Trimethyl(pentacarbonylmanganese)-silane, -germane, and -stannane: Vibrational Spectra and Electron-impact Studies

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The complexes $Me_3MMn(CO)_5$ [M = Si, (I); M = Ge, (II); and M = Sn, (III)] have been examined using vibrational and mass spectroscopy. The i.r. and Raman spectra are consistent with C_{4v} symmetry at the Mn atom; Raman bands at 297 (I), 194 (II), and 178 cm^{-1} (III) are assigned to ν(M–Mn). Appearance potential measurements for ions Me_3M^+ lead to bond dissociation energy values D(M–Mn) near 2·5 eV for all M; a decrease in metal–metal bond strength between (I) and (II) is indicated by approximate force-constants calculated from the ν(M–Mn) frequencies.

ALTHOUGH numerous complexes with bonds between transition and main group metals have been reported,[1] there have been few attempts at a systematic investigation of their spectroscopic properties. Thus while the i.r. spectra of many metal-carbonyl derivatives of the Group IVB elements and related compounds have been subjected [2] to detailed examination in the carbonyl stretching region, frequently with the aim of reaching structural conclusions, full vibrational assignments have rarely been attempted. Likewise, despite interest in the nature of the metal–metal interaction, few relevant bond-stretching vibration frequencies have been reported. A basis for more complete interpretation of the vibrational spectra of compounds of this type is available, however, provided by Risen and his co-workers [3,4] through a detailed study of the tetracarbonylcobalt derivatives $Cl_3MCo(CO)_4$ (M = Si, Ge, or Sn) and $X_3MCo(CO)_4$ (X = Cl, Br, or I: M = Ge or Sn), including full valence force-constant calculations. A partial force-constant treatment and assignment of the i.r. spectra of $X_3SnMn(CO)_5$ (X = Cl, Br, Me, or Ph) have also been published,[5] and detailed empirical assignments for $Me_3SiCo(CO)_4$ [6] and a number of monogermyl–(transition-metal carbonyl) derivatives [7,8] have recently been made. The low probability of extensive mixing between $-GeH_3$ and $-M(CO)_x$ vibrations in the latter also allowed reasonable confidence to be placed in relative values calculated for approximate metal–metal stretching force-constants from observed Raman frequencies.[8]

Equally little attention has been given to the estimation of relative strengths of the metal–metal bonds in these compounds through determination of bond dissociation energies. Published data, all obtained by means of mass spectroscopy, are restricted to the following: $X_3SiCo(CO)_4$ (X = F or Cl) [9] and $MeF_2SiCo(CO)_4$,[10] where D(Si–Co) in the range 440—530 or 310—400 kJ mol^{-1} were determined, depending on the value used for $\Delta H_f°(Co(CO)_4)$; and $Me_3M^1M^2(CO)_3(C_5H_5)$ (M^1 = Ge

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[3] K. L. Watters, J. N. Brittain, and W. M. Risen, *Inorg. Chem.*, 1969, **8**, 1347.

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[8] K. M. Mackay and S. R. Stobart, *J.C.S. Dalton*, 1973, 214.

[9] F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *Inorg. Chem.*, 1968, **7**, 1465; F. E. Saalfeld, M. V. McDowell, A. P. Hagen, and A. G. MacDiarmid, *ibid.*, p. 1665.

[10] F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 1970, **92**, 2324.

or Sn; M^2 = Cr, Mo, or W) where $D(M^1\text{–}M^2)$ values in the range 192—318 kJ mol^{-1} have been reported by Lappert *et al.*,[11] who also made a preliminary attempt to correlate $D(M^1\text{–}M^2)$ values with $\nu(M^1\text{–}M^2)$ measured in the Raman effect.

We have recently reported an investigation[12] of certain aspects of the chemical stability of the metal–metal bond in $Me_3SnMn(CO)_5$; we have further sought to compare the relative strengths of the M–Mn bond in this complex and its Si and Ge analogues by physical means, through a detailed comparison of vibrational and mass spectroscopic properties for all three molecules.

TABLE 1

Vibrational spectra of $Me_3MMn(CO)_5$, M = Si, Ge, or Sn (cm^{-1})

$Me_3SiMn(CO)_5$		$Me_3GeMn(CO)_5$		$Me_3SnMn(CO)_5$		
I.r. (liquid film) [a]	Raman (liquid)	I.r. (KBr disc) [a]	Raman (liquid)	I.r. (liquid film) [a]	Raman (liquid)	Tentative assignment
2960m	2954w(dp)	2980w	2975m(dp)	2980m	2985w(dp)	$\nu_{as}(CH_3)$
2890m	2894m(p)	2910w	2912m(p)	2905m	2917m(p)	$\nu_s(CH_3)$
2091s	2095s(p)	2090s	2095s(p)	2082s	2098s(p)	$\nu(CO)[a_1^{(2)}]$
	2015s(dp)		2015vs(dp)		2012vs(dp)	$\nu(CO)(b_1)$
2000vvs,br	1995s(dp)	1986vvs,br	1991vs(dp)	1980vvs,br	1989vs(dp)	$\nu(CO)(e)$
	(1975m) *		(1975m) *		(1969m) *	$\nu(CO)[a_1^{(1)}]$
1448w						
1404m	1410vw(dp)	1406w	1407w(dp)	1400vvw,br		$\delta_{as}(CH_3)$
				1210w,sh		
1260m,sh	1261vw(p)	1240w,sh	1239s(p)	1195m	1196m(p)	$\delta_s(CH_3)$
1246s	1249vw(dp)	1227m	1228s(dp)	1184m	1186m(dp)	$\delta_{as}(CH_3)$
1095w		1085w		1085w		
1031w		1034w		1030w		
965vw			976vw,br	965vw		
911vw		910vw		901w		
			849m,sh(p)		840vw,br	
			837m,sh(dp)			
838s	839vw(p)	825s	827m(p)	769s	767vw,br	$\rho(CH_3)$
751s	756w(dp)	750m	758vw,br(dp)	700m		$\rho(CH_3)$
665s,sh		665s,sh		660s,sh		$\}\ \delta(MnCO)$
650vs		650vs		647vs		
	682w(dp)	588m	590m(dp)	516m	517m(dp)	$\nu_{as}(MC_3)$
620s	622m(p)	559m	559s(p)	499m	501s(p)	$\nu_s(MC_3)$
486s	485vw	481m		479m		$\nu(MnC)(ax)$
463w,sh	460vw,sh	465w,sh				$\nu(MnC)$?
				426vw,sh	426w,sh(dp)	
410w	418vs(p)	412w	417vs(p)	411w	416s(p)	$\nu(MnC)(eq)$
	297m(p)		194vs(p)		178vs(p)	$\nu(MMn)$
	210s(p)				163m,sh(dp)	$\delta(MC_3)$
	160s(p)		125m,sh			$\rho(MC_3)$
	103vvs(dp)		107vs(dp)		100vs(dp)	skeletal deformations

[a] Vapour phase $\nu(CO)$ frequencies observed as follows: $Me_3SiMn(CO)_5$, 2098s, 2001vvs, 1975m; $Me_3GeMn(CO)_5$, 2101m, 2009vs, 1980w; $Me_3SnMn(CO)_5$, 2093m, 2002vs, 1975w cm^{-1}.

* Solid-state frequencies: see text.

VIBRATIONAL SPECTRA

I.r. and Raman data for all three complexes are collected in Table 1, with approximate descriptions for the observed fundamentals. I.r. frequencies for the germanium and tin compounds are in good agreement with values reported and partially assigned elsewhere.[13] The close relationship of the three molecules is reflected in the obvious similarity of the spectra.

Carbonyl stretching fundamentals observed in the i.r. for a large number of pentacarbonylmanganese derivatives of the Group IVB metals have been discussed[14,15] in terms of an approximation to C_{4v} symmetry at the manganese atom, for which the CO stretching modes are represented as $2a_1 + b_1 + e$. In certain cases the breakdown of this approximation leads to the appearance[15] of the five i.r.-active fundamentals ($3a' + 2a''$) predicted by the expected molecular symmetry of C_s but in general fewer bands have been observed and in particular the b_1 (i.r.-inactive) mode derived from the C_{4v} model has often been only doubtfully distinguished.

We find that for $Me_3MMn(CO)_5$ (M = Si, Ge, or Sn) the observed data are entirely consistent with predictions based on C_{4v} symmetry: thus, three strong i.r. absorptions are attributable to the $a_1^{(2)}$, e and $a_1^{(1)}$ modes, while in the Raman effect a fourth, depolarised band can be assigned to the b_1 fundamental. Raman spectra of solid samples at *ca.* 0 °C allowed all four vibrations to be observed together, through splitting of the e and $a_1^{(1)}$ contours as was found for $GeH_3Mn(CO)_5$ and its rhenium analogue.[8] The frequencies of the b_1 modes measured in the Raman agree well with values

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[11] D. J. Cardin, S. A. Keppie, M. F. Lappert, M. R. Litzow, and T. R. Spalding, *J. Chem. Soc.* (*A*), 1971, 2262.

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[15] W. Jetz, P. B. Simons J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2217.

predicted from observed i.r. data by using force-constants computed from the Cotton–Kraihanzel approximation.[14]

Variations in the frequencies of carbonyl stretching fundamentals, and in the CO stretching force-constants derived therefrom, have each been considered for metal-carbonyl derivatives to be sensitive to the electronic properties of the substituent groups, either in terms of effective electronegativity or of π-acceptor ability.[1,2,14,15] Vapour-phase measurements for $Me_3MMn(CO)_5$, (M = Si, Ge, or Sn) where band positions should be unaffected by intermolecular effects, strongly suggest from the near-equality of $\nu(CO)$ frequencies throughout (Table 1) that which ever of these criteria apply there is little change in the character of the M–Mn bond on going from M = Si to Sn. This conclusion is supported by the invariance of frequency found for the other vibrations of the CO groups: the strong doublet in the i.r. spectra assigned to two of the $\delta(MnCO)$ modes is consistently near 650 cm^{-1}, and frequencies for the axial (strongly i.r.-active) and equatorial (strongly Raman active) $\nu(MnC)$ modes are also identical throughout.

In the spectra of all three compounds features attributable to vibrations of the methyl groups fall within the expected ranges, but as in the case of related trimethyl-halogeno derivatives[16] there is a trend to low frequency of methyl deformation and rocking modes with increasing mass of the Group IV metal atom. Thus for M = Si, Ge, and Sn, $\delta(CH_3)$ modes are found respectively at 1250, 1230, and 1180 cm^{-1} in the Raman effect, and even more pronounced decreases occur for the methyl rocking modes between M = Ge and Sn.

The vibrations of the $-MC_3$ unit (M = Si, Ge, or Sn) are consistent with local C_{3v} symmetry at the *M*-atom. As expected, two bands ($a_1 + e$) are observed for M–C stretching, with that at lower frequency polarised in the Raman (a_1 mode), and show a monotonic decrease in frequency on going from Si to Sn. The lack of exact correlation between bands attributable to the MC_3 deformation vibrations for the three species, particularly in terms of polarisation properties (Table 1), may represent incidence of the non-applicability of the local-symmetry approximation, as was found[7,8] at low frequency for related monogermyl-complexes.

Metal–Metal Stretching Vibrations.—For C_{nv} symmetry $\nu(M{-}M)$ is an a_1 fundamental and should occur as a strong, polarised band at low frequency in the Raman effect. Appropriate features are found at 297, 194, and 178 cm^{-1} for the silane, germane, and stannane respectively. A band at 292 cm^{-1} in the Raman spectrum of $Me_3SiCo(CO)_4$ was assigned[6] to $\nu(SiCo)$, while the $\nu(M{-}M)$ frequencies for the germanium and tin compounds are close to those reported by Lappert *et al.*[11] for related group VIA complexes (Table 2). The Raman band-intensity observed for $Me_3SiMn(CO)_5$ is significantly lower than for the other two complexes, (Table 1) parallelling the observation of Durig and co-workers[6] that for the tetracarbonylcobalt analogue, $\nu(Si{-}Co)$ was also surprisingly weak.

Approximate metal–metal stretching force-constants for $Me_3MMn(CO)_5$, calculated as described elsewhere[8] by one of us, are also listed in Table 1. Lappert and his co-workers have discussed similar results for $Me_3M^1M^2(CO)_3(C_5H_5)$ (M^1 = Ge or Sn: M^2 = Cr, Mo, or W), but the basis for the calculations was not made clear and no values for approximate force-constants were derived.[11] We have therefore determined these latter from the observed M–M frequencies as shown in Table 2, where the two approximations DA and PDA represent extremes in which bonds adjacent to M–M are assumed to have respectively zero and infinite force constants, and the F_{M-M} values thus calculated will lie on either side of the true value. Results obtained using a simple diatomic model [F_{M-M}(DA) values] suggest little effect on the metal–metal force-constant on exchanging germanium for tin, combined with a monotonic increase on descending group VIA, parallelling changes already noted[8] for $H_3M^1M^2(CO)_5$ (M^1 = Si or Ge: M^2 = Mn or Re). This is discussed further below in relation to metal–metal bond dissociation energy terms derived from the mass spectroscopic measurements. Despite the arguments presented by Lappert *et al.*,[11] we attribute less significance to variations in the pseudo-di-atomic[8] values F_{M-M}(PDA) of Table 2.

TABLE 2

Metal–metal stretching frequencies/cm^{-1} and force-constants/mdyn $Å^{-1}$

Compound	$\nu_{obs}(M{-}M)$	F_{M-M}(DA)[a]	F_{M-M}(PDA)[b]
$Me_3SiMn(CO)_5$	297	0·97	3·24
$Me_3GeMn(CO)_5$	194	0·69	1·63
$Me_3SnMn(CO)_5$	178	0·70	1·66
$Me_3GeCr(CO)_3(C_5H_5)$	(191)[c]	0·65	1·59
$Me_3GeMo(CO)_3(C_5H_5)$	180[c]	0·79	1·52
$Me_3GeW(CO)_3(C_5H_5)$	171[c]	0·90	1·50
$Me_3SnCr(CO)_3(C_5H_5)$	183[c]	0·71	1·77
$Me_3SnMo(CO)_3(C_5H_5)$	168[c]	0·88	1·63
$Me_3SnW(CO)_3(C_5H_5)$	165[c]	1·16	1·76

[a] Value calculated assuming a diatomic model. [b] Value calculated assuming a pseudo-diatomic model, ligand masses summed to those of the metal atoms (see text and ref. 8). [c] See ref. 11.

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Summed abundances for important categories of ion-fragments are given in Table 3. Full data with intensities and assignments are listed in Supplementary Publication No. SUP 20688 (6 pp.).* Identical nominal masses for ^{28}Si and CO, and overlapping ions arising from loss of either Me_2 or CO from fragments containing the polyisotopic metals (Ge and Sn) resulted in ambiguities in assignment of certain ion-families, although the second of these factors could usually be resolved by careful examination of relative peak-intensities.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20. Items less than 10 pp. are sent as full size copies.

[16] J. R. Durig K. K. Lau, J. B. Turner, and J. Bragin, *J. Mol. Spectroscopy*, 1969, **31**, 419.

Fragmentation routes for organo-group IVB compounds[17] and metal-carbonyl derivatives[11,18] are well established and are reflected in the spectra for the three complexes; loss of Me and successive loss of CO groups are metastable-supported for the tin compound. Ions in which the metal–metal bond nominally remains intact account for respectively 37, 52, and 59% total ion-current for M = Si, Ge, or Sn, although parent ion-family abundances are comparable for all three complexes (*ca.* 5%). Trends which may reflect decreasing M–C bond strength between M = Si and Sn are a corresponding decrease in the ratio of abundances $Me_3MMn(CO)_y^+/Me_2MMn(CO)_y^+$, and the very low abundance of all ions $MeMMn(CO)_y^+$ (except for $y = 0$) other than for M = Sn. The high stability of ions of the type Me_3M^+ (M = Group IVB metal) has been discussed elsewhere[19] and as expected the base-peak family arises from these fragments in each case. All these features are similar to those described for $Me_3M^1M^2(C_5H_5)(CO)_3$, (M^1 = Ge or Sn; M^2 = Cr, Mo, or W) but one novel observation is that of ions with $m/e = 189$, 191, and 193 in the spectrum of the germane; the only plausible assignment for these peaks seems to be $C_3GeMnCO^+$ for ^{70}Ge, ^{72}Ge, and ^{74}Ge respectively. This is supported by the appearance of an ion with $m/e = 147$ for the silane attributable to $C_3{}^{28}SiMnCO^+$, (although a possible alternative might be $Me_5Si_2O^+$ due to traces of hexamethyldisiloxane; however, no other evidence for the presence of the latter was found and the observed peak-intensity pattern was that of ^nSi rather than $^nSi_2$, $n = 28$, 29, or 30). It is not possible to determine whether loss of hydrogen from methyl, loss of oxygen from carbonyl, or a combination of the two (both of which are known[20] for related compounds) is responsible for the formation of these ions but in either case such extensive retention of carbon atoms is very unusual.

TABLE 3

Ion abundances for $Me_3MMn(CO)_5$ (M = Si, Ge, or Sn) [a]

Ion families [b]	M = Si	M = Ge	M = Sn
$Me_xMMn(CO)_5^+$	7	8	14
$Me_xMMn(CO)_4^+$	3	5	9
$Me_xMMn(CO)_3^+$	5	5	6
$Me_xMMn(CO)_2^+$	4	5	5
$Me_xMMn(CO)^+$	4	2	2
Me_xMMn^+	11	18	20
$Me_3MMn(CO)_y^+$	24	17	14
$Me_2MMn(CO)_y^+$	9	20	32
$MeMMn(CO)_y^+$	1	6	10
Me_3M^+	37	17	21

[a] Expressed as percentage of total metal-containing ions. [b] $x = 3, 2, 1$, or 0; $y = 5, 4, 3, 2, 1$, or 0.

Appearance Potential Measurements.—These were made as described in the experimental section; the values were calculated by the Warren method[21] and are shown in Table 4, together with ionisation potentials, *i.e.* A.P.($Me_3MMn(CO)_5^+$), determined for each compound and derived bond dissociation energies *D*. Nicholson has shown[22] that the Warren method and related semi-log. procedures give results whose minimum uncertainty is *ca.* ±0·1 eV, probably a realistic limit on the data of Table 4 in view of the graphical treatment involved although the consistency of the determinations for A.P.(Me_3M^+) (see Experimental section) is greater. Uncertainties in the range ±0·1 to ±0·4 eV have been placed[9-11] on measurements made on related complexes, although lower limits have been suggested in electron impact studies of some main-group organometallic compounds.[23]

TABLE 4

Ionisation potentials, appearance potentials, and derived bond dissociation energies [a]

	I.P. [b]	A.P.(Me_3M^+) [b]	*D*(M–Mn) [c]	*D*(Me_3M–$Mn(CO)_5^+$)
$Me_3SiMn(CO)_5$	8·85	9·89	2·64	1·04
$Me_3GeMn(CO)_5$	8·76	9·46	2·40	0·70
$Me_3SnMn(CO)_5$	8·63	9·32	2·51	0·69

[a] All values in eV, ±0·1. For a discussion of estimated uncertainties, see text. [b] Assuming I.P.(Ar) = 15·76 eV. [c] Assuming values for I.P.($Me_3M\cdot$) as follows: Si, 7·25; Ge, 7·06; Sn, 6·81 eV, ref. 19.

To be able to use the measured A.P. values for Me_3M^+ to calculate *D*(M–Mn) it must be established that ions of this type originate only from process (1). Considerations discussed by Lappert and co-workers[11] for closely related molecules indicate that this condition

$$Me_3MMn(CO)_5^{+\cdot} \longrightarrow Me_3M^+ + Mn(CO)_5^{\cdot} \quad (1)$$

will be met, a conclusion consistent with the very low ion-abundances at 70 eV of all families $Me_3MMn(CO)_y^+$ except for $y = 0$ or 5. To try to confirm this the mass spectrum of the germane was examined in more detail. At 15 eV the molecular ion and Me_3Ge^+ were much increased in intensity while the abundances of other $Me_3GeMn(CO)_y^+$ families remained very low. A.P. Measurements on the most abundant of the latter, that with $y = 0$, yielded an approximate value of 12—13 eV, very much higher than A.P.(Me_3Ge^+), although a

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[17] D. B. Chambers and F. Glockling, *J. Chem. Soc.* (*A*), 1968, 735; D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.*, 1968, **22**, 317 and references therein.

[18] R. B. King, *Org. Mass Spectrometry*, 1969, **2**, 657; J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, 1968, **1**, 245.

[19] M. F. Lappert, J. B. Pedley, J. Simpson, and T. R. Spalding, *J. Organometallic Chem.*, 1971, **29**, 195.

[20] R. D. George, K. M. Mackay, and S. R. Stobart, *J. Chem. Soc.* (*A*), 1970, 3250; A. Carrick and F. Glockling, *ibid.*, 1968, 913; J. Müller, *Angew. Chem. Internat. Edn.*, 1972, **11**, 653.

[21] J. W. Warren, *Nature*, 1950, **165**, 810.

[22] A. J. C. Nicholson, *J. Chem. Phys.*, 1958, **29**, 1312.

[23] D. B. Chambers, G. E. Coates, and F. Glockling, *J. Chem. Soc.* (*A*), 1970, 741; F. Glockling and R. G. Strafford, *ibid.*, 1971, 1761.

complex shape to the ionisation efficiency curve precluded an accurate determination.*

MacDiarmid and co-workers have reported[10] that they were unable to study the energetics of process (2) due to the formation of Me_3Si^+ from hexamethyldisiloxane present as impurity. The possibility of a similar

$$Me_3SiCo(CO)_4^{+\cdot} \longrightarrow Me_3Si^+ + Co(CO)_4^{\cdot} \quad (2)$$

situation arising in the case of $Me_3SiMn(CO)_5$ was investigated by examining the ionisation efficiency curve for Me_3Si^+ in the mass spectrum of an authentic sample of $Me_3Si{\cdot}O{\cdot}SiMe_3$. A very long ' tail ' prevented a determination of a meaningful value for the A.P. (Me_3Si^+), but the distinctive shape of the curve ruled out presence of this impurity as a complicating factor.

Bond dissociation energies D(M–Mn) were calculated in accordance with process (1) by using literature values[19] for the ionisation potentials of the radicals $Me_3M{\cdot}$, and bond dissociation energies for the molecular ions $D(Me_3M-Mn(CO)_5^+)$ were derived from ionisation potential measurements for the three complexes and are also included in Table 4. In common with other D values derived from mass spectroscopic measurements the present data probably represent upper limits as discussed elsewhere.[24]

DISCUSSION

The derived D(M–Mn) values are in the region of 2·5 eV (*ca.* 250 kJ mol^{-1}), close to the $D(M^1-M^2)$ reported by Lappert and co-workers[11] for $Me_3M^1M^2(C_5H_5)(CO)_3$ (M^1 = Ge or Sn; M^2 = Cr, Mo, or W). Corresponding $D(Me_3M-Mn(CO)_5^+)$ terms are much smaller in magnitude. These calculated bond-dissociation energies can be related to conclusions based on the vibrational spectra in two conflicting ways, one of which indicates a significantly stronger M–Mn bond in the silane while the other provides evidence for roughly equal bond-strengths for M = Si, Ge, or Sn. Thus reference to Tables 2 and 4 shows that force-constant calculations based on simplified models and the $D(Me_3M-Mn(CO)_5^+)$ values (which should provide an estimate of relative changes in M–Mn bond strength) are consistent with one another and with a *ca.* 30% drop in bond order between Si–Mn and Ge–Mn. By contrast, the D(M–Mn) values suggest comparable metal–metal bond strengths in all three compounds [although these results will be dependent in their relative magnitudes on the I.P. ($Me_3M{\cdot}$) terms used in their derivation], and this is confirmed in a qualitative way by the lack of variation in frequency of vibrational fundamentals associated with the CO groups which has already been emphasised. While we note this ambiguity, we attach more significance to the changes in approximate stretching force-constant than to the M–C–O frequencies, and since more assumptions and subsidiary data are required to calculate D(M–Mn) than $D(Me_3M-Mn(CO)_5^+)$ we tentatively conclude that the metal–metal bond strength may decrease significantly between M = Si and Ge. The drop in calculated F_{M-M} between Si–Mn and Ge–Mn might alternatively be accounted for in terms of interaction of ν(SiMn) with other a_1 modes of higher energy, but the absence for the latter of any real variation in frequency across the series (Table 1) seems to indicate that this possibility is less likely.

Although a relationship between approximate force-constant and bond-dissociation energy cannot therefore be clearly established for variation of the Group IVB element, a more encouraging trend is discernible on altering the transition metal. Thus the changes in F_{M-M}(DA) for M^1 = Ge or Sn, M^2 = Cr, Mo, or W (Table 2) do follow the order of increasing $D(M^1-M^2)$ reported[11] previously. It is also interesting to note that $D(M-Cr) < D(M-Mn)$ for M = both Ge and Sn, an observation which may be compared with that of an apparent increase in F_{M-M}(DA) for related metal–metal bonded complexes on progressing across the first transition series.[8]

EXPERIMENTAL

Trimethylsilylpentacarbonylmanganese was prepared through the reaction of decacarbonyldimanganese with trimethylsilane as described by Berry and MacDiarmid,[25] although a lower yield (*ca.* 10%) than that reported by these authors was obtained under the conditions employed (5 mmol scale, sealed 70 ml tube, 135°, 48 h; 15 mmol scale, 0·5 l sealed bulb, 135°, 9 days). Trimethylgermyl- and trimethylstannyl-pentacarbonylmanganese were synthesised as detailed by Bichler *et al.*,[26] the trimethylbromogermane used being being prepared by $GeCl_4$ by published methods.[27]

I.r. spectra were measured using Perkin-Elmer 457 and Grubb-Parsons Spectromajor spectrometers, with calibration from the i.r. spectrum of polystyrene. Raman spectra were obtained with a Cary 83 instrument operating at 488·0 nm (Ar ion laser source), using samples purified by vacuum fractionation and sealed in glass capillaries, and calibration from peaks in the Raman spectrum of indene to give frequencies considered accurate to within ±2 cm^{-1} below 2000 cm^{-1}.

The mass-spectroscopic measurements were made using an AEI MS 902 spectrometer with an ionising voltage of 70 eV for the routine spectra. The samples were triply-sublimed and sealed *in vacuo* and were introduced at 20 °C through an all-glass inlet system. For appearance potential measurements, in the range 7·5—20 eV, a trap-current of

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* *Note added in proof:* During publication of this paper, independent results for M = Si have been reported (F. E. Saalfeld, M. V. McDowell, J. J. DeCorpo, A. D. Berry, and A. G. MacDiarmid, *Inorg. Chem.*, 1973, **12**, 48) which suggest when compared with the data of Table 4 that a further possible source of Me_3Si^+ might be $Me_3SiMn(CO)_4^+$.

[24] H. A. Skinner, *Adv. in Organometallic Chem.*, 1964, **2**, 49 and references therein. For a discussion of this and related topics see also I. Howe, ' Mass Spectrometry,' Chemical Society London, 1971, vol. 1, p. 31.

[25] A. D. Berry and A. G. MacDiarmid, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 601.

[26] R. E. J. Bichler, M. R. Booth, H. C. Clark, and B. K. Hunter, *Inorg. Synth.*, 1970, **12**, 61.

[27] E. H. Brooks and F. Glockling, *Inorg. Synth.*, 1970, **12**, 58; R. E. J. Bichler, M. R. Booth, H. C. Clark, and B. K. Hunter, *ibid.*, p. 64.

20 μA and ion-repeller voltage of −1 to +5 v were used with an accelerating voltage of 6 kV. Results for hexa*methyldisiloxane* were obtained similarly using a commercial sample purified by fractional condensation *in vacuo*. Argon was used in all cases as reference. Up to six determinations were made for A.P.(Me_3M^+), giving values consistent to within ±0·03 eV for M = Si and Sn, and ±0·07 eV for M = Ge where a longer 'tail' in the ionisation efficiency curve was observed.

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