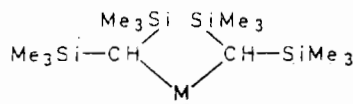


## Subvalent Group 4B Metal Alkyls and Amides. Part II.<sup>1</sup> The Chemistry and Properties of Bis[bis(trimethylsilyl)methyl]tin (II) and its Lead Analogue†

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Bis[bis(trimethylsilyl)methyl]tin,  $\text{SnR}_2$ , has an extensive chemistry, behaving as (i) a Lewis base, (ii) a Lewis acid, or (iii) undergoing oxidative addition (insertion reactions). The following complexes have been isolated, many as well characterised crystals. For class (i), these include ( $M = \text{Cr}$  or  $\text{Mo}$ )  $[\text{M}(\text{CO})_5(\text{SnR}_2)]$ , *trans*- $[\text{M}(\text{CO})_4(\text{SnR}_2)_2]$ ,  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{SnR}_2)]$ ,  $[\text{RhCl}(\text{PPh}_3)_2(\text{SnR}_2)]$ , and  $[\text{PtCl}(\text{PET}_3)(\text{SnR}_2)(\text{SnR}_2\text{Cl})]$ ; for class (ii), the readily thermally-dissociable 1:1 adducts with pyridine, 4-methylpyridine, or piperidine, and for class (iii),  $\text{SnR}_2(\text{A})\text{B}$  ( $\text{AB} = \text{HCl}, \text{HF}, \text{MeI}, \text{RCl}, \text{Cl}_2, \text{Br}_2, \text{O}_2, \text{CH}_2:\text{CMeCMe}:\text{CH}_2$ ,  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{X}]$  ( $\text{X} = \text{H}$  or  $\text{Me}$ ),  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{X}]$  ( $\text{X} = \text{Cl}$  or  $\text{Me}$ ),  $[\text{Fe}(\text{CO})_4\text{X}_2]$ , and  $[\text{PtCl}_2(\text{PET}_3)(\text{SnR}_2)]$ ). An interesting feature is the appearance in the  $^1\text{H}$  n.m.r. spectra of doublets characteristic of diastereotopically distinct  $\text{SiMe}_3$  groups in compounds of the form  $\text{SnR}_2(\text{A})\text{B}$  ( $\text{A} \neq \text{B}$ ). The complex  $[\text{Mo}(\text{CO})_5(\text{PbR}_2)]$  has also been obtained.

THE recently prepared<sup>1</sup> diamagnetic Group 4B alkyls,  $\text{M}[\text{CH}(\text{SiMe}_3)_2]_2$  ( $M = \text{Ge}, \text{Sn},$  or  $\text{Pb}$ ), (I), are formal analogues of singlet carbenes. Thus, whereas the structure of (I;  $M = \text{Sn}$ ) in the solid state has been shown by X-ray crystallography to be dimeric, both (I;  $M = \text{Sn}$ ) and (I;  $M = \text{Ge}$ ) are monomeric in benzene or cyclohexane, and other physical measurements imply that their structures in solution are angular.<sup>1</sup> Such a structural and electronic arrangement suggests that the molecules will be highly reactive compared with the tetraalkyl compounds of Group 4B. Four reaction types may



(I)  $M = \text{Ge}, \text{Sn},$  or  $\text{Pb}$

be considered. First, the molecules may act as Lewis bases and form complexes with various main-group or transition-metal acceptors, in a similar manner to the trivalent alkyls of the adjacent Group 5 elements. Secondly, the presence of the vacant  $p$  orbital may confer Lewis acidity on the molecule, and 1:1 adducts with bases may be formed. In this respect, the chemistry would parallel that of the highly reactive organometallic compounds of Group 3. Species (I) are also co-ordinately unsaturated, and a third reaction type could involve oxidative-addition reactions of molecules  $\text{XY}$  to give four-co-ordinate tetravalent derivatives  $\text{MR}_2(\text{X})\text{Y}$ . (Alternatively, this can be viewed as an 'insertion' of the  $\text{MR}_2$  moiety into the  $\text{X}-\text{Y}$  bond.) Similar reactions are known to occur readily for the trivalent Group 5 alkyls (although usually without oxidation: e.g.  $\text{PR}_3 + \text{RCl} \rightarrow [\text{PR}_4]\text{Cl}$ ) and other

† No reprints available.

<sup>1</sup> Part I, P. J. Davidson, D. H. Harris, and M. F. Lappert, preceding paper.

<sup>2</sup> J. D. Cotton, P. J. Davidson, D. E. Goldberg, M. F. Lappert, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1974, 893.

<sup>3</sup> P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1970, **92**, 2577.

<sup>4</sup> P. G. Harrison, *J.C.S. Chem. Comm.*, 1972, 544; P. G. Harrison and S. R. Stobart, *J.C.S. Dalton*, 1973, 940; P. G. Harrison, T. J. King, and J. A. Richards, *ibid.*, 1975, 2097.

<sup>5</sup> (a) K. D. Bos, E. J. Bulten, and J. G. Noltes, *J. Organometallic Chem.*, 1974, **67**, C13; (b) H.-J. Albert and U. Schröder, *ibid.*, 1973, **60**, C6; (c) K. D. Bos, E. J. Bulten, and J. G. Noltes, *ibid.*, 1972, **39**, C52; 1975, **99**, 397.

bivalent Group 4 compounds. Finally, cleavage reactions of the  $\text{M}-\text{C}$  bond must be considered, since these are well known throughout the Periodic Table, and not least for alkyls of  $\text{Sn}^{\text{IV}}$  or  $\text{Pb}^{\text{IV}}$ . A preliminary account has appeared.<sup>2</sup>

The only previous reports on the chemistry of bivalent Group 4B organometallic compounds have concerned bis(cyclopentadienyl)-tin<sup>3-6</sup> and -lead;<sup>7</sup> several of these papers appeared during the course of this work. In these molecules, the cyclopentadienyl group has  $\eta^5$  co-ordination, with a centrally  $\sigma$ -bonded interaction with the metal. The analogy between  $[\text{N}(\text{SiMe}_3)_2]^-$  and  $[\text{CH}(\text{SiMe}_3)_2]^-$  as ligands in transition-metal chemistry has been discussed<sup>8</sup> and compounds  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$  ( $M = \text{Ge}$ ,<sup>9</sup>  $\text{Sn}$ ,<sup>9,10</sup> and  $\text{Pb}$ <sup>9</sup>) have been prepared. Their chemistry should provide an interesting comparison with that of  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  discussed below.

### RESULTS AND DISCUSSION

**Lewis-base Behaviour.**—Previously, neutral donors could be classified according to whether the ligating atom was carbon (e.g.  $\text{CO}$ ,  $\text{RNC}$ , or nucleophilic carbene) or an element taken from Group 5B or 6B (e.g.  $\text{NH}_3$ ,  $\text{PPh}_3$ , or  $\text{SEt}_2$ ). We now extend the range of donors to include the heavy elements of Group 4B. There is thus an analogy between the Lewis-base behaviour of compounds (I) and tertiary phosphines; results for  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  are summarised in Scheme 1, and some data on the new stannio-complexes (previously named 'stannylenes' complexes by analogy with 'carbene' complexes<sup>2</sup>) and on a lead compound are in Table 1.

U.v. irradiation of  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  and  $[\text{M}(\text{CO})_6]$  ( $M = \text{Cr}$  or  $\text{Mo}$ ) in hexane solution gave moderate yields of the monostannio-complexes,  $[\text{M}(\text{CO})_5(\text{SnR}_2)]$  [ $R = \text{CH}(\text{SiMe}_3)_2$ ], formed by displacement of one molecule of carbon monoxide. Reactions between Lewis bases and Group 6A hexacarbonyls frequently lead to more than

<sup>6</sup> J. Doe, S. Borkett, and P. G. Harrison, *J. Organometallic Chem.*, 1973, **52**, 343.

<sup>7</sup> A. K. Holliday, P. H. Makin, R. J. Puddephatt, and J. D. Wilkins, *J. Organometallic Chem.*, 1973, **57**, C45.

<sup>8</sup> P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209; *Chem. Rev.*, 1976, **76**, 219.

<sup>9</sup> D. H. Harris and M. F. Lappert, *J.C.S. Chem. Comm.*, 1974, 895.

<sup>10</sup> C. D. Schaeffer, jun., and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1974, **96**, 7160.

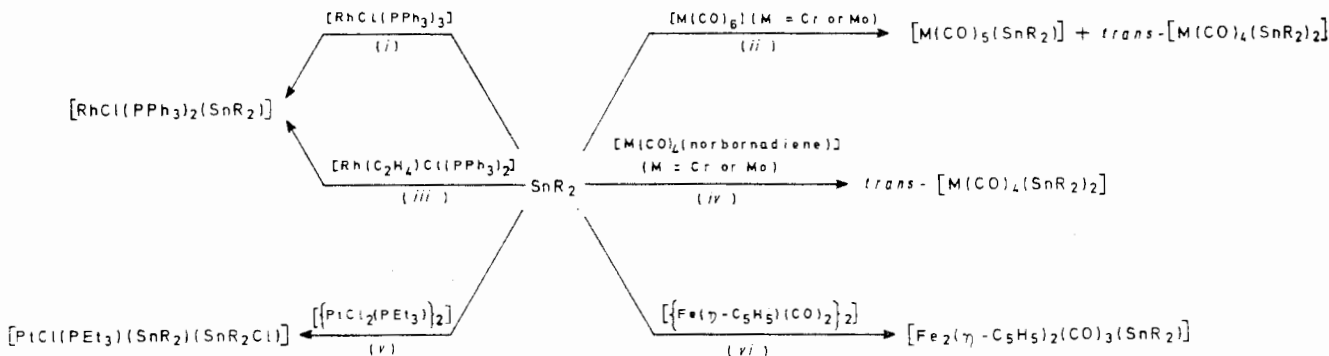
one carbonyl group being substituted,<sup>11</sup> and small amounts of *trans*-disubstituted compounds (identified by i.r.) were also formed. The disubstituted compounds were prepared more conveniently from the respective tetracarbonyl(norbornadiene)metal(0) complexes. Interestingly, no evidence for the formation of *cis* compounds was obtained, but the isolation of an exclusively *trans* product is not unexpected in view of the bulk of the Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> ligand. Bulky tertiary phosphines are known to give *cis-trans* mixtures in analogous ligand-displacement reactions.<sup>11</sup> The reaction between Pb[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and [Mo(CO)<sub>6</sub>] in hexane gave only a very low yield of the yellow monoplumbio-complex, [Mo(CO)<sub>5</sub>(PbR<sub>2</sub>)] [R = CH(SiMe<sub>3</sub>)<sub>2</sub>]. Extensive decomposition to metallic lead was induced by the irradiation,

[Mo(CO)<sub>5</sub>(SnR<sub>2</sub>)] [R = CH(SiMe<sub>3</sub>)<sub>2</sub>] give strong parent ions with appropriate isotope patterns. The main breakdown path for [Mo(CO)<sub>5</sub>(SnR<sub>2</sub>)] involves elimination of CH(SiMe<sub>3</sub>)<sub>2</sub> followed by progressive loss of CO. Although this is significant for [Cr(CO)<sub>5</sub>(SnR<sub>2</sub>)], fragmentation of CO from the parent ion is more important. Both complexes also showed breakdown by loss of Me from the parent ion followed by loss of CO. The strength of the M-Sn bond of these complexes is emphasised by the fact that neither complex showed significant concentrations of the [Sn{CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sup>+</sup> ion, the lower part of the spectra being dominated by [Si{CH(SiMe<sub>3</sub>)<sub>2</sub>}]<sup>+</sup> and its daughter products. The spectrum of the lead analogue was similar although there is some evidence for the elimination of [(Me<sub>3</sub>Si)<sub>2</sub>CHCH(SiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> from the

TABLE 1

Complex <sup>a</sup>	Colour	Physical data for stannio-complexes						
		M.p. (θ/°C)	$\bar{\nu}(\text{CO})^b$ / (cm <sup>-1</sup> )			$\tau(\text{Si-Me})^c$	$\tau(\text{Sn-CH})^c$	$J(^{117/119}\text{SnCH})/\text{Hz}$
[Cr(CO) <sub>5</sub> (SnR <sub>2</sub> )]	Orange	120	2 053s, 1 962s, 1 948vs, 1 942vs, 1 938(sh)			9.69	7.71	53
[Mo(CO) <sub>5</sub> (SnR <sub>2</sub> )]	Yellow	109—110	2 068s, 1 958vs, br, 1 950vs			9.70	7.83	47
<i>trans</i> -[Cr(CO) <sub>4</sub> (SnR <sub>2</sub> ) <sub>2</sub> ]	Orange	215—216	1 901vs			9.55	8.06	52
<i>trans</i> -[Mo(CO) <sub>4</sub> (SnR <sub>2</sub> ) <sub>2</sub> ]	Orange	204—205	1 919vs			9.58	7.85	48
[Mo(CO) <sub>5</sub> (PbR <sub>2</sub> )]	Yellow	93—94	2 072m, 1 960vs, 1 957vs					
[Fe <sub>2</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (CO) <sub>3</sub> (SnR <sub>2</sub> )]	Brown	167—170	1 939vs, 1 770s					
[RhCl(PPh <sub>3</sub> ) <sub>2</sub> (SnR <sub>2</sub> )]	Purple	184—187						

<sup>a</sup> R = CH(SiMe<sub>3</sub>)<sub>2</sub>; for a platinum(II) complex, see Table 2. <sup>b</sup> Hexane solution. <sup>c</sup> Benzene solution.



SCHEME 1 Lewis-base reactions of SnR<sub>2</sub> [R = CH(SiMe<sub>3</sub>)<sub>2</sub>]: (i) PhMe, 100 °C; (ii) n-C<sub>6</sub>H<sub>14</sub>, hv; (iii) C<sub>6</sub>H<sub>6</sub>, 20 °C; (iv) C<sub>6</sub>H<sub>6</sub>, reflux; (v) n-C<sub>6</sub>H<sub>14</sub>, 20 °C; (vi) n-C<sub>6</sub>H<sub>14</sub>, reflux.

and it is unlikely that further photochemical syntheses involving this ligand will be fruitful.

The thermal stability of the stannio- or plumbio-complexes is high, and there is no detectable decomposition below the melting point (above 200 °C for the disubstituted compounds). Solutions are air-sensitive (particularly that of the lead complex), but very much less so than solutions of the parent (I). The solids survive in air over several hours. The extremely high solubility (>1 g cm<sup>-3</sup> at 20 °C) of the complexes in non-polar solvents such as hexane or benzene is striking, and is presumably the result of the envelope of SiMe<sub>3</sub> on the periphery of the molecules. However, the complexes were readily crystallised from concentrated hexane solutions at -30 °C. The materials are virtually insoluble in ethanol, but are slowly decomposed thereby.

All the complexes are sufficiently volatile for mass spectra to be obtained. Both [Cr(CO)<sub>5</sub>(SnR<sub>2</sub>)] and

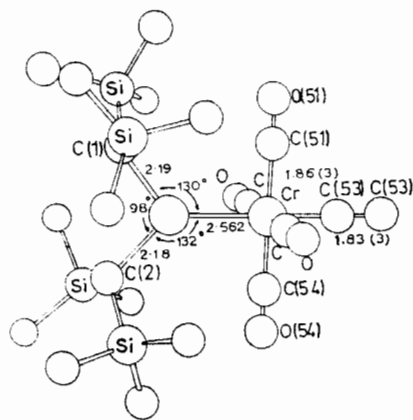
molecule. Mass spectra were also recorded for the bis-stannio-derivatives but some peaks at high *m/e* were poorly resolved. The peaks in the spectrum of the chromium complex were readily identified, except for the parent ion; the more difficult tabulation of the ions in the molybdenum spectrum was assisted by the possibility of counting the differences between some of the peaks. The spectra show many similarities to those of the mono derivatives, with loss of CH(SiMe<sub>3</sub>)<sub>2</sub> followed by progressive removal of CO for the Mo complex, and both this and loss of four CO from the parent ion for the chromium analogue. The main difference is the presence of significant concentrations of the [Sn{CH(SiMe<sub>3</sub>)<sub>2</sub>}]<sup>+</sup> ion in both spectra.

The solution i.r. spectra (Table 1) of the [M'(CO)<sub>5</sub>(MR<sub>2</sub>)] complexes in the carbonyl-stretching region exhibited features consistent with this formulation. Spectra of

<sup>11</sup> T. A. Manuel, *Adv. Organometallic Chem.*, 1965, **3**, 181.

$[M'(CO)_5L]$  species are often analysed on the basis of idealised  $C_{4v}$  point-group symmetry, but severe deviations were observed here. Thus, the  $b_1$  band, formally i.r. forbidden, had unusually strong intensity in  $[Cr(CO)_5(SnR_2)]$ . (However, it was not observed for the other complexes, probably because of accidental degeneracy with the  $e$  mode.) Splitting of the degenerate  $e$  mode was also observed. The single band observed for the bis complexes is consistent with a *trans* configuration. The general similarity of the observed spectra of the  $[M'(CO)_5(MR_2)]$  species to those of the trialkyl- and triaryl-phosphine analogues suggests that the  $\pi$ -acceptor ability of the two ligands may be similar (but see next paragraph). For the  $MR_2$  moiety, back donation of transition-metal  $d$  electrons into the empty  $np$  or higher energy  $nd$  levels on the Group 4B metal is symmetry allowed.

The crystal and molecular structure of  $[Cr(CO)_5(SnR_2)]$  (Figure) also suggests that  $\pi$  interaction between the



Crystal and molecular structure of  $[Cr(CO)_5\{Sn[CH(SiMe_3)_2]\}]$ ; important bond lengths (Å) and angles ( $^\circ$ )

Cr  $3d$  orbitals and vacant  $5p$  or  $5d$  orbitals on tin may be occurring.<sup>2</sup> The molecule has an essentially coplanar arrangement of the  $C_2SnCr$  unit and three carbonyl groups, an appropriate geometry for such an interaction, and the Sn-Cr bond length [2.562(5) Å] is significantly shorter than in  $[Cr(\eta-C_5H_5)(CO)_3(SnPh_3)]$  (2.85 Å)<sup>12</sup> and than the Sn-Mn bond length in  $[Mn(CO)_5(SnMe_3)]$  [2.674(2) Å].<sup>13</sup> The bond shortening could, however, simply reflect the change in the state of orbital hybridisation about the tin atom. The Sn-Cr bond length in  $[Cr(CO)_5(SnR_2)]$  is also shorter than in  $[Cr(CO)_5(SnBu_2py)]$  (py = pyridine) [2.654(3) Å]<sup>14</sup> for which the possibility of  $\pi$  interaction is lowered because of the base molecule attached to tin. The five Cr-C distances are very similar [CrC(51), 1.86(3); CrC(52), 1.84(3); CrC(53), 1.83(3); CrC(54), 1.89(4); CrC(55), 1.85(3) Å],

which suggests also that the  $SnR_2$  ligand is a good  $\pi$  acceptor, and indeed comparable to CO.

Two series of such base-stabilised complexes,  $[Cr(CO)_5(MR'_2 \cdot base)]$ <sup>15</sup> and  $[Fe(CO)_4(MR'_2 \cdot base)]$ ,<sup>16</sup> have recently been prepared by Marks and his co-workers (M = Ge or Sn). The stability of the complexes is dependent on the base strength (for Fe: py > Me<sub>2</sub>CO > tetrahydrofuran > OEt<sub>2</sub>), and attempts to remove the base molecule have led to decomposition. Such behaviour has encouraged the suggestion<sup>14</sup> that three-co-ordinate stannio-complexes of transition metals may only be isolable if the groups attached to tin possess a capacity for  $\pi$  interaction with the vacant  $p$  orbital, to give rise to an 'internal-stabilisation' effect similar to that operative in most carbenometal complexes.<sup>17</sup> Our work demonstrates that neither the ligating base nor internal  $\pi$  stabilisation is a necessary requirement if the alkyl group is very large. Marks' work did, however, suggest to us that the empty  $p$  orbital in the complex might still possess some Lewis acidity. However, we have not succeeded, in our preliminary experiments, in co-ordinating a base molecule to a stannio-complex. Interestingly, the photochemical reaction between  $SnR_2$  and  $[Mo(CO)_5(thf)]$  in tetrahydrofuran (thf) gave only  $[Mo(CO)_5(SnR_2)]$  (by i.r.). It is possible that ligation by thf is discouraged not only by a steric effect but also by back donation into the tin acceptor orbital from electrons in suitable transition-metal  $d$  orbitals.

Mono complexes of germanium(II) or tin(II) halides with Group 6 metal carbonyls were recently reported,<sup>18</sup> and provide a further illustration of the stability, in favourable situations, of germanio- or stannio-complexes without co-ordinated base. However, in some cases, the products (obtained after photochemical irradiation of the reactants in thf) also contained one mole of thf (presumably co-ordinated to the Group 4B element), for example as in  $[Cr(CO)_5(SnCl_2 \cdot thf)]$ . No theme of electronegativity or size of halogen or Group 4B metal seems to run through these observations.

The lack of reaction between  $[Mo(CO)_5(SnR_2)]$  and triphenylphosphine in refluxing benzene is of interest in two ways. First it provides a qualitative indication of the relative donor strength of the two ligands, and secondly it is a further indication of the lack of accessibility of the acceptor tin  $5p$  orbital in such complexes. Comparison with the similar chemistry of carbenometal complexes is of interest. The reaction of tertiary phosphines with  $[Cr(CO)_5\{CR'(OR)\}]$  at 60–80 °C in hexane or benzene gave a *cis-trans* mixture of  $[M(carbene)(CO)_4(PPh_3)]$  complexes.<sup>19</sup> However, at lower temperatures, thermally labile, ylide-type complexes,  $[M(CO)_5\{CR'(OR)(PR''_3)\}]$  were formed.<sup>20a</sup> A similar quinuclidine complex has also been isolated.<sup>20b</sup> These

<sup>12</sup> Yu. T. Struchkov, K. N. Anisimov, O. P. Osipova, N. E. Kolobova, and A. N. Nesmeyanov, *Proc. Acad. Sci. (U.S.S.R.)*, 1967, **172**, 15.

<sup>13</sup> R. F. Bryan, *J. Chem. Soc. (A)*, 1968, 696.

<sup>14</sup> M. D. Brice and F. A. Cotton, *J. Amer. Chem. Soc.*, 1973, **95**, 4529.

<sup>15</sup> T. J. Marks, *J. Amer. Chem. Soc.*, 1971, **93**, 7090.

<sup>16</sup> T. J. Marks and A. R. Newman, *J. Amer. Chem. Soc.*, 1973, **95**, 769.

<sup>17</sup> Cf. D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487.

<sup>18</sup> D. Uhlig, H. Belrens, and E. Lindner, *Z. anorg. Chem.*, 1973, **401**, 233.

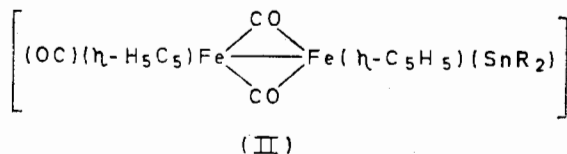
<sup>19</sup> E. O. Fischer and H. Fischer, *Chem. Ber.*, 1974, **107**, 657.

<sup>20</sup> (a) F. R. Kreissl, E. O. Fischer, C. G. Kreiter, and H. Fischer, *Chem. Ber.*, 1973, **106**, 1262; (b) F. R. Kreissl and E. O. Fischer, *ibid.*, 1974, **107**, 183.

aspects of the chemistry of the stannio- and plumbio-complexes may merit further investigation.

The  $^1\text{H}$  n.m.r. spectra of the stannio-complexes in benzene (see Table 1) are similar to that of the parent  $\text{SnR}_2$ ,<sup>1</sup> with the C-H resonance observed *ca.*  $\tau$  2 downfield from the  $\text{SiMe}_3$  singlet. The high solubility of these materials has allowed the identification of the  $^{117/119}\text{Sn}$  satellites about the C-H resonance. The  $^{119}\text{Sn}$  Mössbauer spectra of these complexes showed features consistent with a tin(II) formulation.<sup>21</sup>

The reaction between  $\text{SnR}_2$  and  $[\{\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\}_2]$  in refluxing hexane gave a brown crystalline solid, of stoichiometry  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{SnR}_2)]$ , in moderate yield. The i.r. spectrum (hexane solution) in the carbonyl-stretching region showed only one band in the terminal ( $1\,939\text{ cm}^{-1}$ ) and one in the bridging ( $1\,770\text{ cm}^{-1}$ ) region. The spectrum is similar to those obtained from the reactions between tertiary phosphines or phosphites with  $[\{\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\}_2]$ , where one of the terminal CO ligands is displaced.<sup>22</sup> (In some cases, the product exists partially as the non-bridged isomer.) The spectrum differs markedly from those<sup>23</sup> of the *cis* and *trans* isomers of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{GeMe}_2)]$ , in which the  $\text{GeMe}_2$  and one carbonyl group bridge the Fe-Fe bond,<sup>24</sup> and for each of which two, well-spaced, terminal bands are observed. Likewise the spectrum is different from those of complexes, *e.g.*  $[\{\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\}_2\text{SnCl}_2]$ , which are formed *via* 'insertion' of a tin(II) halide into the Fe-Fe bond, and which, of course, have no bridging carbonyl groups.<sup>25</sup> On these grounds, the formulation of the product as (II) appears reasonable.



The mass spectrum showed a parent ion and a fragmentation pattern consistent with the proposed formulation. The main path involves splitting of the bridge followed by breakdown of the resulting fragments; a strong signal corresponding to  $[\text{SnR}_2]^+$  was also present.

The failure of  $\text{PPh}_3$  to displace  $\text{SnR}_2$  from  $[\text{Mo}(\text{CO})_5(\text{SnR}_2)]$  has already been discussed. Interestingly, the reverse situation obtains in the reaction of a stoichiometric amount of  $\text{SnR}_2$  with Wilkinson's hydrogenation catalyst,  $[\text{RhCl}(\text{PPh}_3)_3]$ , in refluxing toluene, where small yields of the purple crystals of  $[\text{RhCl}(\text{PPh}_3)_2(\text{SnR}_2)]$  were obtained; the major product, however, was  $[\{\text{RhCl}(\text{PPh}_3)_2\}_2]$ . The reaction of  $\text{SnR}_2$  with  $[\text{Rh}(\text{C}_2\text{H}_4)\text{Cl}(\text{PPh}_3)_2]$  also gave the stannio-complex in low yield. It is possible that specific steric or solubilising effects (the rhodium complex is soluble in hydrocarbons) of interest in homogeneous catalysis may arise from the use of the  $\text{SnR}_2$  ligand.

Although the chloride bridge in  $[\{\text{RhCl}(\text{PPh}_3)_2\}_2]$  was

<sup>21</sup> Part III, J. D. Cotton, P. J. Davidson, J. D. Donaldson, M. F. Lappert, and J. Silver, following paper.

<sup>22</sup> R. J. Haines and A. L. du Preez, *Chem. Comm.*, 1968, 1513.

<sup>23</sup> M. D. Curtis and R. C. Job, *J. Amer. Chem. Soc.*, 1972, **94**, 2153.

not readily cleaved by  $\text{SnR}_2$ , reaction with the similarly bridged  $[\{\text{PtCl}_2(\text{PEt}_3)_2\}_2]$  occurred readily in hexane at room temperature. Four molecules of  $\text{SnR}_2$  reacted per mole of platinum complex to give  $[\text{PtCl}(\text{PEt}_3)(\text{SnR}_2)(\text{SnR}_2\text{Cl})]$ ; the latter is formed either by successive cleavage of the bridge by  $\text{SnR}_2$  *trans* to  $\text{PEt}_3$ , and 'insertion' of a further mole of  $\text{SnR}_2$  into one of the terminal Pt-Cl bonds, or by the alternative sequence. This reaction illustrates that the co-ordination chemistry of the heavy-metal donor ligands may be more complicated in scope than that of tertiary phosphines, because of the greater tendency of the former ligands to achieve a higher oxidation state and still be able to bind to a metal site. In accord with our formulation of the  $\text{PtSn}_2$  complex, the Mössbauer spectrum<sup>21</sup> showed isomer shifts characteristic both of  $\text{Sn}^{\text{II}}$  and  $\text{Sn}^{\text{IV}}$ . The  $^1\text{H}$  n.m.r. spectrum is complex: three  $\text{SiMe}_3$  resonances of intensity 1:1:2 were observed. The larger resonance is assigned to the  $\text{SiMe}_3$  protons in the co-ordinated  $\text{Sn}^{\text{II}}\text{R}_2$  group, and the two equivalent smaller peaks to the  $\text{Sn}^{\text{IV}}\text{R}_2\text{Cl}$  system. Similar non-equivalence is observed in other complexes containing the  $\text{SnR}_2\text{Me}$  or  $\text{SnR}_2\text{Cl}$  moiety and is associated with diastereotopic  $\text{SiMe}_3$  environments consequent on a high inversion barrier at tin (see below).

The Lewis-base reactions of cyclopentadienyls of  $\text{Sn}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  with certain main-group metal Lewis acids suggested that similar extension to  $\text{SnR}_2$  might be profitable. Bis(cyclopentadienyl)tin,<sup>3</sup> like the lead analogue,<sup>7</sup> forms a solid 1:1 complex with boron trifluoride at room temperature. In  $\text{Sn}(\text{C}_5\text{H}_4\text{Me})_2 \cdot \text{AlCl}_3$ <sup>6</sup> and  $\text{Sn}(\text{C}_5\text{H}_5)_2 \cdot \text{BF}_3$ ,<sup>3</sup> the angular sandwich structure is retained in the adduct. [It is interesting, however, that in the related molecules  $\text{In}(\text{C}_5\text{H}_5) \cdot \text{BX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or Me}$ ) the cyclopentadienyl group is  $\sigma$  bonded.<sup>26</sup>] However, boron trifluoride and  $\text{SnR}_2$  in  $\text{OEt}_2$  solution did not appear to react over the temperature range  $-30$  to  $50^\circ\text{C}$ , the intense red colour of  $\text{SnR}_2$  persisted and the starting material was recovered unchanged. With boron trichloride, an immediate reaction in 1:1 stoichiometry occurred in hexane solution below  $-30^\circ\text{C}$  to give a white precipitate. Decomposition commenced on warming the mixture to room temperature. The presence of several alkyltin(IV) chlorides was inferred from  $^1\text{H}$  n.m.r. spectra. Although a small amount of  $\text{SnR}_2\text{Cl}_2$  was isolated, complete separation of the complex mixture was not achieved.

*Lewis-acid Behaviour.*—The apparent energetic inaccessibility of the vacant  $5p$  orbital in the co-ordinated  $\text{SnR}_2$  molecule, as shown for example by the poor acceptor power of  $[\text{Cr}(\text{CO})_5(\text{SnR}_2)]$ , suggested that the Lewis acidity of the free molecules (I) might be low. Generally this has been confirmed. Although 1:1 complexes were formed between  $\text{SnR}_2$  and 4-methylpyridine, pyridine, or piperidine, in hexane at  $-30^\circ\text{C}$ , the solids

<sup>24</sup> R. D. Adams, M. D. Brice, and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1080.

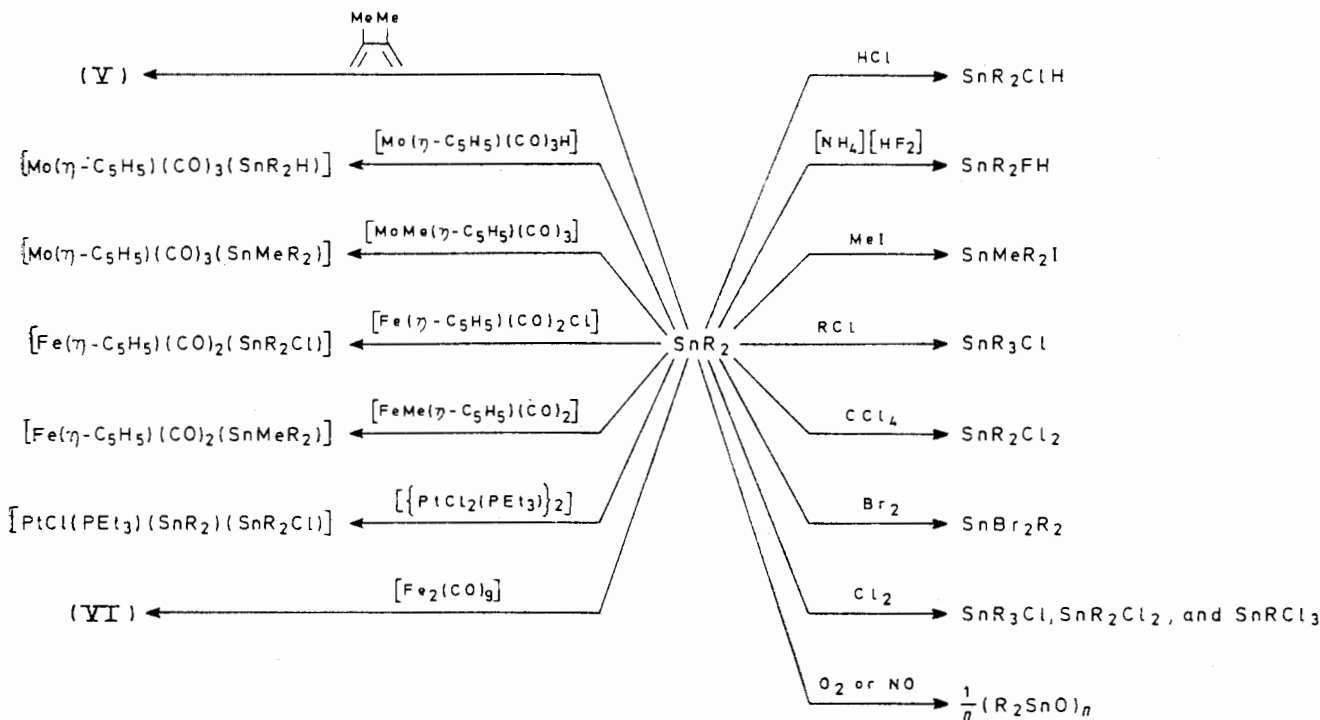
<sup>25</sup> N. Fliteroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1966, 1130.

<sup>26</sup> J. G. Contreras and D. G. Tuck, *Inorg. Chem.*, 1973, **12**, 2596.

(orange for 4-methylpyridine or pyridine, and white for piperidine) were unstable even at room temperature and difficult to characterise. On warming in sealed tubes, the solids gradually turned red ( $\text{SnR}_2$  formation) with concurrent production of the base. The process was reversed by cooling. A 1:1 complex between  $\text{PbR}_2$  and 4-methylpyridine appeared to form in solution but the product was not isolated. The bases  $\text{NEt}_3$ ,  $\text{NMe}_2\text{H}$ ,  $\text{PPh}_3$ ,  $\text{PEt}_3$ , 2,2'-bipyridyl, or quinuclidine did not react detectably with  $\text{SnR}_2$  in hexane at  $-30^\circ\text{C}$ , although  $\text{PMe}_2\text{Ph}$  caused some discharge of the intense red colour at this temperature. Rationalisation of these data is not obvious. The efficiency of complex formation bears no direct relation, for example, to the aqueous base strength, but then, presumably, the heterocyclic nitrogen bases are sterically favoured. However, if such effects

characterisation of the product was not attempted, but  $\text{SnBrR}_3$  was isolated after bromine addition to the solution, and it is probable that  $\text{Li}(\text{SnR}_3)$  is the intermediate species;  $\text{Li}(\text{SnEt}_3)$ <sup>28</sup> and  $\text{Li}(\text{SnPh}_3)$ <sup>29</sup> are formed in an analogous fashion. Attempts by iodination to form a derivative of the pale-brown solution species present after the addition of 3 mol of  $\text{LiR}$  to lead(II) chloride were unsuccessful because of complete Pb-C bond cleavage. The discharge of the characteristic violet colour of  $\text{PbR}_2$  by  $\text{LiR}$  and the fact that lithium triarylpbumbate(II) derivatives are known to be accessible by this method,<sup>30</sup> suggest strongly that  $\text{Li}(\text{PbR}_3)$  was formed.

*Oxidative-addition (or Insertion) Reactions.\**—The planning of our earliest experiments in this area was determined largely by the concept that the substantial steric



SCHEME 2 Oxidative-addition (or insertion) reactions of  $\text{SnR}_2$  [R = CH(SiMe<sub>3</sub>)<sub>2</sub>]

are important, the lack of reaction with quinuclidine is surprising (this is, however, a relatively poor proton acceptor). The colour of the pyridine complexes suggests a charge-transfer interaction between the ring and tin orbitals. The contrast with the behaviour of tin(II) halides which form numerous, thermally stable, 1:1 adducts with nitrogen or oxygen bases is marked.<sup>27</sup>

In the preparation of  $\text{SnR}_2$  by reaction of  $\text{SnCl}_2$  and  $\text{LiR}$ , addition of a third mole of  $\text{LiR}$  in the  $\text{SnCl}_2$ - $\text{LiR}$  reaction caused discharge of the red colour from the solution which then became pale brown. Direct

effect of the CH(SiMe<sub>3</sub>)<sub>2</sub> group was crucial both in stabilising bivalent Group 4B alkyls and in influencing strongly their Lewis acidity and basicity. Accordingly, reactions with small molecules were first explored; all the reactions of  $\text{SnR}_2$  are summarised in Scheme 2. Hydrogen chloride in diethyl ether reacted rapidly with  $\text{SnR}_2$  at room temperature in 1:1 stoichiometry to form  $\text{SnR}_2\text{ClH}$ , which was isolated as a white solid. A bulky analogue,  $\text{SnBu}^t_2\text{ClH}$ , was reported previously.<sup>31</sup> The <sup>1</sup>H n.m.r. spectrum of  $\text{SnR}_2\text{ClH}$  showed two equivalent peaks in the region of the SiMe<sub>3</sub> protons. Several explanations were considered to account for this observation, but we now recognise that all compounds so far prepared of the

<sup>27</sup> H. Gilman and S. D. Rosenberg, *J. Amer. Chem. Soc.*, 1952, **74**, 531.

<sup>28</sup> H. Gilman, L. Summers, and R. W. Leeper, *J. Org. Chem.*, 1952, **17**, 630.

<sup>31</sup> A. K. Sawyer and H. G. Kuivila, *Chem. and Ind.*, 1961, 260.

\* The oxidation state of the tin atom, for many of the compounds discussed in this section, has been established as IV by <sup>119</sup>Sn Mössbauer spectroscopy.<sup>21</sup>

<sup>27</sup> J. S. Morrison and H. M. Haendler, *J. Inorg. Nuclear Chem.*, 1967, **29**, 393.

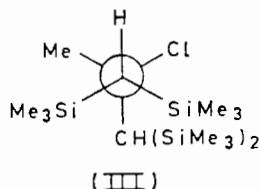
<sup>28</sup> H. Gilman and S. D. Rosenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 250.

TABLE 2  
 Physical data for oxidative-addition products

Compound <sup>a</sup>	Colour	M.p. (θ/°C)	Characteristic i.r. absorptions (cm <sup>-1</sup> )	<sup>1</sup> H N.m.r.				
				Si-Me	Sn-CH	Sn-H	Sn-Me	C <sub>4</sub> H <sub>4</sub>
[PtCl(PEt <sub>3</sub> )(SnR <sub>2</sub> )(SnR <sub>2</sub> Cl)]	Yellow	154—156	ν(SnCl), ν(PtCl) 285(sh), 275m	9.37, 9.67				
[{Fe(CO) <sub>4</sub> } <sub>2</sub> SnR <sub>2</sub> ]	Orange	139—141 (decomp.)	ν(CO) 2 086m, 2 035s, 2 019m, 2 003(sh), 1 998s, 1 987w	9.60	9.73			
[Fe(η-C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (SnR <sub>2</sub> Cl)]	Orange	119.5—120	ν(CO) 2 020w, 2 008s, 1 976w, 1 962s; ν(SnCl) 285m, 280(sh)	9.40, 9.57	9.20			5.51
[Fe(η-C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (SnMeR <sub>2</sub> )]	Yellow-brown	141—142	ν(CO) 1 997s, 1 949s	9.55, 9.57	9.37(?)			5.63
[Mo(η-C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (SnMeR <sub>2</sub> )]	Brown	102—105 (decomp.)	ν(CO) 2 001s, 1 998(sh), 1 930m, 1 922(sh), 1 906s, 1 902(sh)	9.6 <sup>b</sup>	9.62		9.23	5.16
[Mo(η-C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (SnR <sub>2</sub> H)]	Pale yellow	128—130	ν(CO) 1 996(sh), 1 944vs, 1 927(sh), 1 922s, 1 905(sh), 1 903vs	9.53, 9.56	9.83	3.93		6.28
SnR <sub>2</sub> ClH	Colourless	53—54	ν(SnH) 1 845m,br; ν(SnCl) 342(sh), 335w	9.61, 9.75	9.95 <sup>c</sup>	2.21 <sup>c</sup>		
SnR <sub>2</sub> FH	Colourless	90—93 (decomp.)	ν(SnH) 1 832m,br					
SnBrR <sub>2</sub>	Colourless	204—205	ν(SnBr) 230	9.50	9.58			
SnR <sub>2</sub> Cl	Colourless	191—193	ν(SnCl) 315	9.55	9.62			
SnMeR <sub>2</sub>	Colourless	69—71		9.38, 9.67	9.33(?)		8.85	
SnBr <sub>2</sub> R <sub>2</sub>	Colourless	108—109	ν(SnBr) 230	9.59	9.62	9.30		

<sup>a</sup> R = CH(SiMe<sub>3</sub>). <sup>b</sup> Broad and probably could be resolved into a doublet. *J*(H<sub>2</sub>SnCH) ca. 1.5 Hz.

type Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(X)Y show a doublet SiMe<sub>3</sub> <sup>1</sup>H n.m.r. signal, which we attribute to the prochiral tetrahedral tin centre, as a result of which there are two magnetically distinct diastereotopic sets of SiMe<sub>3</sub> environments [see (III)]. Chemical shift non-equivalence of diastereotopic nuclei has been discussed.<sup>32</sup>



In organotin chemistry, the phenomenon is well known for highly-hindered neophyltin compounds such as SnMePh(CH<sub>2</sub>CMe<sub>2</sub>Ph)Cl or SnMe<sub>2</sub>Ph(CH<sub>2</sub>CHMePh).<sup>33</sup> However, without bulky groups at tin there is optical instability possibly associated with the formation of five-coordinate chloride-bridged bi- or poly-nuclear tin compounds. Previous examples of diastereotopy in organotin compounds appear to have been restricted to molecules of type R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>MM'A<sub>2</sub>X (the two groups A are diastereotopic) in which there is one chiral centre (tin or carbon).<sup>34</sup> [Alternatives which we considered, but discarded, for the non-equivalence among the SiMe<sub>3</sub> groups were (i) due to restricted rotation about the Sn-C bonds, or (ii) the possibility that the compound SnR<sub>2</sub>ClY decomposes completely in solution to SnR<sub>2</sub>Cl<sub>2</sub> and SnR<sub>2</sub>Y<sub>2</sub>, but for Y = H the absence of a Sn-H resonance in the region characteristic of dialkyltin dihydrides (ca. τ 5.5) makes (ii) unlikely.] It is noteworthy that the SnCH resonance, which shows a small coupling *J*(HSnCH) of 1.5 Hz, occurs just upfield of the SiMe<sub>3</sub> signal instead of ca. τ 1.5—2.0 below, as in free or complexed SnR<sub>2</sub>; this shift is commonly observed for all the tin(IV) systems formed.

The related compound SnR<sub>2</sub>FH has also been prepared in ether solution from suspended [NH<sub>4</sub>][HF<sub>2</sub>] as an indirect source of HF. The solid, which was obtained after low-temperature crystallisation, was stable at room temperature, but solutions in benzene (for n.m.r.) decomposed rapidly. A similar oxidative-addition of

hydrogen chloride to PbR<sub>2</sub> was unsuccessful and lead(II) chloride was produced. The different reaction course is probably caused by the greater reactivity and relative weakness of the Pb-C bond compared with Sn-C, but the reluctance of lead to achieve the higher oxidation state may also be important. The reaction of SnR<sub>2</sub> with hydrogen halides is in marked contrast with the behaviour<sup>5c</sup> of Sn(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> which is protolysed by hydrogen chloride to give initially Sn(C<sub>5</sub>H<sub>5</sub>)Cl and cyclopentadiene and finally tin(II) chloride. The compound Sn(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> is, in fact, easily protolysed by a variety of alcohols, carboxylic acids, hydroxylamines, etc., and such reactions are sometimes useful in the preparation of otherwise poorly accessible tin(II) salts.<sup>4</sup> The facile cleavage, compared with SnR<sub>2</sub>, is probably a function of the greater basicity of the cyclopentadienide anion, and the greater ionic character of the Sn-C bond in Sn(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>.

We had to modify somewhat our view of the importance of steric effects when we found that SnR<sub>2</sub> reacted readily with either MeI or (Me<sub>3</sub>Si)<sub>2</sub>CHCl (RCl), to give SnMeR<sub>2</sub>I or SnR<sub>3</sub>Cl, respectively. The <sup>1</sup>H n.m.r. spectrum of SnMeR<sub>2</sub>I, which has the typical physical properties of a trialkyltin halide, showed two equivalent SiMe<sub>3</sub> resonances, which again is attributed to the prochiral tin atom. The hypothesis that the inequivalence might be due to substantial restricted Sn-C rotation is gainsaid by the observation that only one resonance in the SiMe<sub>3</sub> region was observed for SnR<sub>3</sub>Cl or SnBrR<sub>3</sub> for which, at first sight, greater steric interactions might have been expected. The high melting points (ca. 200 °C) recorded for both these compounds (cf. SnMe<sub>3</sub>Cl, 37; SnBrMe<sub>3</sub>, 27 °C) and the quadrupole splitting values obtained from their Mössbauer spectra<sup>21</sup> suggest that the compounds may in part relieve steric strain by becoming partially ionic and hence become compressed tetrahedra. Structural studies to explore this possibility are in progress. Bis(cyclopentadienyl)-tin also undergoes oxidative-addition reactions of this type, but at higher temperatures: methyl iodide reacts at 50 °C to give SnMe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>I, and ethyl iodide at 80 °C.<sup>5c</sup> A similar reaction of methyl iodide with PbR<sub>2</sub> rapidly gave PbI<sub>2</sub> at room temperature. Even when warmed, a solution of PbR<sub>2</sub> and RCl in hexane

<sup>32</sup> K. Mislow and M. Raban, *Topics Stereochem.*, 1967, 1, 1.

<sup>33</sup> G. J. D. Peddle and G. Redl, *J. Amer. Chem. Soc.*, 1970, 92, 365.

<sup>34</sup> M. Gielen and H. Mokhtar-Jamai, *J. Organometallic Chem.*, 1975, 91, C33 and refs. therein.

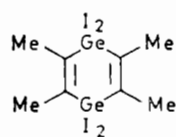


did not react, again reflecting the difficulty of oxidation to  $\text{Pb}^{\text{IV}}$ .

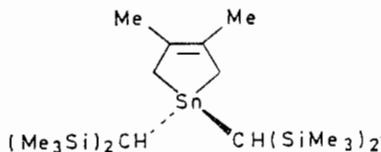
It is noteworthy that bromine adds to  $\text{SnR}_2$  in benzene at  $10^\circ\text{C}$ , to give  $\text{SnBr}_2\text{R}_2$  and that Sn-C bond cleavage was not detected. The reaction with chlorine (in hexane at  $-30^\circ\text{C}$ ) was more complex. A mixture of  $\text{SnR}_3\text{Cl}$ ,  $\text{SnR}_2\text{Cl}_2$ , and  $\text{SnRCl}_3$  was detected by  $^1\text{H}$  n.m.r. but  $\text{SnCl}_2$  was not formed. Similarly, the reaction of iodine with  $\text{Sn}(\text{C}_5\text{H}_5)_2$  led to  $\text{Sn}(\text{C}_5\text{H}_5)_2\text{I}_2$  and its redistribution products,<sup>5a</sup> but under milder conditions, in benzene solution at  $5-10^\circ\text{C}$ ,  $\text{Sn}(\text{C}_5\text{H}_5)_2$  and  $\text{X}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ) gave  $\text{Sn}(\text{C}_5\text{H}_5)_2\text{X}_2$  as the sole product.<sup>5b</sup>

The material obtained by the controlled oxygenation of  $\text{SnR}_2$  in hexane solution was a gummy white solid which analysed for  $\text{SnR}_2\text{O}$  and was presumably polymeric. The same material was obtained from the reaction of  $\text{SnR}_2$  with  $\text{NO}$ . Immediate reaction occurred between chlorinated solvents and  $\text{SnR}_2$  to give mixtures of alkyltin chlorides. Crystals of  $\text{SnR}_2$  were, however, only slowly decomposed by degassed water or ethanol, probably on account of insolubility. However, a methanol-hexane mixture reacted instantly.

Carbene analogues in Group 4B often undergo addition reactions to conjugated dienes or acetylenes. For example,  $\text{GeI}_2$  reacts with buta-1,3-diene and its substituted derivatives to give the metallacyclic products of 1,3-addition<sup>35</sup> and with but-2-yne to yield (IV).<sup>36</sup> The compound  $\text{SnR}_2$  underwent a similar reaction with 2,3-dimethylbuta-1,3-diene giving (V), but there was no



(IV)



(V)

detectable reaction with either tetraphenylbuta-1,3-diene or diphenylacetylene. The compound  $\text{Sn}(\text{C}_5\text{H}_5)_2$  reacts readily with diethyl acetylenedicarboxylate,<sup>5a</sup> and preliminary experiments indicated that  $\text{SnR}_2$  was similarly reactive.

Insertion reactions of tin(II) halides into a variety of transition-metal-transition-metal (*e.g.*<sup>25</sup> Fe-Fe), transition-metal-halogen (*e.g.*<sup>37</sup> Fe-Cl), and transition-metal-carbon (*e.g.*<sup>38</sup> Fe-C) bonds have been extensively explored in recent years. Similar insertion behaviour of  $\text{SnR}_2$  has now been observed in several cases (Scheme 2). Reaction occurred rapidly in benzene at room temperature, with  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{H}]$ , to give colourless crystals of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{SnR}_2\text{H})]$  in high yield. The complex is air-sensitive, particularly in solution, but the solid is thermally stable at room temperature. It

<sup>35</sup> P. Mazerolles and G. Manuel, *Bull. Soc. chim. France*, 1966, 327.

<sup>36</sup> J. V. Scibelli and M. D. Curtis, *J. Organometallic Chem.*, 1972, 40, 317.

<sup>37</sup> M. J. Mays and S. M. Pearson, *J. Chem. Soc. (A)*, 1969, 138.

<sup>38</sup> B. J. Cole, J. D. Cotton, and D. McWilliam, *J. Organometallic Chem.*, 1974, 64, 2231.

<sup>39</sup> D. J. Cardin, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc. (A)*, 1970, 2594.

shows some interesting spectroscopic features; the i.r. spectrum in the carbonyl-stretching region showed three major bands, close to those of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{SnMe}_3)]$ ,<sup>39</sup> each with a shoulder to higher wavenumber. The extra absorptions are probably due to rotational isomers arising from restricted rotation about the Mo-Sn bond, as in  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{SiMe}_3\text{Cl})]$ .<sup>40</sup> The  $^1\text{H}$  n.m.r. spectrum, in which two equivalent  $\text{SiMe}_3$  resonances were observed, but only one  $\text{C}_5\text{H}_5$  resonance, is independent of the above conformational effect. As in all the oxidative-addition products, the CH  $^1\text{H}$  n.m.r. signal occurred just upfield of the  $\text{SiMe}_3$  resonance. It is of some interest that both the former and the SnH signal at  $\tau$  3.93 showed no indication of  $\text{HSnCH}$  coupling. The close proximity of the CH signal (one proton) to the  $\text{SiMe}_3$  doublet (18 protons) precluded positive identification of  $J(^{117/119}\text{SnCH})$  but  $^{117/119}\text{SnH}$  satellites were found by using a concentrated solution and gave values of  $J(^{119}\text{SnH})$  and  $J(^{117}\text{SnH})$  of 1450 and 1386 Hz, respectively. The mass spectrum did not show a significant parent ion, although this may have been obscured by the ion at highest  $m/e$  corresponding to  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{SnR}_2)]^+$ . The isotope patterns of some of the peaks at relatively high  $m/e$  seem to indicate loss of Me and  $(\text{Me} + \text{CO})$  from both the  $\text{P}^+$  and  $[\text{P} - \text{I}]^+$  ions. Other important features are loss of  $\text{CH}(\text{SiMe}_3)_2$  and  $\text{CH}(\text{SiMe}_3)_2 + \text{CO}$  and also the presence of a very strong signal due to  $[\text{SnR}_2]^+$ .

Few tin-transition-metal complexes containing Sn-H bonds have been reported. The attempted protolysis of  $\text{Sn}(\text{C}_5\text{H}_5)_2$  with  $[\text{Mn}(\text{CO})_5\text{H}]$  gave the interesting species  $[\{\text{Mn}(\text{CO})_5\}_4\text{Sn}_2\text{H}_2]$  containing a Sn-Sn bond.<sup>41</sup> The air-stable  $[\{\text{Co}(\text{CO})_3(\text{PBUt}_3)\}_3\text{SnH}]$ <sup>42</sup> and a series of Sn-Mn complexes have been prepared.<sup>43</sup> It is of interest also that  $\text{SnR}_2$  inserted smoothly into the Mo-C bond of  $[\text{MoMe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ . In  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{SnMe}_2)]$ , surprisingly, only one broad  $\text{SiMe}_3$  resonance was observed in the  $^1\text{H}$  n.m.r. spectrum, but for this experiment the performance of the spectrometer was unsatisfactory. The i.r. spectrum again showed the two sets of absorptions associated with restricted rotation about the Sn-Mo bond. Likewise,  $\text{SnR}_2$  reacted rapidly with  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$  or  $[\text{FeMe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  in benzene to give the Fe-Cl or Fe-Me insertion products, together with a small amount of  $[\{\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\}_2]$ . For  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{SnMe}_2)]$  two  $\text{SiMe}_3$  resonances were observed in the  $^1\text{H}$  n.m.r. spectrum, but only one set of carbonyl absorptions in the i.r. On the other hand,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{SnR}_2\text{Cl})]$  showed both the two equivalent  $\text{SiMe}_3$  resonances, and two sets of carbonyl absorptions, the latter presumably due to rotational isomers, as in the case of the molybdenum complexes.

The recent isolation of base-stabilised stannio-complexes, *e.g.*  $[\text{Fe}(\text{CO})_4(\text{SnBu}_2\text{py})]$ ,<sup>16</sup> led us to seek

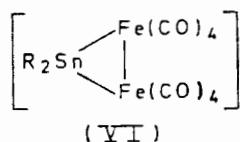
<sup>40</sup> W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1967, 89, 2773.

<sup>41</sup> K. D. Bos, E. J. Bulten, J. G. Noltes, and A. L. Spek, *J. Organometallic Chem.*, 1974, 71, C52.

<sup>42</sup> P. Hackett and A. R. Manning, *J. Organometallic Chem.*, 1974, 66, C1.

<sup>43</sup> J. P. Collman, J. K. Hoyano, and D. W. Murphy, *J. Amer. Chem. Soc.*, 1973, 95, 3424.

the preparation of the parent complex as in  $[\text{Fe}(\text{CO})_4(\text{SnR}_2)]$ . The complex  $[\text{Fe}_2(\text{CO})_9]$  was chosen as the 'source' of  $[\text{Fe}(\text{CO})_4]$  on the basis of previous work, e.g. reactions with a phosphine<sup>44</sup> or pyridine.<sup>45</sup> Unexpectedly, we found that the reagents had reacted in 1:1 stoichiometry and the product is formulated as (VI). Thus, the mass spectrum showed a parent ion



and ions corresponding to progressive loss of eight carbonyl groups, and the base peak was  $[\text{Fe}(\text{SnR}_2)]^+$ . (The breakdown pattern below this ion was complex; there was no significant signal corresponding to  $[\text{SnR}_2]^+$ .) Six terminal carbonyl bands were observed in the i.r. spectrum, but no absorptions associated with bridging carbonyls. The <sup>119</sup>Sn Mössbauer spectral parameters<sup>21</sup> characterise the oxidation state of tin as iv. The formation of (VI) may thus be regarded as displacement of 1 CO from  $[\text{Fe}_2(\text{CO})_9]$  by  $\text{SnR}_2$  with the two remaining bridging CO groups originating from terminal positions. A few similar complexes, e.g.  $[\text{Fe}_2(\text{CO})_8(\text{GePh}_2)]$  (having seven terminal CO absorptions)<sup>46</sup> and  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{GeMe}_2)]$ ,<sup>22</sup> containing a single  $\text{MM}'_2$  ring system have been reported previously. Multiple three-membered metal-ring systems are more common, e.g.  $[\{\text{Fe}(\text{CO})_4\}_4\text{Sn}]$ <sup>47</sup> and  $[\{\text{Ru}(\text{CO})_3(\text{GeMe}_2)\}_3]$ .<sup>48</sup> There was i.r. spectroscopic evidence that a small amount of  $[\text{Fe}(\text{CO})_4(\text{SnR}_2)]$  had also formed. Interestingly, the reaction of a tin(II) halide (Cl or Br),<sup>49</sup>  $\beta$ -ketoenolate,<sup>46</sup> or  $\eta$ -cyclopentadienide<sup>50</sup> with  $[\text{Fe}_2(\text{CO})_9]$  gave  $[\text{Fe}(\text{CO})_4(\text{SnX}_2)]$ , which are dimeric in the solid (the X-ray structure for  $\text{X} = \eta\text{-C}_5\text{H}_5$  shows an  $\text{FeSnFeSn}$  ring),<sup>50</sup> associated in chloroform, but monomeric in pyridine.

The several oxidative-addition reactions described for  $\text{SnR}_2$  seem appropriate to its monomeric nature. Nevertheless, at least in solution, both cyclic and chain polymers of dialkyltin and diaryltin undergo some similar reactions with small molecules; e.g.<sup>50</sup> ethyl iodide reacts with  $(\text{Et}_2\text{Sn})_n$  to give  $\text{SnEt}_3\text{I}$ . The reactivity of these polymeric species has been reviewed.<sup>51</sup> The mechanism of such reactions is not understood, but it is possible that partial rearrangement of the polymers occurs in solution with formation of discrete dialkyl- or diaryl-tin monomers.

#### EXPERIMENTAL

All the experiments were carried out in Schlenk glassware under an atmosphere of high-purity argon.<sup>1</sup> Solvents were freshly distilled from appropriate drying agents as

\* 1 mmHg  $\approx$  13.6  $\times$  9.8 Pa.

<sup>44</sup> P. S. Braterman and W. J. Wallace, *J. Organometallic Chem.*, 1971, **30**, C17.

<sup>45</sup> F. A. Cotton and J. A. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 3438.

<sup>46</sup> E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Amer. Chem. Soc.*, 1968, **90**, 3587.

<sup>47</sup> P. Woodward and P. F. Lindley, *J. Chem. Soc. (A)*, 1967, 382.

required. Melting points were recorded in evacuated tubes and are uncorrected. Microanalyses were either at the Microanalytical Laboratory at the University of Sussex or at the Bernhardt Laboratory. Molecular weights were determined by cryoscopy in benzene under argon, or mass spectrometrically (m.s.) (A.E.I. MS9) when the strongest peak in the parent-ion isotope pattern was recorded. Infrared spectra were recorded on Perkin-Elmer 257 or 457 spectrometers, and <sup>1</sup>H n.m.r. spectra on Varian T60, A60, or HA100 instruments.

*Preparation of Stannio- and Plumbio-complexes.*—(a) *{Bis[bis(trimethylsilyl)methyl]stannio}pentacarbonylchromium(0)*,  $[\text{Cr}(\text{CO})_5(\text{SnR}_2)]$ . Chromium hexacarbonyl (0.548 g, 2.49 mmol) was added to a solution of bis[bis(trimethylsilyl)methyl]tin (1.09 g, 2.49 mmol) in hexane (25 cm<sup>3</sup>) in a Pyrex flask. The stirred mixture was irradiated with u.v. light for 40 h during which time the colour of the solution changed from red to orange. The solution was filtered and the solvent was removed *in vacuo* to give an orange solid. The flask was fitted with an ice-cooled probe and heated to 40 °C at 10<sup>-3</sup> mmHg to sublime out some of the unchanged  $[\text{Cr}(\text{CO})_6]$ .<sup>\*</sup> Recrystallisation of the orange solid from hexane at -30 °C yielded orange crystals. These were crushed and more  $[\text{Cr}(\text{CO})_6]$  was sublimed out. The recrystallisation-sublimation procedure was repeated once more and a final recrystallisation from hexane yielded the product, as orange *needles* (0.669 g, 43%), m.p. 120 °C [Found: C, 36.1; H, 6.0%; *M* (m.s.) 630. C<sub>18</sub>H<sub>38</sub>CrO<sub>5</sub>-Si<sub>4</sub>Sn requires C, 36.25; H, 6.1%; *M* 630].

(b) *{Bis[bis(trimethylsilyl)methyl]stannio}pentacarbonylmolybdenum(0)*,  $[\text{Mo}(\text{CO})_5(\text{SnR}_2)]$ . Using a similar procedure to (a), molybdenum hexacarbonyl (0.721 g, 2.73 mmol) and  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]$  (1.085 g, 2.48 mmol) in hexane (40 cm<sup>3</sup>) yielded the product, as pale yellow *needles* (1.03 g, 64%), m.p. 109–110 °C [Found: C, 33.9; H, 5.8; Sn, 17.8; Mo, 14.0%; *M* (cryoscopy in C<sub>6</sub>H<sub>6</sub>) 672; *M* (m.s.) 674. C<sub>18</sub>H<sub>38</sub>MoO<sub>5</sub>Si<sub>4</sub>Sn requires C, 33.9; H, 5.7; Sn, 17.6; Mo, 14.3%; *M* 674].

(c) *{Bis[bis(trimethylsilyl)methyl]plumbio}pentacarbonylmolybdenum(0)*,  $[\text{Mo}(\text{CO})_5(\text{PbR}_2)]$ . Bis(trimethylsilyl)methyl-lithium (2 mmol, 3 cm<sup>3</sup> of a 0.66 mol dm<sup>-3</sup> diethyl ether solution) in an additional 5 cm<sup>3</sup> of diethyl ether was added over 30 min to anhydrous lead(II) chloride (0.278 g, 1 mmol) in diethyl ether (10 cm<sup>3</sup>) at 0 °C. After stirring at room temperature for 30 min the solution was filtered and diethyl ether was removed under high vacuum. Hexane (20 cm<sup>3</sup>) was added and then taken off under high vacuum to remove trace amounts of diethyl ether. Hexane (20 cm<sup>3</sup>) was added and the purple solution was filtered. Molybdenum hexacarbonyl (0.528 g, 2 mmol) was added and the stirred mixture was irradiated with u.v. light for 16 h. The yellow solution was filtered from the large amount of black solid produced and solvent was removed *in vacuo*. Molybdenum hexacarbonyl was sublimed out (room temperature, 10<sup>-3</sup> mmHg) on to an ice-cooled probe and recrystallisation from hexane at -78 °C yielded yellow crystals. More  $[\text{Mo}(\text{CO})_6]$  was sublimed out and, after a further recrystallisation and sublimation, recrystallisation from hexane (-78 °C) yielded the product, as yellow square *plates* (0.032 g, 4%), m.p. 93–94 °C [Found: C, 30.0; H,

<sup>48</sup> J. Howard and P. Woodward, *J. Chem. Soc. (A)*, 1971, 3648.

<sup>49</sup> A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 2017.

<sup>50</sup> P. Pfeiffer, *Ber.*, 1911, **44**, 1269.

<sup>51</sup> O. M. Nefedov and M. N. Manakov, *Angew. Chem. Internat. Edn.*, 1966, **5**, 1021.



5.1%; *M* (m.s.) 762.  $C_{15}H_{38}MoO_5PbSi_4$  requires C, 30.0; H, 5.0%; *M* 762].

(d) *trans-Bis[bis[bis(trimethylsilyl)methyl]stannio]tetracarbonylchromium(0)*,  $[Cr(CO)_4(SnR_2)_2]$ . Bis[bis(trimethylsilyl)methyl]tin (0.106 g, 0.242 mmol) was added over 5 min to tetracarbonylnorbornadienechromium(0) (0.031 g, 0.121 mmol) in benzene (15 cm<sup>3</sup>) and the solution was heated under reflux for 12 h. Benzene was removed from the orange-red solution *in vacuo* to give an orange solid. A small amount of unchanged chromium(0) complex was sublimed out (40 °C, 10<sup>-3</sup> mmHg) on to an ice-cooled probe. The residue was recrystallised from hexane at -30 °C to yield the product, as orange crystals (0.051 g, 41%), m.p. 215–216 °C (Found: C, 37.0; H, 7.6.  $C_{32}H_{76}CrO_4Si_8Sn_2$  requires C, 37.0; H, 7.4%).

(e) *trans-Bis[bis[bis(trimethylsilyl)methyl]stannio]tetracarbonylmolybdenum(0)*,  $[Mo(CO)_4(SnR_2)_2]$ . Bis[bis(trimethylsilyl)methyl]tin (0.298 g, 0.68 mmol) was added over 5 min to tetracarbonylnorbornadienemolybdenum(0) (0.102 g, 0.34 mmol) in benzene (20 cm<sup>3</sup>). After stirring at room temperature for 1 h, benzene was removed from the orange solution *in vacuo* to give an orange solid. A small amount of unchanged molybdenum(0) complex was sublimed out (40 °C, 10<sup>-3</sup> mmHg) on to an ice-cooled probe. The residue was recrystallised from hexane at -30 °C to yield the product, as orange crystals (0.268 g, 73%), m.p. 204–205 °C (Found: C, 35.5; H, 7.3.  $C_{32}H_{76}MoO_4Si_8Sn_2$  requires C, 35.5; H, 7.1%).

(f) *{Bis[bis(trimethylsilyl)methyl]stannio}tricarbonyldi(η-cyclopentadienyl)di-iron*,  $[Fe_2(η-C_5H_5)_2(CO)_3(SnR_2)]$ . Bis[bis(trimethylsilyl)methyl]tin (0.116 g, 0.265 mmol) was added to dicarbonyl(η-cyclopentadienyl)iron(II) dimer (0.094 g, 0.265 mmol) in hexane (10 cm<sup>3</sup>) at room temperature. There was no visible reaction after stirring at room temperature for 3 h, but 3 h at reflux gave a red-brown solution and some brown solid. The solution was filtered and hexane was removed *in vacuo* to give a red-brown solid. Extraction with hexane (5 cm<sup>3</sup>) at 0 °C resulted in a brown solution which gave brown crystals at -78 °C. These crystals were separated, dissolved in hexane at 0 °C, and recrystallised at -30 °C to give the product, as brown crystals (0.082 g, 41%), m.p. 167–170 °C (decomp.) [Found: C, 42.5; H, 6.8%; *M* (m.s.) 764.  $C_{27}H_{48}Fe_2O_3Si_4Sn$  requires C, 42.5; H, 6.4%; *M* 764].

(g) *Reaction of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with Chlorotris(triphenylphosphine)rhodium(I)*. Bis[bis(trimethylsilyl)methyl]tin (0.148 g, 0.34 mmol) was added to chlorotris(triphenylphosphine)rhodium(I) (0.315 g, 0.34 mmol) in toluene (25 cm<sup>3</sup>). As the temperature was raised to ca. 100 °C the colour changed from red to red-brown and a brown solid was produced. On cooling to room temperature the solution was filtered and solvent was removed *in vacuo* to give a brown solid. Extraction with hexane gave a purple solution which gave purple crystals at -30 °C. Recrystallisation four times from hexane at -30 °C yielded *{bis[bis(trimethylsilyl)methyl]stannio}chlorobis(triphenylphosphine)rhodium(I)* (0.053 g, 14%), m.p. 184–187 °C (Found: C, 54.5; H, 6.3; Cl, 3.1; Sn, 10.6.  $C_{50}H_{88}ClP_3RhSi_4Sn$  requires C, 54.6; H, 6.2; Cl, 3.22; Sn, 10.8%).

(h) *Reaction of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with Chloro(η-ethylene)bis(triphenylphosphine)rhodium(I)*. Chloro(η-ethylene)bis(triphenylphosphine)rhodium(I) (0.455 g, 0.66 mmol) was added over 5 min to Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.289 g, 0.66 mmol) in benzene (20 cm<sup>3</sup>) at room temperature. The deep yellow solution was filtered and benzene was removed *in vacuo* to give a brown solid. Extraction with hexane

gave a purple solution which yielded purple crystals at -30 °C. Recrystallisation from hexane at -30 °C yielded the stanniorhodium(I) complex (0.073 g, 10%).

*Preparation of [PtCl(PEt<sub>3</sub>)(SnR<sub>2</sub>)(SnR<sub>2</sub>Cl)]*.—Bis[bis(trimethylsilyl)methyl]tin (0.240 g, 0.55 mmol) was added slowly with stirring at room temperature to  $[PtCl_2(PEt_3)_2]$  (0.100 g, 0.13 mmol) suspended in hexane (10 cm<sup>3</sup>). The initial red colour caused by the dissolution of tin(II) alkyl quickly disappeared. On completion of addition, the solution was orange and all the sparingly soluble platinum complex had reacted. The solution was filtered, concentrated to ca. 2 cm<sup>3</sup>, and cooled to -30 °C to give pale-orange crystals of the product (0.26 g, 80%), which was purified by recrystallisation from hexane, m.p. 154–156 °C (Found: C, 32.5; H, 7.5; Cl, 5.7; Sn, 18.4.  $C_{34}H_{91}Cl_2P_2PtSi_8Sn_2$  requires C, 32.4; H, 7.3; Cl, 5.6; Sn, 18.9%).

A similar experiment with Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.27 mmol) and  $[PtCl_2(PEt_3)_2]$  (0.13 mmol) gave a significantly reduced yield (ca. 30%), and unchanged  $[PtCl_2(PEt_3)_2]$  was recovered.

*Lack of Reaction between [Mo(CO)<sub>5</sub>(Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>)] and Triphenylphosphine*.—A mixture of the molybdenum complex (0.407 g, 0.6 mmol) and triphenylphosphine (0.157 g, 0.6 mmol) in benzene (10 cm<sup>3</sup>) was heated under reflux for 3 h. I.r. spectroscopy indicated no reaction had taken place and PPh<sub>3</sub> (0.128 g, 82%) was recovered by removing the benzene and washing the residue with hexane at -50 °C.

*Reactions of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with Main-group Lewis Acids*.—(a) *Boron trifluoride*. An equimolar quantity of the purified trifluoride was frozen on to a mixture of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.300 g, 0.686 mmol) and diethyl ether (5 cm<sup>3</sup>) at -196 °C. No reaction was apparent on warming up to 50 °C or after the addition of a four-fold excess of BF<sub>3</sub>; Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was recovered unchanged after removal of volatiles and crystallisation from hexane.

(b) *Boron trichloride*. An equimolar amount of boron trichloride was condensed at -196 °C on to a frozen solution of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.163 g, 0.373 mmol) in hexane (5 cm<sup>3</sup>). At ca. -30 °C, reaction occurred; the deep-red colour was discharged and the solution became colourless. A slight amount of a white precipitate was formed. The solution rapidly became yellow on warming to room temperature. Work-up *via* the usual recrystallisations from hexane was hampered by continuous decomposition; small amounts of a white, foul-smelling, gummy material (Found: C, 10.7; H, 4.0%) were isolated. The <sup>1</sup>H n.m.r. spectrum of the solution suggested a mixture of alkyltin chlorides, SnR<sub>4-n</sub>Cl<sub>n</sub> [R = CH(SiMe<sub>3</sub>)<sub>2</sub>]. A small quantity of a white solid, m.p. 79–80 °C, was separated after repeated recrystallisation and sublimation. Analysis (Found: C, 33.9; H, 7.9%) showed this might have been impure SnR<sub>2</sub>Cl<sub>2</sub> (Calc. for C<sub>14</sub>H<sub>38</sub>Cl<sub>2</sub>Sn: C, 33.1; H, 7.5%); ν(Sn-Cl) at 340s and 328m cm<sup>-1</sup>; ν(Sn-C) at 499m cm<sup>-1</sup>.

*Reactions of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with Lewis Bases*.—(a) *4-Methylpyridine*. 4-Methylpyridine (47 μl, 0.48 mmol) in benzene (5 cm<sup>3</sup>) was added over 40 min to Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.191 g, 0.44 mmol) in benzene (15 cm<sup>3</sup>) at 20 °C. The colour of the solution changed slightly from red to orange-red. After stirring at 20 °C for 2 h, benzene was removed *in vacuo* to give a mixture of orange and red crystals and an orange oil. Addition of hexane (10 cm<sup>3</sup>) gave a red solution which on cooling to -30 °C became pale-orange and slowly deposited orange crystals. These were isolated and dried *in vacuo* at -30 °C to give *bis[bis(trimethylsilyl)methyl]-(4-methylpyridine)tin* (0.150 g, 65%), m.p. 77–81 °C (decomp.) (Found: C, 45.1; H, 8.4; N, 2.5.  $C_{20}H_{45}NSi_4Sn$

requires C, 45.3; H, 8.6; N, 2.6%). It was necessary to remove all traces of solvent at  $-30^{\circ}\text{C}$  since if any solvent was present when the compound was allowed to warm to room temperature noticeable dissociation to the starting materials took place.

(b) *Piperidine* (0.074 cm<sup>3</sup>, 0.75 mmol) in hexane (5 cm<sup>3</sup>) was added dropwise to a solution of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.290 g, 0.663 mmol) in hexane (5 cm<sup>3</sup>) with stirring at 0 °C. The deep red colour was discharged and the solution became pale orange. The volume was reduced to ca. 2 cm<sup>3</sup> by evaporation at  $-5^{\circ}\text{C}$  and the solution was cooled to  $-30^{\circ}\text{C}$ . Colourless crystals of the 1:1 adduct (0.32 g, 92%) (Found: C, 43.4; H, 9.3; N, 2.4. C<sub>15</sub>H<sub>41</sub>N<sub>2</sub>Si<sub>4</sub>Sn requires C, 43.7; H, 9.5; N, 2.7%) were isolated at this temperature, after washing with cold ( $-30^{\circ}\text{C}$ ) hexane (2 × 1 cm<sup>3</sup>), and drying at  $-30^{\circ}\text{C}$ . The solid yellowed slightly, in sealed vessels, on warming to room temperature, and turned red, with the formation of a colourless liquid, as the temperature was increased. The decomposed solid melted at 85–90 °C to a deep red liquid. The process was reversible.

(c) *Pyridine or other nitrogen or phosphorus bases.* The reaction between Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and a 10% molar excess of pyridine was carried out in hexane in a similar manner. The solid 1:1 adduct formed was less soluble than the piperidine analogue and more highly orange-coloured. The compound decomposed slowly at room temperature, and satisfactory analyses were not obtained.

Under similar conditions, no reaction was detected between SnR<sub>2</sub> and triethylamine, dimethylamine, 2,2'-bipyridine, triethylphosphine, triphenylphosphine, or quinuclidine.

*Reaction of Bis[bis(trimethylsilyl)methyl]lead with 4-Methylpyridine.*—4-Methylpyridine (68 μl, 0.7 mmol) was added to bis[bis(trimethylsilyl)methyl]lead (0.371 g, 0.7 mmol) in hexane (10 cm<sup>3</sup>) at room temperature. The colour changed from purple to pale yellow, but attempts to crystallise the product were unsuccessful. Hexane was removed *in vacuo* to give a pale yellow oil which on prolonged evacuation gave the starting lead alkyl.

*Oxidative-addition Reactions.*—(a) *Preparation of SnBr[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>.* A diethyl ether solution (5.0 cm<sup>3</sup>, 3.45 mmol) of Li[CH(SiMe<sub>3</sub>)<sub>2</sub>] (0.69 mol dm<sup>-3</sup>) was added dropwise to a suspension of tin(II) chloride (0.218 g, 1.15 mmol) in diethyl ether (5 cm<sup>3</sup>), with stirring at 0 °C. A white precipitate formed, and the supernatant progressively became orange, deep red, and finally light brown after the addition of the first, second, and third equivalents of the lithium reagent. Bromine (0.06 cm<sup>3</sup>, 1.15 mmol) in benzene (6 cm<sup>3</sup>) was added dropwise at 0 °C. A white precipitate formed and the brown colour was discharged. The solvent was pumped off and the residue extracted with hexane (5 cm<sup>3</sup>). The filtered solution was concentrated to ca. 0.5 cm<sup>3</sup> and cooled to  $-30^{\circ}\text{C}$  to give hexagonal-shaped colourless crystals (0.25 g, 32%) of the product, which was further purified by recrystallisation from hexane and sublimation (Found: C, 37.4; H, 8.3; Br, 11.5. C<sub>21</sub>H<sub>57</sub>BrSi<sub>6</sub>Sn requires C, 37.3; H, 8.5; Br, 11.8%), m.p. 204–205 °C.

(b) *Preparation of SnMe[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>I.* Methyl iodide (ca. 1% v/v in hexane) was added dropwise to a solution of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.215 g, 0.49 mmol) in hexane (5 cm<sup>3</sup>) until the deep red colour was discharged. The solution was filtered, concentrated to ca. 0.5 cm<sup>3</sup>, and cooled ( $-30^{\circ}\text{C}$ ) to give a white solid (0.17 g, 63%). This was purified by sublimation [70 °C (10<sup>-2</sup> mmHg) on to a  $-78^{\circ}\text{C}$  probe] to give the product (Found: C, 31.3; H, 7.1; I, 21.6.

C<sub>15</sub>H<sub>41</sub>ISi<sub>4</sub>Sn requires C, 31.1; H, 7.1; I, 21.9%) as a white solid, m.p. 69–71 °C.

(c) *Preparation of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Cl.* The product (70%) (Found: C, 40.1; H, 9.1; Cl, 5.8. C<sub>21</sub>H<sub>57</sub>ClSi<sub>6</sub>Sn requires C, 39.9; H, 9.1; Cl, 5.6%), m.p. 191–193 °C, was similarly obtained as colourless crystals from the reaction in hexane between Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and (Me<sub>3</sub>Si)<sub>2</sub>CHCl.

(d) *Preparation of SnBr<sub>2</sub>[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.* Bromine (0.020 cm<sup>3</sup>, 0.39 mmol) in benzene (10 cm<sup>3</sup>) was added dropwise at room temperature to Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.171 g, 0.39 mmol) in benzene (5 cm<sup>3</sup>). The solution quickly became colourless. Benzene was removed, residual solid redissolved in hexane (10 cm<sup>3</sup>), the solution filtered, concentrated to ca. 0.5 cm<sup>3</sup>, and cooled ( $-30^{\circ}\text{C}$ ). Colourless crystals (0.15 g, 64%) of the product (Found: C, 28.5; H, 6.4; Br, 26.9. C<sub>14</sub>H<sub>38</sub>Br<sub>2</sub>Si<sub>4</sub>Sn requires C, 28.2; H, 6.4; Br, 26.8%) were isolated and purified by sublimation [70 °C (10<sup>-2</sup> mmHg) on to a  $-78^{\circ}\text{C}$  probe].

(e) *Preparation of bis[bis(trimethylsilyl)methyl]chlorostannane.* Anhydrous hydrogen chloride (1.03 mmol, 5.8 cm<sup>3</sup> of a 0.18 mol dm<sup>-3</sup> solution in diethyl ether) was added over 13 min to Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.449 g, 1.03 mmol) in diethyl ether (10 cm<sup>3</sup>) at room temperature. The solution became yellow, and solvent was removed *in vacuo* to give a pale yellow oil. A hexane solution of this oil yielded colourless crystals at  $-78^{\circ}\text{C}$  which were recrystallised ( $-78^{\circ}\text{C}$ ) to yield the product (0.276 g, 57%), m.p. 53–54 °C (Found: C, 35.9; H, 8.6; Cl, 7.2. C<sub>14</sub>H<sub>38</sub>ClSi<sub>4</sub>Sn requires C, 35.5; H, 8.3; Cl, 7.5%), as colourless crystals.

(f) *Preparation of bis[bis(trimethylsilyl)methyl]fluorostannane.* (i) *From [NH<sub>4</sub>][HF<sub>2</sub>].* A mixture of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.20 g, 0.46 mmol) and [NH<sub>4</sub>][HF<sub>2</sub>] (0.050 g, 0.87 mmol) was prepared in diethyl ether (5 cm<sup>3</sup>) at room temperature. After 1 h, the deep red colour was discharged and the solution became pale yellow. The diethyl ether was pumped off, and the residual oil extracted into hexane. Concentration of the solution and cooling to  $-30^{\circ}\text{C}$  gave colourless crystals of the product (0.05 g, 22%) (Found: C, 36.2; H, 8.2. C<sub>14</sub>H<sub>38</sub>FSi<sub>4</sub>Sn requires C, 36.8; H, 8.6%).

(ii) *From impure OEt<sub>2</sub>·BF<sub>3</sub>.* Hydrogen fluoride, present in undistilled OEt<sub>2</sub>·BF<sub>3</sub>, reacted readily to give the product (55%) (Found: C, 37.0; H, 8.8; F, 4.0%). The reaction procedure was generally similar.

(g) *Reaction of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with carbon tetrachloride.* Carbon tetrachloride (ca. 1% v/v in benzene) was added to Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.150 g, 0.343 mmol) in hexane (5 cm<sup>3</sup>) until the red colour was completely discharged. Solvent was pumped off, and the frothy white residue was extracted into hexane and filtered. Crystallisation from hexane at  $-30^{\circ}\text{C}$  could not be induced. The <sup>1</sup>H n.m.r. spectrum of the solution showed two strong peaks in the SiMe<sub>3</sub> region, at τ 9.50 and 9.60. Attempted crystallisation of the gum obtained from acetone-methanol mixtures gave small amounts (ca. 10 mg) of a white solid, probably Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub> (Found: C, 33.0; H, 7.2. C<sub>14</sub>H<sub>38</sub>Cl<sub>2</sub>Si<sub>4</sub>Sn requires C, 33.1; H, 7.4%). The <sup>1</sup>H n.m.r. (benzene) spectrum showed SiMe<sub>3</sub> protons at τ 9.51; ν(Sn-Cl) (Nujol mull) at 340 and 320 cm<sup>-1</sup>.

(h) *Reaction of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with chlorine.* Small aliquot portions of chlorine were condensed on to a frozen solution of Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.300 g, 0.68 mmol) in hexane (5 cm<sup>3</sup>) until the characteristic deep red colour of the thawed solution was discharged. The resulting pale yellow solution was filtered, concentrated to ca. 1 cm<sup>3</sup>, and cooled ( $-30^{\circ}\text{C}$ ), but crystallisation did not occur. The <sup>1</sup>H n.m.r. (in benzene) spectrum of the oil remaining after removal of

the hexane, showed three major  $\text{SiMe}_3$  resonances at *ca.*  $\tau$  9.48, 9.52, and 9.62.

(i) *Preparation of*  $\text{Sn}(\text{CH}_2\text{CMe}:\text{CMeCH}_2)[\text{CH}(\text{SiMe}_3)_2]_2$ . A solution of 2,3-dimethylbuta-1,3-diene (0.050  $\text{cm}^3$ , 0.443 mmol) in hexane (5  $\text{cm}^3$ ) was added dropwise to  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  (0.194 g, 0.443 mmol) at room temperature. After stirring for 1 h, the colour of the solution had changed from deep red to pale yellow. Concentration of the solution to *ca.* 0.5  $\text{cm}^3$  followed by cooling to  $-30^\circ\text{C}$  gave colourless crystals which were washed with  $3 \times 0.5 \text{ cm}^3$  of cold ( $-40^\circ\text{C}$ ) hexane and dried at room temperature. After sublimation [ $50^\circ\text{C}$  ( $10^{-2}$  mmHg) on to a probe at  $0^\circ\text{C}$ ], these were identified as the *product* (0.15 g, 65%), m.p.  $56\text{--}58^\circ\text{C}$  (Found: C, 46.2; H, 9.7; Sn, 23.0.  $\text{C}_{20}\text{H}_{48}\text{Si}_4\text{Sn}$  requires C, 46.2; H, 9.3; Sn, 22.8%).

(j) *Reaction of methanol with*  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ . A dilute solution of methanol in hexane was added dropwise to a solution of  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  (0.15 g, 0.34 mmol) in hexane (5  $\text{cm}^3$ ), at room temperature, until the red colour was discharged. A trace amount of white precipitate was filtered off, and the volatiles were removed from solution leaving a pale yellow oil. Attempted crystallisation from hexane, toluene, or toluene-methanol was unsuccessful. The  $^1\text{H}$  n.m.r. (benzene solution) spectrum indicated the presence of at least three  $\text{SiMe}_3$ -containing species. I.r. spectra showed a broad weak peak at *ca.*  $1815 \text{ cm}^{-1}$ , in the region characteristic of  $\nu(\text{Sn-H})$ .

(k) *Autoxidation of*  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ . Controlled oxidation of either hexane solutions of  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ , or the solid, gave a hexane-insoluble, gummy, hygroscopic material with composition approximating to  $\text{SnR}_2\text{O}$  (Found: C, 36.3; H, 8.7.  $\text{C}_{14}\text{H}_{38}\text{OSi}_4\text{Sn}$  requires C, 37.1; H, 8.5%).

Nitrogen mono-oxide reacted instantly with hexane solutions of  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  to give a white precipitate. The i.r. spectrum corresponded to that of the oxidation product (Found: C, 35.6; H, 8.5; N, 0%), with typical  $\text{CH}(\text{SiMe}_3)_2$  spectral features.

(l) *Preparation of*  $\mu\text{-}\{[\text{bis}[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{stannio}\}\text{-bis}(\text{tetracarbonyliron})$ . Nonacarbonyl-di-iron(0) (0.364 g, 1 mmol) was added to  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  (0.438 g, 1 mmol) in semi-solid benzene (20  $\text{cm}^3$ ) at  $4^\circ\text{C}$  and the mixture was allowed to warm slowly to room temperature. After stirring at  $20^\circ\text{C}$  for 7 h the iron complex slowly reacted and the colour of the solution changed from red to orange-brown. The solution was filtered, and benzene, together with a small amount of pentacarbonyliron(0), was removed *in vacuo* to give a brown oil. A hexane solution of this oil yielded orange crystals at  $-78^\circ\text{C}$  which were recrystallised from cold ( $-78^\circ\text{C}$ ) hexane to yield the product, as orange crystals (0.128 g, 21%), m.p.  $139\text{--}141^\circ\text{C}$  (decomp.) [Found: C, 34.2; H, 5.0%; M (m.s.) 774.  $\text{C}_{22}\text{H}_{38}\text{Fe}_2\text{O}_3\text{Si}_4\text{Sn}$  requires C, 34.2; H, 4.95%; M 774].

(m) *Preparation of*  $\{[\text{bis}[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{hydrido-stannio}\}\text{tricarbonyl}(\eta\text{-cyclopentadienyl})\text{molybdenum(II)}$ . Bis- $[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{tin}$  (0.250 g, 0.57 mmol) was added to tricarbonyl( $\eta\text{-cyclopentadienyl}$ )hydridomolybdenum(II) (0.146 g, 0.57 mmol) in benzene (15  $\text{cm}^3$ ). The solution was stirred for 4 h, whereafter the colour had changed from red to yellow. Removal of benzene *in vacuo* yielded a yellow solid which was recrystallised from hexane to give the product, as pale-yellow crystals (0.341 g, 86%), m.p.  $128\text{--}130^\circ\text{C}$  (Found: C, 38.8; H, 6.8.  $\text{C}_{22}\text{H}_{44}\text{MoO}_3\text{Si}_4\text{Sn}$  requires C, 38.7; H, 6.5%).

(n) *Preparation of*  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{SnMeR}_3)]$ . The

complex  $[\text{FeMe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  (0.141 g, 0.73 mmol) in benzene (5  $\text{cm}^3$ ) was added dropwise at room temperature over 0.5 h to  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  (0.319 g, 0.73 mmol) in benzene (5  $\text{cm}^3$ ). Stirring was continued for a further 1 h, and the colour of the solution changed from deep red to pale brown. The solution was evaporated to an oil, extracted into hexane (5  $\text{cm}^3$ ), and filtered. Concentration to *ca.* 1  $\text{cm}^3$  and cooling ( $-30^\circ\text{C}$ ) gave a yellow solid, which was recrystallised from hexane to give the product, as yellow-brown crystals (0.17 g, 37%), m.p.  $141\text{--}142^\circ\text{C}$  (Found: C, 42.1; H, 7.7; Sn, 18.6.  $\text{C}_{22}\text{H}_{46}\text{FeO}_2\text{Si}_4\text{Sn}$  requires C, 42.0; H, 7.4; Sn, 18.9%).

(o) *Preparation of*  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{SnR}_2\text{Cl})]$ . The compound  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  (0.17 g, 0.39 mmol) was added slowly, with stirring at room temperature, to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$  (0.80 g, 0.38 mmol) in benzene (5  $\text{cm}^3$ ). The colour of the solution changed from orange-red to pale brown. Solvent was removed and the residue extracted with hexane (8  $\text{cm}^3$ ), filtered, concentrated to *ca.* 2  $\text{cm}^3$ , and cooled to  $-30^\circ\text{C}$  to give a yellow solid. This was recrystallised from hexane to give the product as yellow-orange needles (0.18 g, 71%), m.p.  $119.5\text{--}120^\circ\text{C}$  (Found: C, 38.8; H, 6.9; Cl, 5.6.  $\text{C}_{21}\text{H}_{43}\text{ClFeO}_2\text{Si}_4\text{Sn}$  requires C, 38.8; H, 6.7; Cl, 5.5%).

(p) *Preparation of*  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{SnMeR}_2)]$ . The product (63%), m.p.  $103\text{--}105^\circ\text{C}$  (decomp.) (Found: C, 39.9; H, 6.8.  $\text{C}_{23}\text{H}_{46}\text{MoO}_3\text{Si}_4\text{Sn}$  requires C, 39.6; H, 6.7%), was obtained from the reaction of equimolar quantities of  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  and  $[\text{MoMe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$  in hexane, in a manner similar to that described in (o).

*Reaction of*  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  *with Octacarbonyldicobalt(0)*.—Hexane (10  $\text{cm}^3$ ) was added slowly to  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  (0.280 g, 0.64 mmol) and octacarbonyldicobalt(0) (0.218 g, 0.64 mmol) at  $-78^\circ\text{C}$  and the mixture was allowed to warm slowly to room temperature. Reaction commenced at *ca.*  $-20^\circ\text{C}$  to give a yellow solution which was stirred at room temperature for 1 h. After filtration, the solvent was removed *in vacuo* to give a yellow solid. Hydrogen-1 n.m.r. and i.r. spectroscopy indicated the presence of a mixture of products and attempts to separate these were unsuccessful.

*Attempted Oxidative-addition Reactions involving*  $\text{Pb}[\text{CH}(\text{SiMe}_3)_2]_2$ .—The following experiments were carried out on a sample of  $\text{Pb}[\text{CH}(\text{SiMe}_3)_2]_2$  prepared from lead(II) chloride (4.0 mmol) and  $\text{Li}[\text{CH}(\text{SiMe}_3)_2]$  in diethyl ether. The purple solution was evaporated to an oil, which was extracted into hexane. The filtered hexane solution (30  $\text{cm}^3$ ) was divided into aliquot portions (10  $\text{cm}^3$ ).

(a) *Reaction with hydrogen chloride*. A 0.10 mol  $\text{dm}^{-3}$  solution of hydrogen chloride in diethyl ether was added dropwise to a hexane solution of  $\text{Pb}[\text{CH}(\text{SiMe}_3)_2]_2$  until the purple colour was completely discharged. The white precipitate of lead(II) chloride was filtered off and dried; an i.r. spectrum showed the absence of any  $\text{CH}(\text{SiMe}_3)_2$  absorptions.

(b) *Reaction with*  $(\text{Me}_3\text{Si})_2\text{CHCl}$ . Addition of excess of  $(\text{Me}_3\text{Si})_2\text{CHCl}$  to  $\text{Pb}[\text{CH}(\text{SiMe}_3)_2]_2$  in hexane at room temperature did not discharge the characteristic purple colour. At  $60^\circ\text{C}$ , metallic lead formed slowly.

(c) *Reaction with methyl iodide*. Addition of methyl iodide in hexane to  $\text{Pb}[\text{CH}(\text{SiMe}_3)_2]_2$  in hexane at room temperature immediately discharged the purple colour to give a clear solution and a trace amount of white precipitate. Attempted work-up of the solution was hampered by slow formation of lead(II) iodide, even below  $0^\circ\text{C}$ . No addition product was isolated.