Reactivity of the Metal–Metal Bond in Trimethylstannylpentacarbonylmanganese

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Reaction between Me_3SnH and $Mn_2(CO)_{10}$ affords $Me_3SnMn(CO)_5$ (I), but in much poorer yield than other established routes. Unlike its trimethylsilyl analogue, (I) is unaffected by water, methanol, and also aqueous NaOH. Cleavage of the tin–manganese bond occurs quantitatively with 1,2-dibromoethane and $HgCl_2$, and with RHgX (R = Me or Ph; X = Cl or Br) to give products dependent on R and X. With CF_3COCl and $HSiCl_3$, displacement of one methyl group from tin occurs yielding $Me_2ClSnMn(CO)_5$ (II), whereas $SnCl_4$ successively cleaves all three tin–carbon bonds. In the Raman spectrum of (II), ν(Sn–Mn) is at 194 cm^{-1}, compared with 178 cm^{-1} for (I).

NUMEROUS examples of organotin derivatives of the transition metals are now known, but while much information is available regarding the synthesis of such compounds and their molecular structures, little attention has yet been given to their chemical behaviour, and in particular to the stability of the tin–transition metal bond.[1] An exception is trimethylstannylpentacarbonylmanganese; since the first report of its preparation[2] this complex has been the subject of a number of studies, mainly by Clark and his co-workers. Thus while halogens and certain inorganic halides cleave the tin–manganese bond, hydrogen halides react to give methyl(halogeno)tin derivatives;[3,4] fluoro-olefins and sulphur dioxide insert into the metal–metal bond.[5,6] As part of an examination of the properties of a range of organotin–transition metal compounds we have explored some further reactions of $Me_3SnMn(CO)_5$, the results of which are reported here.

Unlike analogous reactions involving trialkylsilanes,[7,8] trimethylstannane when heated with decacarbonyldimanganese gives only low yields (*ca.* 7%) of $Me_3SnMn(CO)_5$. Thus while two other syntheses from $Mn_2(CO)_{10}$, involving reaction with either Me_6Sn_2 or $(C_5H_5)SnMe_3$, have been reported by Abel,[9,10] the most important route to the complex remains that reported[2] by Clark and Tsai [equation (1)], following a preparative method established earlier by Gorsich.[11]

$$Me_3SnCl + NaMn(CO)_5 \longrightarrow Me_3SnMn(CO)_5 + NaCl \quad (1)$$

The product is sufficiently volatile to be readily handled in a conventional vacuum system and also to show a vapour-phase i.r. spectrum at room temperature, with conspicuous carbonyl stretching absorptions at 2100 and 2013 cm^{-1} (rather higher frequencies than for the liquid phase), and with a strong doublet at 668 and 655 cm^{-1} (MnCO deformation). The Raman spectrum of the liquid includes a strong, polarised band at 178 cm^{-1}, attributable to the Sn–Mn stretching vibration; the mass spectrum shows the expected high proportion of ion-current (*ca.* 50%) carried by fragments containing both metal atoms, and also a high abundance for the Me_3Sn^+ ion. A more detailed study of these spectroscopic properties, and of those of trimethyl-silyl and -germyl analogues, is in progress.[12]

The high resistance towards protolysis shown by $Me_3SnMn(CO)_5$ is in marked contrast to the rapid and complete reaction of the silyl analogue with both water and methanol.[7] No evidence for the formation of $HMn(CO)_5$ or hexamethyldistannoxane was obtained with either of these reagents, or with NaOH in a water/ether mixture, although in the latter case ineffective mixing of the two reactants may have occurred.

Reaction with 1,2-dibromoethane was essentially quantitative according to equation (2). Similar cleavage of related metal–metal bonded complexes has been observed,[13] the highly selective nature of the reaction favouring a multicentre molecular mechanism. Recent work has shown that while cleavage of group IVB–mercury bonds by organic dibromo-compounds is almost certainly a molecular process,[14] that of the metal–metal bond in disilanes and digermanes under similar conditions appears to proceed *via* a free-radical (S_H2) mechanism.[15] These observations suggest that bond polarity might be a significant factor in determining by which of these mechanisms reaction occurs. In platinum(II) complexes with Pt–Si or Pt–Ge bonds an oxidative addition

$$Me_3SnMn(CO)_5 + C_2H_4Br_2 \longrightarrow Me_3SnBr + C_2H_4 + BrMn(CO)_5 \quad (2)$$

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[1] F. Glockling and S. R. Stobart, *MTP Internat. Rev. Science, Inorg. Chem.*, 1972, **6**, 63.

[2] H. C. Clark and J. H. Tsai, *Inorg. Chem.*, 1966, **5**, 1407.

[3] M. R. Booth, D. J. Cardin, N. A. D. Carey, H. C. Clark, and B. R. Sreenathan, *J. Organometallic Chem.*, 1970, **21**, 171.

[4] E. W. Abel and G. V. Hudson, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2339.

[5] R. E. J. Bichler, M. R. Booth, and H. C. Clark, *J. Organometallic Chem.*, 1970, **24**, 145; H. C. Clark, J. D. Cotton, and J. H. Tsai, *Inorg. Chem.*, 1966, **5**, 1582.

[6] N. A. D. Carey and H. C. Clark, *Canad. J. Chem.*, 1968, **46**, 643.

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

[8] B. K. Nicholson and J. Simpson, *J. Organometallic Chem.*, 1971, **32**, C29.

[9] E. W. Abel and S. Moorhouse, *J. Organometallic Chem.*, 1970, **24**, 687.

[10] E. W. Abel, S. A. Keppie, M. F. Lappert, and S. Moorhouse, *J. Organometallic Chem.*, 1970, **22**, C31.

[11] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.

[12] R. A. Burnham and S. R. Stobart, to be published.

[13] E. H. Brooks and F. Glockling, *J. Chem. Soc.* (*A*), 1966, 1241; A. Carrick and F. Glockling, *J. Chem. Soc.* (*A*), 1968, 913.

[14] S. W. Bennett, C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Organometallic Chem.*, 1971, **27**, 195.

[15] A. Hosomi and H. Sakurai, *J. Amer. Chem. Soc.*, 1972, **94**, 1384.

of $C_2H_4Br_2$ to Pt has been proposed.[16] Reaction (2) is thus apparently a general one and may be useful in an analytical sense.

In contrast to the specific action of $C_2H_4Br_2$, methyl iodide reacted slowly to give a complex mixture of products in which iodination at both tin and manganese was indicated, and with Me_4Sn as the only methylated species together with some methane. No reaction was observed with ethyl chloride, nor with C_6F_5Br, unlike CF_3I which cleaved the Sn–Mn bond.[3] U.v. irradiation with CF_3COCl gave in rather low yield $Me_2ClSnMn(CO)_5$ with no indication of extensive fission of the metal–metal bond.

In common with other group IVB–transition metal complexes, $Me_3SnMn(CO)_5$ was quantitatively cleaved by mercuric chloride in THF solution [reaction (3)].

$$2Me_3SnMn(CO)_5 + HgCl_2 \longrightarrow 2Me_3SnCl + Hg[Mn(CO)_5]_2 \quad (3)$$

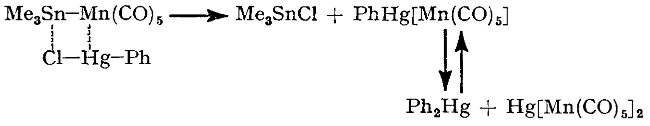
Similarly, organomercuric halides also cleaved the Sn–Mn bond, but the products obtained varied with the mercury compound used. With methylmercuric bromide quantitative reaction occurred as in equation (4). By contrast,

$$2Me_3SnMn(CO)_5 + MeHgBr \longrightarrow Hg[Mn(CO)_5]_2 + Me_4Sn + Me_3SnBr \quad (4)$$

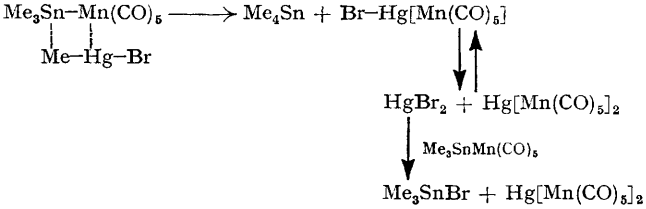
reaction with phenylmercuric chloride afforded products indicating cleavage in the opposite sense [equation (5)]. Methylmercuric chloride yielded only 76% of the

$$2Me_3SnMn(CO)_5 + 2PhHgCl \longrightarrow Ph_2Hg + Hg[Mn(CO)_5]_2 + 2Me_3SnCl \quad (5)$$

$Hg[Mn(CO)_5]_2$ expected by analogy with (4), together with Me_4Sn, Me_3SnCl, and traces of Me_2Hg, indicating a reaction which was not completely selective. These results suggest a four-centre molecular mechanism for Sn–Mn bond cleavage, similar to that proposed for insertion of fluoro-olefins into the Sn–Mn bond by Clark and his co-workers,[5] who have also emphasised the possible dependence of the type of products formed on Sn–Mn bond polarity. Likewise, variations in the polarity of the organomercury derivatives may contribute to the difference between reactions (4) and (5): thus with PhHgCl, initial formation of $PhHgMn(CO)_5$ followed by disproportionation (Scheme 1) would account for the observed products, there being no reaction between Ph_2Hg and $Me_3SnMn(CO)_5$ (analogously, the complex was found to be unaffected by Me_2Hg). A change in polarity on going to MeHgBr would yield $BrHgMn(CO)_5$ as in Scheme 2, when further reaction either directly or *via* disproportionation to $HgBr_2$ would give Me_4Sn, Me_3SnBr, and $Hg[Mn(CO)_5]_2$. The action of MeHgCl presumably represents the intermediate case, the reaction products being consistent with rather lower Hg–Cl bond polarity in MeHgCl than in PhHgCl.



SCHEME 1



SCHEME 2

To investigate its stability towards strongly nucleophilic reagents the complex was treated with lithium aluminium hydride. Extensive cleavage of the tin–manganese bond was observed, a high proportion of the tin being recovered as trimethylstannane. Under milder conditions, using sodium borohydride in methanol–THF, a similar reaction was evident. This rather ready reductive cleavage of the metal–metal bond is in contrast to the behaviour of $Cl_2Ge[Fe(C_5H_5)(CO)_2]_2$, reported[17] to be reduced in high yield to $H_2Ge[Fe(C_5H_5)(CO)_2]_2$.

Exchange reactions involving displacement of one group IV metal by another, usually in the form of a triorganometal hydride, have recently been reported[16,18] for group IV–transition metal complexes. These reactions proceed readily if the transition metal is coordinatively unsaturated, probably through oxidative addition of R_3MH to the transition metal. This type of mechanism is clearly unlikely for $Me_3SnMn(CO)_5$ but although no reaction was observed with Me_3SiH, on heating the complex with Bu_3SnH small amounts of Me_3SnH were detected. By contrast, $HSiCl_3$ attacked the tin–carbon bond under both mild and free-radical conditions, reaction (6) occurring without any indication of further substitution at Sn.

$$Me_3SnMn(CO)_5 + HSiCl_3 \longrightarrow Me_2ClSnMn(CO)_5 + MeHSiCl_2 \quad (6)$$

Of the reactions with the group IVB tetrahalides investigated, the only one to occur rapidly was that with $SnCl_4$, where n.m.r. measurements showed convincingly that successive replacement of methyl groups by chlorine was taking place [equation (7)] giving eventually $Cl_3SnMn(CO)_5$.

$$Me_3SnMn(CO)_5 + xSnCl_4 \longrightarrow Me_{3-x}Cl_xSnMn(CO)_5 + xMeSnCl_3 \quad (7)$$

This behaviour is analogous to a range of other redistribution reactions involving $SnCl_4$ and is consistent with recent reports[19] of its effectiveness as a selective

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[16] A. F. Clemmitt and F. Glockling, *J. Chem. Soc.* (*A*), 1971, 1164.

[17] N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1130.

[18] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3147; F. Glockling and J. G. Irwin, *Inorg. Chim. Acta*, 1972, **6**, 355.

[19] J. E. Bentham, S. Cradock, and E. A. V. Ebsworth, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1077.

chlorinating agent. The n.m.r. data reported in the Experimental section are interesting in that all the chemical shifts appear *ca.* 0·35 p.p.m. downfield in $SnCl_4$ relative to values found for CCl_4 solutions, and they also illustrate the usefulness of tin–(methyl-proton) coupling constants in assigning the spectra: values at the low end of the scale for organotin compounds (*ca.* 40 Hz) are typical for transition-metal derivatives.[20,21]

The i.r. spectrum of $Me_2ClSnMn(CO)_5$ has been reported previously, both in the carbonyl stretching region [21] and also at lower frequency.[22] Raman data recorded for this complex are shown in the Table together with approximate descriptions of the vibrations. An assignment of the carbonyl stretching modes in terms of local C_{4v} symmetry at the Mn atom is indicated, the i.r.-inactive b_1 vibration giving rise to a strong band at 2047 cm^{-1}. One other notable feature is the strong band at 194 cm^{-1}, assigned to ν(Sn–Mn); this frequency is 16 cm^{-1} above that in $Me_3SnMn(CO)_5$, in agreement with the far-i.r. values observed and discussed by Carey and Clark.[22] Attempted reduction of $Me_2ClSnMn(CO)_5$ using lithium aluminium hydride afforded dimethylstannane as the only volatile product, paralleling the behaviour of $Me_3SnMn(CO)_5$.

Raman spectrum of $Me_2ClSnMn(CO)_5$

Frequency cm^{-1}	Tentative assignment	Frequency cm^{-1}	Tentative assignment
2922m	$\nu(CH_3)$	528m	$\nu_{as}(SnC_2)$
2102s	$\nu(CO)\ a_1^{(2)}$	518vs	$\nu_s(SnC_2)$
2047vs	$\nu(CO)\ b_1$	414vs	ν(MnC)
2034vs	$\nu(CO)\ a_1^{(1)}$	304m	ν(SnCl)
1991m	$\nu(CO)\ e$	194vs	ν(SnMn)
		165vs	δ(CSnC)
1191 1176 } s	$\delta_{sym}(CH_3)$	126s,sh	δ(CSnCl)
		116 vs	δ(CMnC) + δ(CMnSn)

The incidence of tin–carbon rather than tin–manganese bond cleavage with a variety of reagents emphasises the high chemical stability of the Sn–Mn bond in $Me_3SnMn(CO)_5$ revealed by these and related studies. Extensive cleavage of the metal–metal bond has been observed only with strong nucleophiles or where ready formation of multicentre reaction intermediates is suspected. The tin complex is much less susceptible to hydrolytic cleavage than the analogous silane derivative,[7] in contrast to the relative behaviour towards unsaturated species like SO_2, where it is the tin compound which reacts readily to give insertion products while the silane is recovered unchanged.[7]

EXPERIMENTAL

Reactions were carried out in evacuated break-seal tubes, using a standard vacuum system for manipulations, unless otherwise stated. Ethers were twice distilled from sodium onto calcium hydride and were stored under a nitrogen atmosphere. I.r. spectra were obtained using a Perkin-Elmer 457 spectrometer, Raman spectra with a Cary 83 spectrometer operating at 488·0 nm, mass spectra with an AEI MS902, and n.m.r. spectra with a Varian A60D instrument. Reactants were either obtained commercially or prepared and purified by literature methods. Trimethylstannylpentacarbonylmanganese was prepared by the method of Clark and Tsai,[2,23] the product being purified by sublimation and subsequently handled by vacuum manipulation; it could be pumped through a trap at 0° but was held at −25°. Gas volumes are expressed as ml at 0°/760 mmHg.

Reaction of Trimethylstannane with Decacarbonyldimanganese.—$Mn_2(CO)_{10}$ (240 mg, 0·62 mmol) and an excess of Me_3SnH (*ca.* 1·3 mmol) were sealed in a Carius tube and heated at 60° for 1 week, during which time a metallic mirror was deposited. Fractionation yielded incondensable gas, unchanged Me_3SnH, a trace of $HMn(CO)_5$, Me_4Sn, and $Me_3SnMn(CO)_5$ (30 mg, 0·08 mmol, 7%); Me_6Sn_2 and $Mn_2(CO)_{10}$ remained in the tube. (All products were identified by i.r. spectroscopy).

Reactions of Trimethylstannylpentacarbonylmanganese.—*With water.* The complex (188 mg, 0·52 mmol) was sealed with water (0·5 ml) and Et_2O (1·0 ml). After 1 week at 20° with occasional shaking, recovery yielded $Me_3SnMn(CO)_5$ (93%), leaving traces of an involatile, carbonyl-containing residue.

With methanol. The complex (183 mg, 0·51 mmol) and AnalaR methanol (1·0 ml) were allowed to react for 1 week at 20°. Yellowing of the solution was noted, but only MeOH and $Me_3SnMn(CO)_5$ (91%) were found as volatiles.

With sodium hydroxide solution. The complex (166 mg, 0·46 mmol) was sealed off with NaOH (111 mg, 2·78 mmol), water (0·5 ml), and Et_2O (0·5 ml). On warming to 20° the ether layer immediately turned yellow; after 8 days recovery of volatiles gave $Me_3SnMn(CO)_5$ (77%). During the final stages of fractionation the involatile residue turned dark green; i.r. spectroscopy showed that this was not a carbonyl compound.

With 1,2-*dibromoethane.* The complex (193 mg, 0·54 mmol) and $C_2H_4Br_2$ (1559 mg, 8·30 mmol) were allowed to react for 8 days at 45°, during which time the solution turned yellow and orange crystals were deposited. Fractionation of volatiles afforded ethylene [10·93 ml, 91% based on $Me_3SnMn(CO)_5$]; mass spectroscopy showed the presence of Me_3SnBr in the recovered $C_2H_4Br_2$ fraction, and also revealed traces of $Me_2BrSnMn(CO)_5$. The orange crystals were identified as $BrMn(CO)_5$ (Found: C, 21·65; Br, 29·1. Calc. for C_5BrMnO_5: C, 21·85; Br, 29·05%).

With methyl iodide. The complex (200 mg, 0·56 mmol) and MeI (1450 mg, 10·2 mmol) were heated at 65° for 5 weeks. The solution turned deep red and an orange solid formed. Recovery yielded methane (1·6 ml), Me_4Sn, some unchanged $Me_3SnMn(CO)_5$, and an inseparable mixture of a variety of tin- and carbonyl-derivatives: the presence of $IMn(CO)_5$, $I_2Mn_2(CO)_8$, $IMe_2SnMn(CO)_5$, $I_2MeSnMn(CO)_5$, and $Me_2Sn[Mn(CO)_5]_2$ was inferred from i.r. and mass spectroscopy.

With ethyl chloride. No reaction was observed with EtCl during 2 weeks at 70°.

With pentafluorobromobenzene. No reaction occurred with C_6F_5Br under u.v. irradiation during 8 h.

With trifluoroacetyl chloride. The complex (197 mg, 0·55 mol) was sealed in a Carius tube with CF_3COCl (221 mg,

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[20] S. Onaka, Y. Sasaki, and H. Sano, *Bull. Chem. Soc. Japan*, 1971, **44**, 726.

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

[22] N. A. D. Carey and H. C. Clark, *Inorg. Chem.*, 1968, **7**, 94.

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

1·67 mmol). After 12 days at room temperature, fractionation afforded $Me_3SnMn(CO)_5$ (78%). In a further reaction, the complex (0·54 mmol) with an excess of CF_3COCl was irradiated (u.v.) for 6 h. *Ca.* 0·25 mmol of CF_3COCl reacted, giving $Me_2ClSnMn(CO)_5$ along with unchanged $Me_3SnMn(CO)_5$. Two volatile products were tentatively identified as CF_3COMe and $CF_3COMn(CO)_5$ by gas-phase i.r. and mass spectroscopy.

With mercuric chloride. The complex (195 mg, 0·55 mmol), $HgCl_2$ (74 mg, 0·27 mmol), and THF (2·5 ml) reacted rapidly at room temperature with deposition of a pale yellow solid. The reaction tube was opened after 5 days, when sublimation gave Me_3SnCl. The residual yellow needles were identified by Raman spectroscopy[24] as bis(pentacarbonyl-manganese)mercury (157 mg, 0·26 mmol, 98% based on $HgCl_2$) (Found: Hg, 33·85. Calc. for $C_{10}O_{10}HgMn_2$: Hg, 33·95%).

With methylmercuric chloride. The complex (206 mg, 0·57 mmol), MeHgCl (67 mg, 0·27 mmol), and THF (1·0 ml) formed a yellow precipitate rapidly at 20°. After 17 h volatile products isolated were Me_4Sn, Me_3SnCl, and traces of Me_2Hg (all identified by i.r.) as well as unchanged starting compounds. Yellow crystals of $Hg[Mn(CO)_5]_2$ (120 mg, 0·20 mmol) remained.

With methylmercuric bromide. The complex (155 mg, 0·43 mmol) was treated with MeHgBr (59 mg, 0·20 mmol) in THF (1·0 ml) to yield Me_4Sn and Me_3SnBr (identified by i.r. spectroscopy and g.l.c.), and $Hg[Mn(CO)_5]_2$ (112 mg, 0·19 mmol) (Found: C, 20·4; Hg, 33·6. Calc. for $C_{10}HgMn_2O_{10}$: C, 20·35; Hg, 34·0%). In a further reaction in the absence of THF, only starting materials were recovered after six days at 60°.

With dimethylmercury. No reaction occurred with Me_2Hg in THF during 1 week at 50°.

With phenylmercuric chloride. The complex (194 mg, 0·54 mmol) and PhHgCl (85 mg, 0·27 mmol) were shaken in THF (1·0 ml) to give a mixed white and yellow precipitate. After 26 days at 20° removal of volatiles [including unchanged $Me_3SnMn(CO)_5$ and Me_3SnCl], and extraction with benzene gave $Hg[Mn(CO)_5]_2$ (45 mg, 0·076 mmol, 56%); evaporation of the benzene extract afforded Ph_2Hg (22 mg, 0·063 mmol, 46%) (Found: C, 41·15; H, 2·95; Hg, 55·2. Calc. for $C_{12}H_{10}Hg$: C, 40·65; H, 2·8; Hg, 56·5%).

With trimethylsilane. No reaction occurred with Me_3SiH during 16 days at 60°.

With tributylstannane. The complex (190 mg, 0·53 mmol) and an excess of Bu_3SnH (*ca.* 0·5 ml) were heated at 60° for 14 days. Fractionation gave Me_3SnH (6 mg, 0·03 mmol), identified by its i.r. spectrum. Most of the $Me_3SnMn(CO)_5$ was recovered, along with large quantities of hydrogen and Bu_6Sn_2.

With trichlorosilane. The complex (145 mg, 0·40 mmol) was sealed in a Carius tube with $HSiCl_3$ (190 mg, 1·40 mmol) and heated at 50° for 5 days, when fractionation yielded an inseparable mixture of $HSiCl_3$ and $MeHSiCl_2$ (identified by its gas-phase i.r. spectrum). Sublimation of the residue gave unchanged $Me_3SnMn(CO)_5$ together with traces of $Me_2Sn[Mn(CO)_5]_2$ (identified mass spectroscopically) and left $Me_2ClSnMn(CO)_5$ (88 mg, 0·23 mmol) (Found: C, 22·15; H, 1·45; Cl, 9·1. $C_7H_6ClMnO_5Sn$ requires C, 22·15; H, 1·6; Cl, 9·35%). In a further experiment the complex (158 mg, 0·44 mmol) was irradiated (u.v.) for 6 h with $HSiCl_3$ (251 mg, 1·85 mmol) to give as products $MeHSiCl_2$, traces of Me_3SnCl, and $Me_2ClSnMn(CO)_5$ (150 mg, 0·40 mmol, 90%).

With group IVB tetrahalides. These reactions were initially investigated using ^1H n.m.r. spectroscopy. The complex (*ca.* 20 mg) was sealed in evacuated n.m.r. tubes with MCl_4 (M = C, Si, Ge, or Sn), reaction over 30—40 days at 60° being monitored by recording the spectrum, relative to external Me_4Si, at appropriate intervals. No reaction was observed with CCl_4 or $SiCl_4$; a slow reaction was evident with $GeCl_4$ but could not be followed satisfactorily owing to concurrent deterioration of the spectrum. With $SnCl_4$, however, a rapid reaction occurred and the following n.m.r. data were obtained: initially, one signal, $\tau = 8·65$, $J(^{119}SnCH) = 45$ Hz, $J(^{117}SnCH) = 42$ Hz; after 24 h, this signal had disappeared leaving new peaks at $\tau = 8·29$, $J(^{119}SnCH) = 45$ Hz, $J(^{117}SnCH) = 42$ Hz, and $\tau = 8·07$, $J(^{119}SnCH) = 99$ Hz, $J(^{117}SnCH) = 94$ Hz; slow disappearance of the τ 8·29 peak left only that at τ 8·07 after 30 days. Independent determination of the ^1H n.m.r. spectrum of $MeSnCl_3$ in $SnCl_4$ solution gave parameters identical with those of the τ 8·07 signal. Those at τ 8·65 and 8·29 are thus assigned to $Me_2ClSnMn(CO)_5$ and $MeCl_2SnMn(CO)_5$ respectively.

With stannic chloride. The complex (177 mg, 0·49 mmol) and $SnCl_4$ (1700 mg, 6·5 mmol) were allowed to react at 95° for 22 days; during this time colourless crystals and a pale yellow solid formed. Fractionation afforded $SnCl_4$, traces of $COCl_2$ and CCl_4, and $MeSnCl_3$; solid $Cl_3SnMn(CO)_5$ (150 mg, 0·36 mmol, 73%) remained. (All products were identified by i.r. spectroscopy).

With lithium tetrahydroaluminate. The complex (160 mg, 0·45 mmol) was stirred at room temperature for 2 h in di-n-butyl ether (8 ml) with $LiAlH_4$ (100 mg, 2·9 mmol); the mixture turned deep brown, and fractionation yielded Me_3SnH (47 mg, 0·29 mmol). A brown, pyrophoric residue remained.

With sodium tetrahydroborate. The complex (118 mg, 0·33 mmol) and $NaBH_4$ (100 mg, 2·7 mmol) were stirred at 20° for 1 h in a mixture of methanol (1 ml) and THF (5 ml). Some hydrogen was formed, and fractionation afforded solvents and Me_3SnH (detected by i.r. spectroscopy). The yellow residue turned orange in air, and gave a small amount of a carbonyl complex on extraction with cyclohexane; this was identified as $Mn_2(CO)_{10}$ (i.r.).

Reaction of Dimethylchlorostannylpentacarbonylmanganese with Lithium Tetrahydroaluminate.—$Me_2ClSnMn(CO)_5$ (150 mg, 0·40 mmol) and $LiAlH_4$ (200 mg, 5·8 mmol) were stirred at 20° in THF (6 ml) for 2 h. Removal of volatiles afforded an inseparable mixture of THF and dimethylstannane; the latter was identified by its gas-phase i.r. spectrum. I.r. spectroscopy also indicated that the metallic-looking, brown, involatile residue contained carbonyl groups but extraction with cyclohexane gave no soluble component.

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[24] D. M. Adams and A. Squire, *J. Chem. Soc.* (*A*), 1968, 2817.