^1—M^2)$ have been calculated for compounds with transition metal to Main Group IV metal bonds, $L_nM^1M^2X_3$, using measured appearance potentials (*AP*) of $M^2X_3^+$ ions (X = Me) and literature values of ionisation potentials (*IP*) of Me_3M^2 radicals [7]. Other workers [8—11] have estimated $D(M^1—M^2)$ values from *AP*s of ions other than $M^2X_3^+$ and appropriate thermochemical data, though this less direct method may be subject to greater error. The present study follows on from the recent investigation of the effect of ligands, L, on D(Mo—Sn) in $Cp_2Mo(L)SnMe_3$, and M^1, M^2, and X on $D(M^1—M^2)$ in several compounds of Mo, W, Ta, Mn, Re and Co [1], and includes the compounds of Fe (Ia—Ie).

$Cp(CO)(L)FeMX_3$

(Ia) L = CO, M = Si, X = Me
(Ib) L = PPh_3, M = Si, X = Me
(Ic) L = CO, M = Sn, X = Me
(Id) L = CO, M = Sn, X = Ph
(Ie) L = CO, M = Sn, X = Cl

$(CO)_4CoSnMe_3$
(II)

$(CO)_5MnSiMe_3$
(III)

Experimental

All compounds used in this work have been reported previously [1,12].

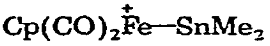
Mass spectra were recorded on an AEI MS9 mass spectrometer at 70 eV with an accelerating voltage of 8000 V and source temperature of between 60—100°C above ambient. Samples were introduced either by the direct insertion probe or by sublimation directly into the source from a breakseal attached via an all glass system. *IP* and *AP* data were collected as previously described [7] and originally processed using the semi-logarithmic plot method. However, the more recent method of Johnstone and McMaster, [13] was preferred for the reasons discussed in detail elsewhere [14] and the results were recalculated. During this time some similar work was published [4,6] using the extrapolated voltage difference method for calculation of *AP*s.

Discussion

Mass spectral fragmentation. Compounds Ia [15], Ic [6], Id [16] Ie [17], II and III [1] have been discussed previously and the present work agreed reasonably well. The spectrum obtained for Ia agreed better with that reported by King et al. [15] than Innorta et al. [6]. The more detailed spectrum of Ic revealed, in 1—2% of the total ion current of metal containing ions, $CpFeSnCH_n^+$ ($n = 2, 3$) $CpFeSn^+$, $FeSn^+$, and $CpFe^+$ not previously mentioned [6].

The phosphine complex Ib showed a parent molecular ion as the second most abundant ion. The base peak was $CpFePPh_3^+$ and $FePPh_3^+$ was also very abundant. Fragmentation by initial loss of $Me^{\cdot}$, CH_4, or CO and subsequently $H^{\cdot}$ and H_2, or loss of $H^{\cdot}$ and H_2 from $CpFePPh_n^+$ ($n = 2, 3$) and $FePPh_3^+$ provided notably abundant ions. Rearranged ions $C_6H_nFe^+$ ($n = 4$—6), $C_6H_mSi^+$ ($m = 7, 8$) were observed. The Me_3Si^+ ion and expected fragment ions [7] were abundant. Metastable peaks corresponding to CO loss from the parent molecular ion, and H_2 loss from $CpFePPh_n^+$ ($n = 2, 3$) were identified.

An interesting feature in the spectra of Ia—Ie, $(CO)_4CoSnMe_3$, and $(CO)_5MnSiMe_3$ which has also been observed in several related compounds [2—6] and $Cp_2Mo(L)SnMe_3$ derivatives [1] was the ion formed by loss of one X radical. In a number of cases this ion is highly abundant, especially for M^2 = Sn or Pb, X = Me where it may be the most abundant of metal containing ions e.g. from $(CO)_5MnSnClMe_2$ and $(CO)_5ReSnMe_3$ [1]. The stability of these ions may be enhanced if the Me_2M^2 group bonds as a stannylene ligand and the transition metal retains an 18 electron valence shell, e.g. IV. An alternative stable configuration would be that with the positive charge retained at a tricoordinate M^2 centre, e.g. V. It has been generally found that ions containing the Me_2M^2 group such as IV and V became more abundant as M^2 changes from Si through to Pb [6], reflecting perhaps the relative compatibility or orbitals of M^1 and M^2, and the ability of the Me_2M^2 group to stabilise a positive charge. This is consistent with the suggestion of Innorta et al. [6] that the initial ionisation of $Cp(CO)_2FeM^2Me_3$



$Cp(CO)_2\overset{+}{Fe}—SnMe_2$

(IV)

$Cp(CO)_2Fe—\overset{+}{Sn}Me_2$

(V)

may involve a Fe—M^2 σ-bonding level for M^2 = Sn or Pb rather than the central metal d orbitals as in the case of Si.

As far as the mass spectra are concerned, of course, relative ionic bond dissociation energies including $D(M^2—Me)^+$ and $D(L—M^1)^+$ are important in determining fragmentation patterns. It is seen from Table 1 that $D(M^2—Me)^+$ is much greater for Si—Me bonds than Sn—Me in $Cp(CO)_2FeM^2Me_3$ compounds. Consideration of the other data in Table 1 such as the larger value of $D(Sn—Me)^+$ compared to $D(Co—CO)^+$ from II provides some explanation of the observed fragmentation patterns [1,3,6].

Loss of CO (or L) is important in all spectra of compounds such as Ia—Ie, II and III. Values for $D(M^1—CO)^+$ eV from Ia (0.66), Ib (0.73), and II (0.39) may be compared with corresponding values of 1.34 from $Cp(CO)_3CrGeMe_3$ [2], 0.88 from $Cr(CO)_6$ [18] and 0.57 [19], or 1.47 [20] for $Fe(CO)_5$. It is noteworthy that the energy required for cleavage of a Ph_3P group (0.57 eV) from the parent molecular ion of Ib is slightly lower than for the cleavage of CO (0.73 eV) although the overall abundance of $FePPh_3$-containing ions is much greater than ions containing the FeCO-group.

Loss of the second CO from $L_{n-1}M^1M^2Me_3$ requires 1.42 eV from Ia and 0.81 eV from II compared to values (eV) of 0.69 [19], and 1.28 [19], or 0.3 [20] from $Cr(CO)_6$ and $Fe(CO)_5$ respectively.

Ionisation and appearance potentials of $M^2X_3^+$ *ions.* Values of *IP*s and *AP*s of $M^2X_3^+$ ions from Ia—Ie are given in Table 2, together with previous results by Innorta et al. [6] and Clark and Rake [5]. There is reasonable agreement between the data bearing in mind the different methods used to interpret ionisation efficiency curves.

The marked decrease by 1.02 eV of the *IP* of Ia on replacing one CO by Ph_3P finds analogy with previous results (eV) for $Cp(CO)_3Mn$ (8.12) and $Cp(CO)_2(PPh_3)$-Mn (6.93) [21], and $Fe(CO)_5$ (7.96) [20] and $Fe(CO)_4(P\text{-}n\text{-}Bu_3)$ (7.29) [22]. This has been interpreted as showing an increased charge density at the central metal atom in the phosphine complexes caused by the better σ-donor ability of the phosphine compared to CO [22]. The increased $D(Fe—Si)$ in Ib compared to Ia can also be rationalised in terms of the effects of σ-donor and π-acceptor

TABLE 1

APPEARANCE POTENTIALS OF FRAGMENT IONS FORMED BY LOSS OF L OR Me GROUPS FROM $L_nM^1M^2Me_3$

Compound	Ion	*AP* ±0.1 (eV)	$D(\text{parent—X})^+$ (eV)
$(CO)_5MnSiMe_3$	$(CO)_5MnSiMe_2^+$	10.75	2.23
$Cp(CO)_2FeSiMe_3$	$Cp(CO)_2FeSiMe_2^+$	10.41 [a]	2.28
	$Cp(CO)FeSiMe_3^+$	8.54	0.66
	$CpFeSiMe_3^+$	9.96	1.42 [b]
$Cp(CO)(PPh_3)FeSiMe_3$	$Cp(PPh_3)FeSiMe_3^+$	7.59	0.73
	$Cp(CO)FeSiMe_3^+$	7.43	0.57
$Cp(CO)_2FeSnMe_3$	$Cp(CO)_2FeSnMe_2^+$	8.04 [a]	0.31
$(CO)_4CoSnMe_3$	$(CO)_4CoSnMe_2^+$	10.12	1.91
	$(CO)_3CoSnMe_3^+$	8.60	0.39
	$(CO)_2CoSnMe_3^+$	9.41	0.81 [b]

[a] From ref. 6. [b] Value for $D([\text{parent—CO}]—CO)^+$.

TABLE 2

IONISATION AND APPEARANCE POTENTIALS, AND BOND DISSOCIATION ENERGIES (eV) FROM Ia—Ie

Compound	*IP* ± 0.1 (eV)		*AP* ± 0.1 (eV)		*D*(M^1—M^2) (eV)	*D*(M^1—M^2)$^+$ (eV)	*D*(M^2—X) [e] (eV)
$Cp(CO)_2FeSiMe_3$	7.88 [c]	8.13 [b]	9.22 [a]	8.98 [b]	1.97 [d]	1.34 [a]	3.21
$Cp(CO)(PPh_3)FeSiMe_3$	6.86 [a]	—	9.48 [a]	—	2.23 [d]	2.62 [a]	3.21
$Cp(CO)_2FeSnMe_3$	7.77 [a]	7.73 [b]	9.12 [a]	9.40 [b]	2.31 [d]	1.35 [a]	2.84
$Cp(CO)_2FeSnPh_3$	—	—	8.87 [a]	9.16 [c]	2.58 [e]	—	2.95
$Cp(CO)_2FeSnCl_3$	—	8.70 [b]	12.06 [a]	—	3.06 [e]	—	3.17

[a] This work. [b] From ref. 6. [c] From ref. 5; note however, that the value of *AP* Ph_3Sn^+ given does not agree with the reported *D*(Fe—Sn) = 54 ± 9 kcal mol^{-1} using the estimated *IP* $Ph_3Sn^{\cdot}$ = 6.85 eV. [d] Using *IP* $Me_3M^{\cdot}$ from ref. 7. [e] *IP* $Ph_3Sn^{\cdot}$ = 6.29 eV; *IP* $Cl_3Sn^{\cdot}$ estimated at 9.0 eV; *D*(M^2—X) from ref. 23.

ability of PPh_3 compared to CO in these complexes. Similar conclusions have been drawn from the study of *D*(Mo—Sn) in $(Cp)_2Mo(L)SnMe_3$, although the trend in these complexes was less marked [1].

An increase in *D*(M^1—M^2) on changing M^2 from Si through Ge to Sn has been found in compounds of Cr, Mo, W [2], Re and Co [4]. However, in the case of Mn it appears that *D*(Mn—Si) > *D*(Mn—Sn) [1,3,6], and the position of *D*(Mn—Ge) [3,6] is ambiguous. In the present study *D*(Fe—Si) < *D*(Fe—Sn) and this is in agreement with a previous result [6].

The effect on *D*(Fe—Sn) of changing X from Me through Ph to Cl is to increase the bond dissociation energies in that order, Table 2. An increase in *D*(M^1—Sn) of about 0.1 eV with M^1 = Mn or Re has been reported on changing X from Me to Ph [1]. A much larger increase, 0.3 eV, was found in this study with a further 0.5 eV increase on changing Ph to Cl. In the latter case it should be remembered that the *IP* $Cl_3Sn^{\cdot}$ (9.0 eV) was estimated [23] and exceeds an estimated value of *IP* $CpFe^{\cdot}(CO)_2$ (7.7 eV) [5]. Therefore any excess energy produced in the fragmentation of the parent molecular ion of Ie will be more likely to be transferred to Cl_3Sn^+, consequently giving an anomalously high *AP*. Unfortunately the *AP* of $CpFe(CO)_2^+$ could not be measured since other species such as $CpFe(CO)_2Cl$ were contributing to its abundance. However, results from $(CO)_5MnSnMe_2X$ (X = Me or Cl) [1], also show an increase in *D*(Mn—Sn) on changing X = Me to Cl, and it seems probable that at least a similar increase would occur from Ic to Ie. Metal—metal bond distances in Id and Ie, and some related Mn compounds are given in Table 3. They correspond closely to the bond dissociation energies. It is also of note that the (Mn—Sn) bond length decreases on replacing one CO group in $(CO)_5MnSnMe_3$ by PPh_3 paralleling the increased *D*(Fe—Si) in Ib compared to Ia discussed above.

Results from Mössbauer spectroscopy indicate that $CpFe(CO)_2$ is a better σ-donor and/or weaker π-acceptor than $Mn(CO)_5$ [24]. From the differences in *D*(M^1—Sn), Table 3, it would appear that the predominance of σ-inductive effects over any π-bonding effects is greater in the Fe—Sn compounds than in Mn—Sn compounds.

Finally, it is noted that *D*(Fe—M^2) reported, Table 2, are less than the corresponding M^2—X values.

TABLE 3

BOND DISTANCES AND DISSOCIATION ENERGIES FROM $L_nM^1M^2X_3$

Compound	$d(M^1—M^2)$ (pm)	$D(M^1—M^2)$ (eV)
$(CO)_5MnSnMe_3$	267 [25]	2.04
$(CO)_5MnSnPh_3$	267 [26]	2.09
$(CO)_5MnSnCl_3$	259 [27]	—
$(CO)_5MnSnMe_2Cl$	—	2.24 [1]
trans-$(CO)_4(PPh_3)MnSnPh_3$	263 [28]	—
$Cp(CO)_2FeSnMe_3$	—	2.30
$Cp(CO)_2FeSnPh_3$	254 [29]	2.58
$Cp(CO)_2FeSnCl_3$	247 [30]	3.06

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