Subvalent Group 4B Metal Alkyls and Amides. Part III.[1] Mossbauer Spectroscopy Studies of Bis[bis(trimethylsilyl)methyl]tin(II) and its Derivatives†

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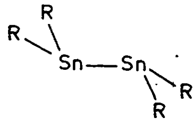
Mossbauer spectra of SnR_2 [R = $CH(SiMe_3)_2$] and of 16 of its derivatives have been recorded. The latter fall into two classes: (*i*) the dialkylstannylene complexes such as [$Cr(CO)_5(SnR_2)$] in which bivalent Sn is three-co-ordinate: and (*ii*) dialkylstannylene insertion products into C–X, M–H, M–Cl, M–Me, or M–M bonds (M = a transition metal, X = halogen) such as [$Fe(\eta$-$C_5H_5)(CO)_2(SnR_2Cl)$], in which quadrivalent tin is four-co-ordinate. The compound SnR_2 and class (*i*) complexes are characterised by isomer shifts of 2.15 ± 0.1 mm s^{-1} relative to $BaSnO_3$ and large quadrupole splittings [2.31 (for SnR_2) or 4.25 ± 0.2 mm s^{-1} for class (*i*)]. Class (*ii*) complexes show lower isomer shifts (1.49 ± 0.25 mm s^{-1}) and quadrupole splittings (<2.37 mm s^{-1}). Magnetic Mössbauer measurements on SnR_2 and [$Cr(CO)_5(SnR_2)$] show that for both complexes the sign of the quadrupole coupling constant eQV_{zz} is negative and hence V_{zz}, the principal component of the field gradient tensor, is positive.

WIDESPREAD application has recently been made of ^{119}Sn Mössbauer spectroscopy in the structural analysis of tin complexes and in the interpretation of the electronic arrangement around the tin atoms therein.[2] Data for tin(II) organometallic complexes (*i.e.*, SnC compounds) and their derivatives are, however, very limited, being restricted to the compounds $Sn(C_5H_5)_2$,[3] $Sn(C_5H_5)X$ (X = Cl or Br),[4] $B_9C_2{}^{1,2}Sn^3H_{11}$,[5] and $Sn(Ph\overline{CB_{10}H_{10}C})_2$,[6] in each of which the tin atom is in an unusual electronic environment. The recent discovery of the dialkyl derivative $Sn[CH(SiMe_3)_2]_2$,[7,8] which is monomeric in benzene or cyclohexane solution, has provided a unique compound for Mössbauer comparison. In this paper we discuss the Mössbauer parameters for this compound, and for a variety of 'stannylene' complexes, *e.g.* [$Cr(CO)_5(SnR_2)$], in which this moiety acts, in the manner of a tertiary phosphine, as a σ donor to a transition-metal Lewis acid. With the exception of the complexes [$Cr(CO)_5(SnI_2)$] and [$Mo(CO)_5(SnCl_2)$] which were reported [9] during the course of this work, these are the only known tin(II) complexes of transition metals in which there may be a trigonal arrangement about the ligating atom.[1] A Mössbauer study has recently been made of related complexes of the type [$M(CO)_x(SnBu^t{}_2\cdot$base)] [M = Fe, x = 4, and base = dimethyl sulphoxide (dmso) or pyridine; M = Cr, x = 5, and base = tetrahydrofuran (thf), dmso, or pyridine] which bear an additional base ligand on the tin atom.[10] The data were interpreted as suggestive of a tin(IV) formulation.

The solid-state structure of $Sn[CH(SiMe_3)_2]_2$, recently derived from single-crystal *X*-ray data,[8,11] shows the molecule to be a centrosymmetric dimer, (I). The



(I) R = $CH(SiMe_3)_2$

environment about each tin atom is perhaps best described as distorted tetrahedral, with the sum of bond angles at tin as 342°; for 'pure' sp^3 Sn this would be *ca.* 327° and 'pure' sp^2, 360°. The Sn–Sn bond length of 2.76 Å is similar to that in Sn_2Ph_6 or in tetrahedral tin. The solid is diamagnetic. Such a structure is in keeping with the observed formation of complexes with Lewis bases, *e.g.* 4-methylpyridine (electron-pair donation into the vacant $5p_z$ orbital on tin) and with transition-metal Lewis acids as in [$Cr(CO)_5(SnR_2)$] where the sp_xp_y lone pair of electrons on tin is utilised.[1] The potential Lewis basicity of monomeric $Sn[CH(SiMe_3)_2]_2$ had also been suggested by the He(I) photoelectron (p.e.) spectrum which showed a doublet at low ionisation energy (7.42 and 8.33 eV).[7,12,‡] The $5p$ level in atomic tin lies at 7.32 eV. (In the vapour, as in

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† No reprints available.

‡ 1 eV ≈ 1.60×10^{-19} J.

[1] Part II, J. D. Cotton, P. J. Davidson, and M. F. Lappert, preceding paper.

[2] (*a*) G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59; (*b*) J. J. Zuckerman, *Adv. Organometallic Chem.*, 1970, **9**, 21; (*c*) R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, 101.

[3] (*a*) P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1969, **91**, 6885; (*b*) *ibid.*, 1970, **92**, 2577.

[4] K. D. Bos, E. J. Bulten, and J. G. Noltes, *J. Organometallic Chem.*, 1972, **39**, C52.

[5] R. W. Rudolph and V. Chowdhry, *Inorg. Chem.*, 1974, **13**, 248.

[6] A. Yu. Aleksandrov, V. I. Bregadse, V. I. Goldanskii, L. I. Zakharkin, O. Yu. Okhlobystin, and V. I. Khrapov, cited in ref. 2*b*.

[7] P. J. Davidson and M. F. Lappert, *J.C.S. Chem. Comm.*, 1973, 317.

[8] Part I, P. J. Davidson, D. H. Harris, and M. F. Lappert, *J.C.S. Dalton*, 1976, 2268.

[9] D. Uhlig, H. Behrens, and E. Lindner, *Z. anorg. Chem.*, 1973, **401**, 233.

[10] G. W. Grynkewich, B. Y. K. Ho, T. J. Marks, D. L. Tomaja, and J. J. Zuckerman, *Inorg. Chem.*, 1973, **12**, 2522.

[11] D. E. Goldberg, D. H. Harris, M. F. Lappert, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1976, 621.

the solution in C_6H_6 or n-C_6H_{14}, the compound is believed to be a monomer of C_{2v} symmetry.[1,12]) The coplanarity of the C_2SnCr unit in $[Cr(CO)_5(SnR_2)]$, together with the CSnC bond angle of 98°, shows similarity, with regard to the tin environment, to the unco-ordinated molecule.[1,8,11]

A variety of quadrivalent tin complexes has also been prepared *via* facile oxidative-addition reactions to $Sn[CH(SiMe_3)_2]_2$.[1] Their Mössbauer spectra have also been recorded and are compared with those previously measured for similar systems.

RESULTS AND DISCUSSION

The Mössbauer parameters for $Sn[CH(SiMe_3)_2]_2$, and for previously reported tin(II) organometallic derivatives, are listed in the Table. Compared with the other species, the isomer shift of $Sn[CH(SiMe_3)_2]_2$ is very low, and lies only just above the value for α-tin (2.05 mm s^{-1}) which is often regarded as the borderline between tin(II) compounds whose values lie above and Sn^{IV} which lie below.*

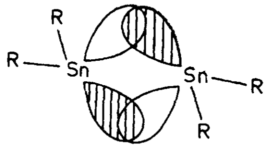
Mossbauer parameters (mm s^{-1})

Compound [a]	Isomer shift (± 0.03)[b]	Quadrupole splitting (± 0.05)	Ref.
SnR_2	2.16	2.31	*c*
$Sn(C_5H_5)_2$	3.74	0.86	3
$Sn(C_5H_5)Cl$	3.70	1.05	4
$SnBr(C_5H_5)$	3.69	0.99	4
$Sn(Ph\overline{CB_{10}H_{10}C})_2$	2.95	1.90	6
$B_9C_2{}^{1,2}Sn^3H_{11}$	4.67	3.83	5
$[Cr(CO)_5(SnR_2)]$	2.21	4.43	*c*
$[Mo(CO)_5(SnR_2)]$	2.15	4.57	*c*
trans-$[Cr(CO)_4(SnR_2)_2]$	2.21	4.04	*c*
trans-$[Mo(CO)_4(SnR_2)_2]$	2.13	4.24	*c*
$[PtCl(PEt_3)(SnR_2)(SnR_2Cl)]$	2.05, 1.73	4.23, 2.66	*c*
$Sn(C_5H_5)_2 \cdot BF_3$	3.79	0.90	3*b*
$[Cr(CO)_5(SnBu^t{}_2 \cdot thf)]$	2.11	4.14	10
$[Cr(CO)_5(SnBu^t{}_2 \cdot py)]$	2.01	3.44	10
$[Fe(CO)_4(SnCl_2)]$	2.01	2.09	*d*
$[\{Fe(CO)_4\}_2SnR_2]$	1.73	1.53	*c*
SnR_3Cl	1.27	2.18	*c*
$SnBrR_3$	1.24	2.05	*c*
$SnMeR_2I$	1.48	2.24	*c*
$[Fe(\eta\text{-}C_5H_5)(CO)_2(SnR_2Cl)]$	1.54	2.37	*c*
$[Fe(\eta\text{-}C_5H_5)(CO)_2(SnMeR_2)]$ [e]	1.48	0	*c*
$[Mo(\eta\text{-}C_5H_5)(CO)_3(SnR_2H)]$	1.39	0.67	*c*
$[Mo(\eta\text{-}C_5H_5)(CO)_3(SnMeR_2)]$	1.35	0.71	*c*
$[Fe(\eta\text{-}C_5H_5)(CO)_2(SnCl_3)]$	1.77	1.82	23
$[Fe(\eta\text{-}C_5H_5)(CO)_2(SnMe_3)]$ [e]	1.35	>0	13*b*
$[Mo(\eta\text{-}C_5H_5)(CO)_3(SnMe_3)]$	1.36	1.25	13*b*

[a] R = $CH(SiMe_3)_2$. [b] Relative to $BaSnO_3$ or SnO_2 at *ca.* 20 °C. [c] This work. [d] A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 2017. [e] The full linewidth at half-height, Γ, was 1.34 for $[Fe(\eta\text{-}C_5H_5)(CO)_2(SnMeR_2)]$ or[13b] 1.16 for $[Fe(\eta\text{-}C_5H_5)(CO)_2(SnMe_3)]$.

The crystal structure and Mössbauer data of $Sn[CH(SiMe_3)_2]_2$ distinguish it from formally similar compounds of the type $Sn(C_5H_5)_2$, $Sn(C_5H_5)Cl$, $SnBr(C_5H_5)$, and $(SnBu^n{}_2)_n$. The cyclopentadienyl compounds have no Sn–Sn bonding and their isomer-shift values, which are only just below that for $SnCl_2$ (4.07 mm s^{-1}), are characteristic of tin(II) compounds with a non-bonding electron pair on each tin atom. The compound $(SnBu^n{}_2)_n$ is polymeric, with strong Sn–Sn interaction, and its isomer shift is definitely characteristic of quadrivalent tin (1.5 mm s^{-1}).[14] Hence the formally non-bonding pairs on the tin atoms in the $SnBu^n{}_2$ monomer have clearly been used in the formation of the Sn–Sn bonds on polymerisation. The zero quadrupole splitting for $(SnBu^n{}_2)_n$ is characteristic of tin(IV) compounds containing both Sn–C and Sn–Sn bonds.

The bonding in crystalline $\{Sn[CH(SiMe_3)_2]_2\}_2$ is shown schematically in (II), which accounts for the *X*-ray and the magnetic-susceptibility data and indicates that the Sn–Sn interaction is weak, as shown by its solution and chemical behaviour.[8] The bent bonds arise from overlap between the lone-pair on each tin atom and the empty *p* orbital on the neighbouring tin atom. The isomer-shift value (2.16 mm s^{-1}) lies between that for $Sn(C_5H_5)_2$ (no Sn–Sn interaction) and $(SnBu^n{}_2)_n$ (strong Sn–Sn interaction), as is consistent with weak interaction between two $Sn[CH(SiMe_3)_2]_2$ monomers to form the dimer. The presence of an electrical-field gradient at the Sn atoms, shown by the quadrupole splitting of the Mossbauer resonance line, is also consistent with the crystal structure. On each tin atom there is one direction (that of the empty orbital) in which any electron density on the Sn must arise from the weak interaction with the lone pair on the neighbouring Sn atom and this produces the field gradient.



(II) R = $CH(SiMe_3)_2$

Magnetic Mossbauer measurement on $Sn[CH(SiMe_3)_2]_2$ [Figure 1(*a*)] gives further structural information. The sign of the quadrupole coupling constant eQV_{zz} is negative.[15] Since eQ for tin is also negative, this requires that V_{zz}, the principal component of the field gradient tensor, is positive. We interpret the positive value of V_{zz} on the basis of previous similar analyses on tin(II) systems[16] as indicating a deficit of *p*-electron density in the principal direction of the field gradient.

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* Some workers[2b] prefer to use the isomer shift for β-tin (2.56 mm s^{-1}) as the crossover point between oxidation states. However, the isomer shifts of several genuine tin(II) basic salts and hydroxostannates are below this value.[13a] This, together with the observation that the formal sp^3 electronic arrangement in the diamond-like structure of α-tin can be regarded as the covalent limit for Sn^{IV}, and intermediate in *s*-electron density between the extreme Sn^{2+} and Sn^{4+} electronic situations, suggest to us that the α-tin dividing line is more realistic. We note in addition that there are dangers in the allocation of a *formal oxidation state to tin compounds* on this basis and that isomer-shift values may often be more appropriately used to assign the *valence state of a tin atom.*[13b]

[12] D. H. Harris, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J.C.S. Dalton*, 1976, 945.

[13] (*a*) A. G. Davies and J. D. Donaldson, *J. Chem. Soc.* (*A*), 1968, 946; (*b*) S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *ibid.*, 1971, 1311.

[14] V. I. Goldanskii, V. Ya. Rochev, and V. I. Khrapov, *Doklady Akad. Nauk S.S.S.R.*, 1964, **156**, 909.

[15] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, *Proc. Phys. Soc.*, 1962, **79**, 416.

[16] T. C. Gibb, B. A. Goodman, and N. N. Greenwood, *Chem. Comm.*, 1970, 774; J. D. Donaldson, E. J. Filmore, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1109.

We also suggest that the V_{zz} lies along the direction of the weak Sn–Sn interaction forming the dimer.

A striking physical property of $Sn[CH(SiMe_3)_2]_2$ is that the colour of the solid, which is red at room temperature, fades reversibly to pale yellow on cooling to liquid-nitrogen temperature.[7,8] This suggests close-lying, thermally accessible, electronic states for this molecule. However, it is possible that a structural change occurs on cooling. In this regard, we emphasise that the Mossbauer spectrum was recorded at 77 K, and note that satisfactory data could not be obtained at room temperature.

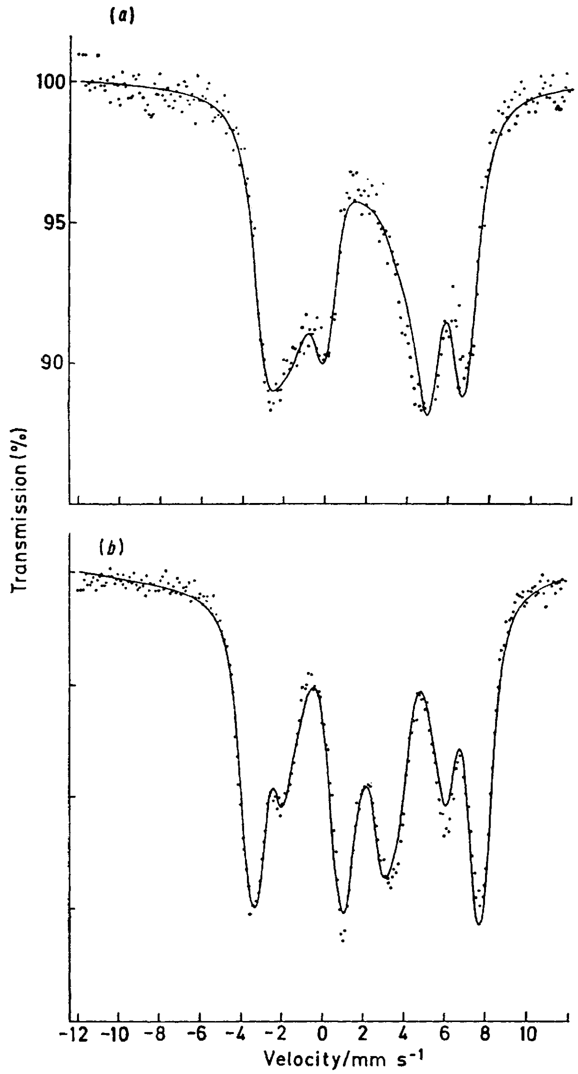

FIGURE 1 ^{119}Sn Mossbauer spectra of (*a*) SnR_2 and (*b*) $[Cr(CO)_5(SnR_2)]$ in an applied magnetic field [$R = CH(SiMe_3)_2$]

The quadrupole splitting values for the three-co-ordinate stannylene transition-metal complexes are very much larger than that for $Sn[CH(SiMe_3)_2]_2$, and in fact are among the largest recorded for organotin systems. A magnetic Mössbauer study of $[Cr(CO)_5\{Sn[CH(SiMe_3)_2]_2\}]$ has been carried out and, like $Sn[CH(SiMe_3)_2]_2$, indicates [Figure 1(*b*)] that eQV_{zz} is negative and, hence, V_{zz} positive. As before, the direction of V_{zz} can be identified with that of the vacant $5p_z$ orbital on tin. In this case, however, there are no weak interactions between Sn and any atom in the *z* direction. This produces a larger *p* imbalance between the *z* and the *x* and *y* directions and leads to the larger value for the quadrupole splitting. Interestingly, the quadrupole splittings for the four-co-ordinate tin complexes, *e.g.* $[Cr(CO)_5(SnBu^t_2{\cdot}thf)]$ and $[Cr(CO)_5(SnBu^t_2{\cdot}py)]$, in which the base lone-pair ' occupies ' the vacant $5p$ orbital, are again large, but decrease with increase of base strength.[10] Magnetic Mössbauer data for these materials are not available for comparison. The Mössbauer spectrum of a three-co-ordinate stannylene complex of $Sn(C_5H_5)_2$ with the main-group Lewis acid BF_3 has been recorded.[3b] In this case, the quadrupole splitting is small (0.90 mm s^{-1}) and only slightly higher than that of the free $Sn(C_5H_5)_2$ moiety.

The isomer shifts for our five stannylene complexes do not differ markedly from that for $Sn[CH(SiMe_3)_2]_2$ which suggests that the *s*-electron density at the Sn nucleus is similar in each case; in all the compounds, the tin is, of course, three-co-ordinate. No significant change in isomer shift occurs in going from mono- to di-substituted products. The lack of sensitivity of isomer shift has a parallel in the values observed for $Sn(C_5H_5)_2$ (3.74 mm s^{-1}) and $Sn(C_5H_5)_2{\cdot}BF_3$ (3.79 mm s^{-1}).[3b] Direct comparison of these data may be misleading, for while $Sn(C_5H_5)_2$ and $Pb(C_5H_5)_2$ have discrete angular structures in the gas phase,[17] the crystal structure of $Pb(C_5H_5)_2$ indicates polymerisation through bridging η-cyclopentadienyl groups.[18] Such polymerisation could modify the isomer-shift value of $Sn(C_5H_5)_2$ from the value typical of an isolated molecule, although, as the interactions involved are probably substantially ionic, the variation may be small.

The isomer shifts of the base-complexed molecules, *e.g.* $[Cr(CO)_5(SnBu^t_2{\cdot}thf)]$ and $[Cr(CO)_5(SnBu^t_2{\cdot}py)]$, studied [10] by Zuckerman and his co-workers lie slightly below those of our stannylene compounds. Together with *X*-p.e. and ^1H n.m.r. coupling-constant data, these shifts have been interpreted as favouring a tin(IV) formulation.[10] However, in our opinion, a strict classification into a formal oxidation state is of limited value for compounds of this type. Such a decrease in isomer shift, on co-ordination of a base to a tin(II) species, has a parallel in the value obtained for $SnCl_2$ (4.01 mm s^{-1}) and $SnCl_2{\cdot}py$ (3.24 mm s^{-1}).[19]

During the course of this work, tin(II) halide complexes $[M(CO)_5(SnX_2)]$ ($X = I$, $M = Cr$; $X = Br$, $M = W$; and $X = Cl$, $M = Mo$ or W) were prepared. In other cases, thf complexes, which by analogy with $[Cr(CO)_5(SnBu^t_2{\cdot}py)]$ probably have the base molecule co-ordinated to the tin atom, were isolated using the same synthetic procedure.[9] These complexes provide an ideal series for further evaluation of the factors affecting

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[17] A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organometallic Chem.*, 1967, **7**, 97.

[18] C. Panattoni, G. Bombieri, and U. Croatto, *Acta Cryst.*, 1966, **21**, 823.

[19] J. D. Donaldson, D. G. Nicholson, and B. J. Senior, *J. Chem. Soc.* (*A*), 1968, 2928.

both isomer shifts and quadrupole splittings in such systems. Data on the thermally unstable base adducts [1] of $Sn[CH(SiMe_3)_2]_2$ will also be pertinent.

The Mossbauer spectrum of $[PtCl(PEt_3)(SnR_2)(SnR_2Cl)]$ [$R = CH(SiMe_3)_2$] proved useful in the characterisation of this complex (Figure 2). Two sets of Mössbauer parameters were identified: (*i*) the isomer shift of 2.05 mm s^{-1} and the associated quadrupole splitting of 4.23 mm s^{-1} are clearly characteristic of a co-ordinated SnR_2 group; while (*ii*) the isomer shift of 1.73 mm s^{-1} and quadrupole splitting of 2.66 mm s^{-1} are appropriate to quadrivalent tin bound to a transition metal.[2] The formation of this complex, a rare example of an organometallic complex containing a metal in two oxidation states, can be envisaged as involving cleavage (probably *trans* to the phosphine) of the chloride bridge in $[\{PtCl_2(PEt_3)\}_2]$ by SnR_2, and insertion of a further mole of SnR_2 into one of the Pt–Cl bonds.[1]

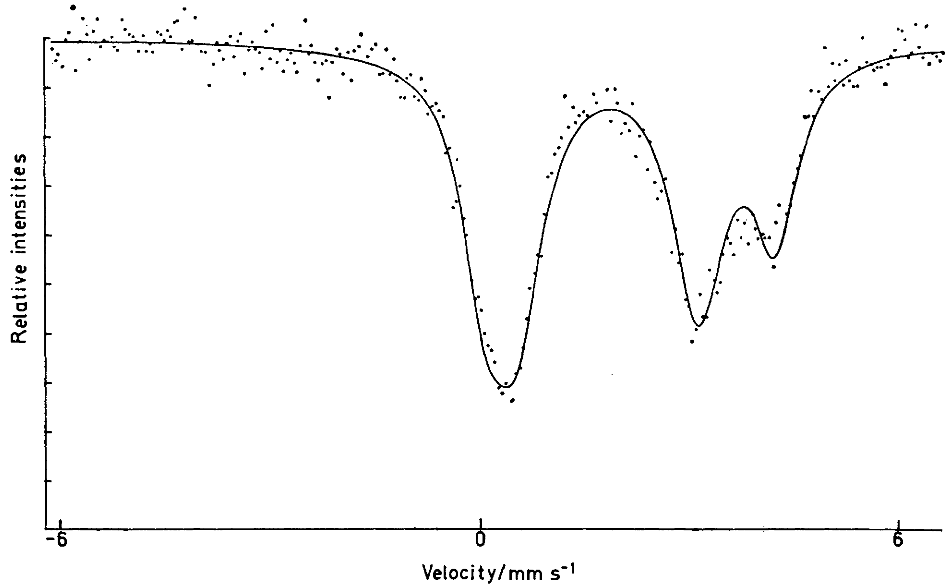
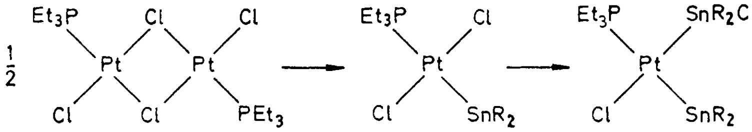


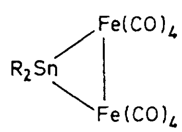
FIGURE 2 ^{119}Sn Mossbauer spectrum of $[PtCl(PEt_3)(SnR_2)(SnR_2Cl)]$



Mössbauer measurements have also been helpful in the assignment of a valence state of four to a variety of other complexes formed *via* the insertion of SnR_2 into M–H, M–alkyl, M–Cl, or M–M {for (III); strictly, this is not an insertion into an Fe–Fe ' bond ' of $[Fe_2(CO)_9]$} bonds. The data are shown in the Table.

The isomer shift and quadrupole splitting for $[\{Fe(CO)_4\}_2SnR_2]$ clearly rule out a stannylene formulation and are consistent with a triangulated structure (III). The isomer-shift value (1.73 mm s^{-1}) compares closely with that of $[\{Fe(CO)_4(SnBu^t_2)\}_2]$ (1.83 mm s^{-1}) which has a four-membered Fe_2Sn_2 ring, but the quadrupole splitting is slightly larger (1.53 *versus* 1.16 mm s^{-1}).[10] This higher value may be associated with the greater distortion from a tetrahedral geometry expected in the three-membered ring system. (Compare, *e.g.*, the FeSnFe bond angle of 69° in $[\{Fe(CO)_4\}_4Sn]$,[20] a molecule with two Fe_2Sn triangles, with the SnFeSn bond angle of 103° in $[\{Fe(CO)_4(SnMe_2)\}_2]$.[21])

The isomer-shift values for the series SnR_3Cl, $SnBrR_3$, and $SnMeR_2I$ [$R = CH(SiMe_3)_2$] are generally similar to those of other trialkyltin halides.[2] The quadrupole-splitting values for SnR_3Cl and $SnBrR_3$ are, however, lower (*cf.*[22] for $SnBu^n_3I$, δ 1.152 and Δ 2.96 mm s^{-1}). This suggests either that $CH(SiMe_3)_2$, when attached to Sn, is less electron withdrawing than Me, Et, or Ph, or, more probably, that the bulky halides are monomeric in the solid state possibly with significant ionic character. The $CH(SiMe_3)_2$ group is generally regarded as electron releasing.[22]



(III) $R = CH(SiMe_3)_2$

Data were also collected for four new complexes containing tin(IV)–transition-metal bonds. The isomer shifts agree well with those reported for analogous molecules (see Table). The small quadrupole splitting

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[20] P. Woodward and P. F. Lindley, *J. Chem. Soc.* (*A*), 1967, 382.

[21] C. J. Gilmore and P. Woodward, *J.C.S. Dalton*, 1972, 1387.

[22] *cf.*, M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 293.

for [Mo(η-C_5H_5)$(CO)_3$(SnR_2H)] is interesting and suggests that there is little difference in the character of the Sn–C, Sn–H, and Sn–Mo bonds. The larger splitting for [Fe(η-C_5H_5)$(CO)_2$(SnR_2Cl)] reflects the *p*-orbital imbalance between the Sn–Cl and Sn–C bonds.

EXPERIMENTAL

The Mossbauer data were obtained at 80 K using a $BaSnO_3$ source supplied by The Radiochemical Centre, Amersham. The chemical shift of the reference material, α-Sn, from $BaSnO_3$ was measured as 2.05 mm s^{-1}. The Mossbauer apparatus has been described elsewhere.[23] Preparative details for the compounds discussed have been published separately.[1,7]

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[6/353 *Received*, 19*th February*, 1976]

[23] S. R. A. Bird, J. D. Donaldson, A. F. LeC. Holding, B. J. Senior, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1616.