

Electron Impact Study of Compounds with Main Group IV Element to Transition Metal Bonds

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The mass spectra of several compounds with bonds between transition metals and main group IV elements are discussed. Ionization potentials (*I*) and appearance potentials of $[M'X_3]^+$ ions (*A*) were measured and bond dissociation energies $D(M-M')$ calculated. Values of $D(Mo-Sn)$ from $(\eta-C_5H_5)_2Mo(L)SnMe_3$ with $L = H, Cl, Br, I,$ or $-C(CO_2Me):CH(CO_2Me)$ were all about 2.5 ± 0.13 eV. Replacement of molybdenum in $(\eta-C_5H_5)_2M(H)SnMe_3$ by tungsten resulted in an increase in $D(M-Sn)$. The related tantalum compound $(\eta-C_5H_5)_2Ta(H)_2SnMe_3$ had a value slightly lower than the tungsten com-

pound. Complexes $(CO)_5MnM'X_3$ showed the sequence of decreasing bond strengths for $M'X_3$ as $SiMe_3 \geq SnClMe_2 > SnPh_3 \approx SnMe_3$. The corresponding rhenium complexes with $M'X_3$ as $SnPh_3$ and $SnMe_3$ had considerably higher $D(M-M')$ values than the manganese derivatives. The $D(Co-Sn)$ in $(CO)_4CoSnMe_3$ was very similar to the $D(Mn-Sn)$ in $(CO)_5MnSnMe_3$. These observations are discussed with reference to reported structural data where available.

Introduction

Continuing the investigation of compounds containing bonds between main group elements and

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TABLE I. Ionisation Potentials (*I*), Appearance Potentials (*A*) and Bond Dissociation Energies $D(M-M')$, eV.

Compound	(<i>I</i>)	(<i>A</i>)	$D(M-M')$ ^a	
1	$(\eta-C_5H_5)_2Mo(H)(SnMe_3)$	6.48 ± 0.11	9.19 ± 0.15	2.38
2	$(\eta-C_5H_5)_2Mo(Cl)(SnMe_3)$	6.55 ± 0.12	9.30 ± 0.14	2.49
3	$(\eta-C_5H_5)_2Mo(Br)(SnMe_3)$	6.60 ± 0.13	9.36 ± 0.12	2.55
4	$(\eta-C_5H_5)_2Mo(I)(SnMe_3)$	6.51 ± 0.09	9.42 ± 0.15	2.61
5	$(\eta-C_5H_5)_2Mo(vy)(SnMe_3)^b$	6.80 ± 0.13	9.44 ± 0.13	2.63
6	$(\eta-C_5H_5)_2W(H)(SnMe_3)$	6.18 ± 0.11	9.73 ± 0.12	2.92
7	$(\eta-C_5H_5)_2Ta(H)_2(SnMe_3)$	6.77 ± 0.12	9.46 ± 0.11	2.65
8	$(CO)_5MnSiMe_3^c$	8.52 ± 0.10	9.81 ± 0.11	2.56
9	$(CO)_5MnSnMe_3$	8.24 ± 0.11	8.85 ± 0.13	2.04
10	$(CO)_5MnSnClMe_2$	8.21 ± 0.12	9.74 ± 0.12	2.2^e
11	$(CO)_5MnSnPh_3$	7.94 ± 0.11	8.38 ± 0.15	2.09^e
12	$(CO)_5ReSnMe_3$	8.30 ± 0.10	9.59 ± 0.13	2.78
13	$(CO)_5ReSnPh_3$	7.98 ± 0.09	9.16 ± 0.11	2.87^e
14	$(CO)_4CoSnMe_3^d$	8.21 ± 0.11	9.06 ± 0.15	2.25

^aCalculated using $I Me_3M\cdot$ in ref. 13. ^b(vy) is $-C(CO_2Me)=CH(CO_2Me)$. ^cFrom photoelectron spectrum $I = 8.47$ eV.

^dFrom photoelectron spectrum $I = 8.25$ eV. ^eCalculated using $I Me_2ClSn\cdot = 7.5 \pm 0.2$ eV (estimated) and $I Ph_3Sn\cdot = 6.29 \pm 0.16$ eV in ref. 15.

TABLE II. Abundance of Ions from Compounds (2)–(4) ($\eta\text{-C}_5\text{H}_5$)₂Mo(L)SnMe₃ and Me₃SnL [19] (L = Cl, Br or I) at $m/z \geq 92$.^a

Composition of Ion	(2)	Me ₃ SnCl	(3)	Me ₃ SnBr	(4)	Me ₃ SnI
	L = Cl		L = Br		L = I	
(C ₅ H ₅) ₂ MoLSnMe ₃	0.7	–	3.5	–	1.4	–
(C ₅ H ₅) ₂ MoLSnMe ₂	1.7	–	4.2	–	1.5	–
(C ₅ H ₅) ₂ MoSnMe ₃	0.6	–	1.4	–	1.1	–
(C ₅ H ₅) ₂ MoSnMe ₂	1.4	–	1.1	–	3.4	–
(C ₅ H ₅) ₂ MoSnMe	3.0	–	–	–	0.6	–
(C ₅ H ₅) ₂ MoSn	0.5	–	–	–	2.1	–
(C ₅ H ₅) ₂ MoL	2.5	–	6.1	–	1.5	–
(C ₅ H ₅) ₂ MoMe	4.1	–	4.1	–	2.1	–
(C ₅ H ₅) ₂ Mo	16.6	–	27.0	–	19.4	–
(C ₅ H ₅)MoC ₃ H ₃ L	1.8	–	–	–	–	–
(C ₅ H ₅)MoC ₃ H ₃	4.6	–	3.3	–	3.0	–
Mo	0.5	–	0.8	–	0.7	–
Me ₃ SnL	5.7	–	1.6	1.6	1.1	2.8
Me ₂ SnL	10.7	24.9	16.4	21.0	2.8	11.3
Me ₃ Sn	14.3	10.9	8.9	4.8	35.6	18.3
MeSnL	10.3	4.0	4.1	4.1	1.3	3.5
Me ₂ Sn	4.8	3.6	1.8	2.3	6.0	1.6
LSn	4.4	7.5	4.1	2.7	1.1	7.1
MeSn	6.1	5.3	4.0	4.2	8.2	8.5
CH ₂ Sn	0.5	1.5	1.0	0.8	1.0	2.0
HSn	1.9	0.9	1.0	0.8	1.2	1.3
Sn	2.7	3.4	1.8	2.6	2.7	4.5
C ₅ H ₅ Sn	0.7	–	3.8	–	2.2	–

^aIons with intensity >0.5% of the total ion current are represented.

transition metals [1], L_nM–M'X₃, it was decided to study the effects of changing groups L, X and M and M' on bond dissociation energies D(M–M'). Previous work on compounds of main group IV elements bonded to transition metals Mo, W [2], Mn [1, 3–5], Re [6], Fe [1, 4, 7], and Co [1, 6, 8–10] has been reported. Compounds (1)–(14) were used in this study, Table I.

Experimental

The preparations of all the compounds used in this study have been reported previously; (1)–(7) [11], (8)–(14) [4, 5, 12].

Samples contained in 'breakseal' tubes were directly attached to the AEI MS9 mass spectrometer via an all glass inlet system. Steady ion currents were obtained by direct sublimation into the source. For some samples, gentle heating (40–60 °C) with a hot air blower was required to obtain sufficient ion source pressures; with others the 'breakseal' tube had to be cooled in low temperature (–45–0 °C) baths.

Spectra were recorded at 70 eV with an accelerating voltage of 8000 V and source temperature of between 70–100 °C above ambient. *I* and *A* data were recorded as previously described [2, 13] and interpreted with the critical slope curve matching (CSCM) method [14].

The He(I) photoelectron spectra of (8) and (14) were recorded by Dr. G. J. Sharp of University of Sussex using as Perkin-Elmer PS 16 instrument. The resolution (full width at half height) was of the order of 35 meV, as measured on the argon doublet.

Results and Discussion

Mass Spectra

As expected by comparison with related compounds, the most abundant ions in the spectra of (1)–(14) were due to loss of L, X or M'X₃ groups and ions derived from M'X₃ species [1–10, 16]. Few metastable peaks were recorded. Monoisotopic spectra of ions with intensity ≥ 0.5 per cent of the total ion current from compounds (2)–(4) are given

in Table II, and Table IV lists the abundances of M-Sn containing ions from (10) and (12)-(14) which are produced in $\geq 1.0\%$ of the ion current of such ions. Only novel features in the spectra of (1)-(14) will be discussed here.

Compounds (1)-(7)

All showed weak to moderately abundant parent molecular (pm) ions. Base peaks were due to $[M(C_5H_5)_2]^+$ in every case except (4) which gave $[SnMe_3]^+$. Compound (5) showed $[Mo(C_5H_5)_2(vy)]^+$, $[Mo(C_5H_5)_2(vy - OMe)]^+$ and $[Mo(C_5H_5)_2(vy - CO_2Me)]^+$ in similar abundances, exceeded only by the base peak and $[SnMe_3]^+$.

Initial loss of a methyl group gave abundant $[pm-Me]^+$ ions from (1)-(5) and (7); from (6) this ion had comparable intensity to the base peak. The stability of these ions may be enhanced if they contain either an eighteen valence electron, positively charged transition metal centre with $SnMe_2$ bonding as a stannylene ligand, or alternatively, if the positive charge was located at a tricoordinate tin atom as in $[SnMe_2Y]^+$, with Y being the eighteen valence electron transition metal centred $M(C_5H_5)_2(L)$ -group. A general feature in the spectra of (1)-(12) is the predominance of ions of the type $[SnX_2Y]^+$ over their $[SnX_3Y]^+$ and $[SnXY]^+$ counterparts. The stability of tricoordinate tin-centred ions is well known [16].

The rearranged ion $[SnC_5H_5]^+$ which is quite common from other $M(C_5H_5)(SnX_3)$ -containing compounds was observed in moderate abundance from (1)-(7). Another rearranged ion $[M(C_5H_5)_2(CH_3)]^+$ was found in reasonable abundance from all compounds (1)-(7), and from (7) $[TaCH_3]^+$ was also observed. Transfer of an alkyl group to a transition metal was not previously found from $\eta-C_5H_5M(CO)_3(M'Me_3)$ [2], although both hydride, e.g. from $\eta-C_5H_5Mo(CO)_2(GeH_3)(PPh_3)$ [17], and phenyl group transfer, e.g. from $\eta-C_5H_5Fe(CO)_2(SnPh_3)$ [18], have been reported in the spectra of related compounds.

Other rearranged ions $[Me_nSnL]^+$ ($n = 0-3$) were particularly noticeable from (2)-(4). The possibility that these ions were formed via decomposition of (1)-(7) in the mass spectrometer prior to ionisation caused us to compare the relative abundances of relevant ions from (1)-(7) and the parent Me_3SnL compounds. In all cases the abundances of the fragments observed from (1)-(7) were significantly dissimilar to those from the parent Me_3SnL compound [19]. For example, the $[SnMe_3]^+$ ion was always found in greater abundance from (2)-(4) being 1.3, 1.9 and 2.0 times as abundant for $L = Cl, Br$ and I respectively, Table II. This suggests that a significant proportion of $[SnMe_3]^+$ ions were produced from (1)-(7) directly which has obvious relevance to the appearance potential measurements discussed below.

Metastable ions were identified for the following reactions. Loss of $SnMe_2$ from $[W(C_5H_5)_2(H)(SnMe_2)]^+$ (calc. for ^{184}W and ^{120}Sn isotopes 213.4, found 213.7); loss of $HsnMe_2$ from $[Ta(C_5H_5)_2(H)_2(SnMe_2)]^+$ (calc. for ^{181}Ta and ^{120}Sn isotopes 223.7, found 223.8); loss of H from $[Ta(C_5H_5)_2(H)(Me)]^+$ (calc. for ^{181}Ta isotope 323.0, found 323.0).

Compounds (8)-(14)

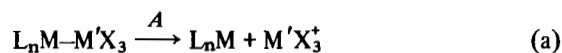
Only (10) and (13) have not been reported previously. The spectrum of the other compounds were in good agreement with published data [3, 4, 6]. The majority of the ions were of the types $[M(CO)_n(M'X_m)]^+$ with ($n = 0-5$ for $M = Mn$ or Re and $n = 0-4$ for $M = Co$; $m = 0-3$) or were derived from the $M'X_3$ group. Reasonably abundant parent molecular ions were observed for (10) and (13), and the base peaks were $[SnMe]^+$ and $[SnPh_3]^+$ respectively.

The most abundant ion containing both M and M' from (10) and (12) was $[pm-Me]^+$. This type of ion also contributed significantly to the spectrum of (9), as did $[pm-Ph]^+$ from (13). Its stability may be expected for similar reasons to those discussed above for the related species from (1)-(7). It may be noted here that the compound $[(CO)_5MnSnMe_2]BF_4$ has been isolated [20]. As with the previously reported $(CO)_5MnM'X_2Y$ ($M' = Ge$ or Sn) [3], a larger proportion of the ion current was carried by $[Mn(CO)_n(M'XY)]^+$ compared to $[Mn(CO)_n(M'X_2Y)]^+$ ions from (10), (12) and (13), but this was not the case for (8) [3], (11) or (14) which showed the reverse.

Rearrangement ions with X transferred to Mn were strong features in the spectra of (9)-(11), e.g. from (10) ions such as $[Mn(CO)_nCl]^+$ and $[MnCH_3]^+$ were observed. Such transfers were negligible in the spectra of (12)-(14).

Ionisation and Appearance Potential Measurements; $D(M-M')$ Values

In all cases, the reaction producing $[M'X_3]^+$ with the lowest A was assumed to be (a), with the usual reservations about such an assumption [2, 16]. Previously some evidence has been produced from



the compounds $\eta-C_5H_5M(CO)_3M'Me_3$ [2], and $(CO)_5MnM'Me_3$ [3]. We are confident that the same situation applies in our study except perhaps in compound (4) discussed below. Values of I , A , and $D(M-M')$ are given in Table I.

Compounds (1)-(7)

The relatively limited range of I 's (6.6 ± 0.2 eV) and A 's (9.35 ± 0.2 eV) is noteworthy from (1)-(5). These correspond to values of $D(Mo-Sn)$ in the range 230 to 254 $kJ\ mol^{-1}$. Ionic bond dissociation energies

$D(\text{Mo-Sn})^*$ are slightly higher since I 's are below I Me_3Sn^* (6.81 eV) [13]. Although a variation of the bond dissociation energies with L is discernable, the values for $D(\text{Mo-Sn})$ are all within twice the standard deviations, *i.e.* 2.5 ± 0.15 eV. It is therefore difficult to draw any firm conclusions about the effect of L other than it does not appear to be very significant. There does not appear to be any obvious correlations between $D(\text{Mo-Sn})$ in (1)–(5) and other reported spectroscopic data such as ^{119}Sn n.m.r. chemical shifts [21]. One may compare the present results with the value of $D(\text{Mo-Sn})$ of 293 kJ mol^{-1} (using I $\text{Me}_3\text{Sn}^* = 6.81$ eV) from $\eta\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{SnMe}_3$ [2]. This earlier value was, however, calculated via the semi-log plot method.

The observation of ions derived from Me_3SnL in the spectra of (1)–(4), especially for L = halogen, was interesting particularly in the light of the evidence from the X-ray structural analyses of $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{Br})\text{SnBr}_3$ [22], and $(\text{bipy})(\text{CO})_3\text{Mo}(\text{Cl})\text{SnMeCl}_2$ [23], showing weak (L)---SnX₃ interactions. Although no evidence for a direct reductive elimination of Me_3SnL was found in the chemistry of $(\eta\text{-C}_5\text{H}_5)_2\text{M}(\text{L})\text{SnMe}_3$ [11], it is possible that reactions giving Me_3SnL or $[\text{Me}_3\text{SnL}]^\ddagger$ could occur in the mass spectrometer. A comparison of $D(\text{Mo-Sn})$ values from (1)–(4), Table I, with $D(\text{Me}_3\text{-Sn-L})$ {kJ mol⁻¹, L = H(146) [24], Cl(392) [15], Br(318) [24] or 380 [25]}, I(259) [24] or 322 [25]}, suggests that Mo-Sn and not Sn-L bond dissociation energies were being measured in every case except perhaps L = I.

The results from (1) and (6) show the W-Sn bond (282 kJ mol^{-1}) to be stronger than the corresponding Mo-Sn bond (230 kJ mol^{-1}). This sequence was also found for $(\eta\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{SnMe}_3$ compounds [2].

The $D(\text{W-Sn})$ was also stronger than $D(\text{Ta-Sn})$ in $(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{H})_2\text{SnMe}_3$ (256 kJ mol^{-1}). Although it is not possible to assess the relative importance of electronic effects with W(d²) and Ta(d⁰), and steric effects, the experimental results do not appear too surprising.

Compounds (8)–(14)

Values of $D(\text{M-M}')$ for several of these compounds have been published previously. Results reported for $D(\text{Mn-Si})$ from (8), 2.47 ± 0.3 eV [4] and 2.64 ± 0.1 eV [3], are in agreement with the present work (2.56 ± 0.11 eV) and a value 2.37 ± 0.3 eV [4] for $D(\text{Mn-Sn})$ from (9) is comparable with 2.04 ± 0.13 eV but another value [3] of 2.51 ± 0.1 eV is higher.

However, more significant differences are apparent from (11) 2.71 ± 0.24 eV [4] compared to 2.09 ± 0.15 eV, (12) 3.7 ± 0.1 eV [6] compared to 2.78 ± 0.13 eV, and (14) 2.8 ± 0.1 eV [6] compared to 2.25 ± 0.15 eV. It is difficult to understand why there are

TABLE III. Single Bond Covalent (r) Radii of M' in M'X₃ and M in (CO)₅M.

Species	M or M'	r(pm)	Ref.
Me_3Si	Si	117	32
$(\text{Me}_3\text{Si})_3\text{Si}$	Si	118	33
Me_3Sn	Sn	138	34
Ph_3Sn	Sn	138	35
$(\text{CO})_5\text{Mn}$	Mn	138	31
$(\text{CO})_5\text{Re}$	Re	151	31

such large discrepancies in the last three cases. Some difference would be expected since the previous figures were calculated using the extrapolated voltage difference method whilst the present work used the more recent critical slope curve matching (CSCM) method of Johnstone and McMaster [14]. This method was preferred for the reasons discussed elsewhere [26] and because I values of (8) and (14) obtained with it were in good agreement with photoelectron spectroscopic results, Table I.

Comparison of $D(\text{M-Sn})$ from (9) 197 kJ mol^{-1} and (11) 201 kJ mol^{-1} and with $D(\text{Re-Sn})$ from (12) 269 kJ mol^{-1} and (13) 276 kJ mol^{-1} suggests that the strengthening of the M-Sn bond which occurs is not greatly affected by changing R from Me to Ph. Since there are bond length data $d(\text{M-M}')$ available for $(\text{CO})_5\text{M-M}'\text{X}_3$ compounds (M = Mn or Re, M'X₃ = SiMe₃ [27a, b], Si(SiMe₃)₃ [28a, b] and SnPh₃ [29a, b]), and $(\text{CO})_5\text{Mn-SnMe}_3$ [30], it was decided to attempt to correlate the bond length and bond strength data. The single bond covalent radii of M' in M'X₃ species and M in (CO)₅M-species are given in Table III. The choice of radii for Mn and Re is problematic [28a, 31] and the values suggested by Birykov and Struchkov have been used [31]. In every case the $d(\text{M-M}')$ values are less than the sum of the corresponding covalent radii. Expressed as a percentage contraction (δ) from the sum of the covalent radii, the respective values are $\delta(\text{Mn-Si})$ 2.0%, $\delta(\text{Mn-Sn})$ 3.3%, $\delta(\text{Re-Si})$ 3.0%, and $\delta(\text{Re-Sn})$ 52%. While this series appears consistent with the stronger $D(\text{Re-Sn})$ compared to $D(\text{Mn-Sn})$ it is not possible to conclude if the difference of $\delta(\text{Re-Sn}) - \delta(\text{Mn-Sn})$ is equivalent to a difference of $D(\text{Re-Sn}) - D(\text{Mn-Sn})$ of 0.8 eV, Table I, or 1.2 eV [6]. Further, any attempt to correlate the $\delta(\text{M-M}')$ values with corresponding increases in bond strengths is frustrated at present by the lack of value of $D(\text{Re-Si})$ and two different values of $D(\text{Mn-Mn})$ [16]. An alternative approach circumventing the choice of the single covalent radii of Mn and Re is to refer to the difference $\Delta\{d(\text{Re-M}'\text{X}_3) - d(\text{Mn-M}'\text{X}_3)\}$, (for M'X₃ = SiMe₃ [27], Si(SiMe₃)₃ [28], GePh₃ [29b, 31], and SnPh₃ [29]). The values of Δ are 10, 11, 9 and 7 pm respectively, again suggestive

TABLE IV. Abundance of M-Sn Containing Ions from Compounds (10) and (12) to (14).

Composition of Ion	(10)	(12)	(13)	(14)
(CO) ₅ MnSnX ₂ Y	5.4	1.6	2.6	—
(CO) ₅ MnSnXY	16.8	33.6	16.6	—
(CO) ₅ MnSnX ₂	5.0	—	—	—
(CO) ₅ MnSnX	—	—	12.7	—
(CO) ₄ MnSnX ₂ Y	9.4	—	—	4.7
(CO) ₄ MnSnXY	5.3	—	—	—
(CO) ₄ MnSnX ₂	1.2	6.1	—	1.5
(CO) ₄ MnSnX	—	1.2	1.0	—
(CO) ₄ MnSn(X-H)	—	3.5	—	—
(CO) ₃ MnSnX ₂ Y	—	—	—	8.7
(CO) ₃ MnSnXY	1.5	—	—	—
(CO) ₃ MnSnX ₂	1.0	4.4	18.8	1.5
(CO) ₃ MnSnX	—	1.1	—	—
(CO) ₃ MnSn(X-H)	—	4.3	—	—
(CO) ₃ MnSn	—	9.7	—	—
(CO) ₂ MnSnX ₂ Y	3.9	—	—	10.1
(CO) ₂ MnSnXY	7.6	—	—	—
(CO) ₂ MnSnX ₂	1.0	—	3.0	3.4
(CO) ₂ MnSn(X-H)	—	2.1	—	—
(CO) ₂ MnSn(X-2H)	—	1.9	—	—
(CO) ₂ MnSn	—	6.3	—	—
(CO)MnSnX ₂ Y	5.1	—	—	6.3
(CO)MnSnXY	3.2	—	—	—
(CO)MnSnX ₂	—	—	5.5	3.9
(CO)MnSnX	—	—	1.1	1.9
(CO)MnSn(X-H)	—	5.0	—	—
(CO)MnSn(X-2H)	—	2.0	—	—
(CO)MnSn	—	6.4	—	1.9
MnSnX ₂ Y	10.8	—	2.5	3.7
MnSnX(X-H)Y	—	—	—	1.0
MnSnXY	5.4	—	—	—
MnSn(X-H)Y	2.3	—	—	—
MnSnX ₂	1.9	—	18.3	4.3
MnSnX(X-H)	—	—	8.7	—
MnSn(X-H) ₂	—	—	3.3	—
MnSnC ₁₀ H ₈	—	—	2.1	—
MnSnX	2.1	1.8	1.7	28.7
MnSn(X-H)	1.6	5.8	2.1	2.6
MnSn(X-2H)	—	1.5	—	—
MnSnY	6.0	—	—	—
MnSn	3.5	1.7	—	15.8

of a strengthening of the (Re-M') bonds as M' changes through Si, Ge to Sn. However, it is not possible to relate these values to differences in bond strengths directly for the reasons given above. Bearing in mind the assumptions made in the determination of *A*s, and the errors in the measurements it is

perhaps more useful to study the trends in bond strengths obtained using one method. Thus a stronger D(Mn-Si) 247 kJ mol⁻¹ bond in (8) compared to D(Mn-Sn) 197 kJ mol⁻¹ in (9) is found and this is in agreement with previous results [3, 4]. Whereas a change of X from methyl to phenyl in (CO)₅Mn-SnX₃ has little effect, replacement of one methyl group by a chlorine atom appears to strengthen the Mn-Sn bond by almost 20 kJ mol⁻¹, Table I. This concurs with numerous results from X-ray studies of similar compounds (see ref. [31]), and results from Mössbauer spectroscopy [36] which have been interpreted in terms of the charge donating and accepting abilities of the SnX₃ groups, however, the experimental error in *A* measurement and the error in the estimated *I*•SnMe₂Cl makes the apparent small difference in D(Mn-Sn) in these compounds questionable.

Changing the transition metal from Mn to Re in compounds (CO)₅M-SnMe₃ increases the D(M-Sn) value by 71 kJ mol⁻¹. A similar effect was observed in η-C₅H₅M(CO)₃SnMe₃ compounds where D(W-Sn) was 93 kJ mol⁻¹ higher than D(Cr-Sn) [2].

The stronger D(Co-Sn) 217 kJ mol⁻¹ in (14) than D(Mn-Sn) 197 kJ mol⁻¹ in (9) agrees with a previous study [3], but once again the difference is within the combined experimental errors. Comparison of these values can be made with 222 kJ mol⁻¹ from η-C₅H₅Fe(CO)₂SnMe₃ [1], and 220 kJ mol⁻¹ from η-C₅H₅Cr(CO)₃SnMe₃ [2]. However it should be noted that the *A* value for D(Cr-Sn) was calculated using the semi-log. plot method to interpret the ionisation efficiency curve, whereas the CSCM method was used for all the other compounds.

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