X-Ray Crystal Structure Analysis, Nuclear Magnetic Resonance and Mössbauer Parameters of *trans*-Tetrachlorobis(triethylphosphine)tin(IV)

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Crystals of the title compound are monoclinic, space group $P2_1/n$ with $Z = 2$ in a cell of dimensions $a = 7{\cdot}189(8)$, $b = 12{\cdot}053(15)$, $c = 12{\cdot}028(14)$ Å, $\beta = 91° 10'(20)$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to R 9·9% for 1206 visually estimated reflections. The centrosymmetric molecules have bond angles at tin within 1·3° of 90°; Sn–P is 2·615(5) Å, and Sn–Cl are 2·445(5) and 2·455(5) Å. The bond lengths are compared with those in phosphine complexes of transition- and Group B metal chlorides. The results are consistent with an earlier suggestion from Mössbauer studies that the Sn–P bonds have high tin 5*s*-character, and an approximate analysis of Sn–P n.m.r. coupling constants further supports this. An explanation is offered for the different modes of variation of ^1J(M–P) for complexes of the phosphines $R_nPh_{n-3}P$.

THE examination of a variety of spectroscopic parameters in conjunction with bond-length measurements has led to the recognition of substantial variations in the σ-bond characters of metal–ligand bonds in phosphine complexes of transition-metal chlorides.[1-3] Although spectroscopic parameters are often available for phosphine complexes of non-transition metals, very few bond lengths have been determined, and none are known for octahedral complexes. In order to obtain bond lengths suitable for comparison with known values in transition-metal compounds, we have undertaken an *X*-ray crystal structure analysis of the complex $[SnCl_4(Et_3P)_2]$. A *trans*-structure previously inferred from vibrational spectroscopy [4,5] has been confirmed by the present study, so direct comparison with the series of transition-metal complexes *trans*-$[MCl_4Y_2]$ (M = W, Re, Os, Ir, Pt; Y = phosphine) is possible.[2] The bond-length measurements are also highly relevant to the interpretation of Mössbauer and ^{31}P n.m.r. parameters of phosphine complexes of tin(IV) chloride which have been reported recently.[5,6]

EXPERIMENTAL

Complex.—The complex was prepared from anhydrous tin(IV) chloride (1 mol) and triethylphosphine (2 mol) in oxygen-free dried benzene by the method of ref. 7. Addition of dry hexane gave white prisms, m.p. 135—137 °C (lit.,[7] 145—150 °C) (Found: C, 29·8; H, 6·3. Calc. for $C_{12}H_3OCl_4P_2Sn$: C, 29·0; H, 6·9%), which proved suitable for *X*-ray analysis.

Crystal Data.—$C_{12}H_{30}Cl_4P_2Sn$, $M = 496{\cdot}7$, Monoclinic, $a = 7{\cdot}189(8)$, $b = 12{\cdot}053(15)$, $c = 12{\cdot}028(14)$ Å, $\beta = 91° 10'(20)$, $U = 1042{\cdot}0$ Å^3, $Z = 2$, $D_m = 1{\cdot}60$ (by flotation), $D_c = 1{\cdot}583$, $F(000) = 500$. Space group $P2_1/n$. (This result was reported by others after completion of this work.[6]) Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 161·4 cm^{-1}.

Crystallographic Measurements.—A single crystal in the shape of a needle-like prism of cross-section 0·25 × 0·25 mm was used for data collection. Cell dimensions were obtained from precession photographs taken with Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å). Three-dimensional intensity data were collected from equi-inclination Weissenberg photographs of the 0—5*kl* levels and estimated visually. Data were corrected for Lorentz polarisation effects but not for absorption (the good agreement between chemically equivalent bond lengths indicates that this does not significantly affect positional parameters). A total of 1204 non-zero independent reflections were obtained, and were placed on the same scale through common reflections.

Structure Analysis.—All calculations were carried out on the ATLAS computer of the S.R.C. Chilton Laboratory by use of the *X*-Ray System programmes.† The space-group symmetry of this structure requires that the tin atom lies on a centre of symmetry. This atom was placed at the origin and its positional co-ordinates held constant throughout the analysis. Interpretation of the three-dimensional Patterson synthesis gave in addition the co-ordinates of the two independent chlorine atoms. A structure-factor calculation based on these three atoms gave R 32%. The phosphorus atom and five of the six independent carbon atoms were located from the resulting electron density map, and the remaining carbon atom was easily identified from a difference-Fourier synthesis based on the atoms previously found. Full-matrix least-squares refinement with all atoms having individual isotropic temperature factors resulted in R 12·3%, which was reduced to 10·2% after the assignment of anisotropic temperature factors to the tin, chlorine, and phosphorus atoms. Atomic scattering factors were taken from ref. 8 except those for tin which were taken from ref. 9. The factors for tin, chlorine, and phosphorus were corrected for real and imaginary components of anomalous dispersion.[10] A difference-Fourier map calculated at this stage showed ten of the fifteen hydrogen atom positions above background at heights 0·3—0·6 eÅ^{-3}. The remaining hydrogen positions could be calculated and all were included, though not refined, in the final three cycles of full-matrix least-squares calculations

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† '*X*-Ray System', version of July 1970, ed. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

[1] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1707; A. Pidcock and J. F. Nixon, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

[2] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Comm.*, 1970, 30.

[3] S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**, 6669.

[4] I. R. Beattie and G. A. Ozin, *J. Chem. Soc.* (*A*), 1970, 370; R. Rivest, S. Singh, and C. Abraham, *Canad. J. Chem.*, 1967, **45**, 3137; P. G. Harrison, B. C. Lane, and J. J. Zuckerman, *Inorg. Chem.*, 1972, **11**, 1537.

[5] A. J. Carty, T. Hinsperger, L. Mihichuk, and H. D. Sharma, *Inorg. Chem.*, 1970, **9**, 2573.

[6] J. F. Malone and B. E. Mann, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 819.

[7] J. A. C. Allison and F. G. Mann, *J. Chem. Soc.*, 1949, 2915.

[8] 'International Tables for Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[9] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[10] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

which converted at R 9·9% for the 1206 independent reflections. The hydrogen atoms were arbitrarily assigned isotropic temperature factors of B 5·0 for this purpose. The weighting scheme used in the least-squares refinement was $w = 1{\cdot}0/(A + B|F_o|)$, where $A = 1{\cdot}0$ and $B = 0{\cdot}04$, chosen from an analysis of the variance. In the last cycle of refinement parameter shifts were all $< 0{\cdot}05\ \sigma$.

RESULTS AND DISCUSSION

Final atomic parameters are given in Table 1 for the numbering scheme of Figure 1; the first digit of a hydrogen atom number refers to the carbon atom to which it is attached. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20732 (2 pp., 1 microfiche).* Bond lengths and angles are listed in Table 2 and the molecular structure and unit-cell contents are illustrated in Figures 1—3. There are no short intermolecular contacts and the deviations from 90° valence angles about the tin atom are very small.

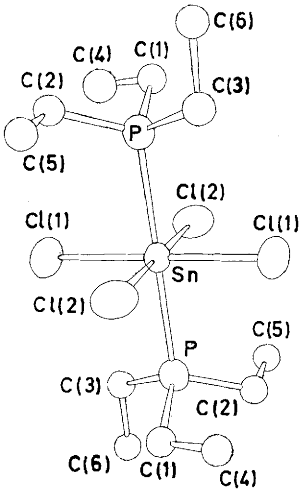

FIGURE 1 Structure of the molecule showing the numbering scheme

Bond lengths.—Bond lengths have not been determined in other *trans* complexes of tin(IV) chloride, but a variety of *cis*-complexes have been examined by X-ray crystallography as have several adducts of the methyltin chlorides.[11] The mean Sn–Cl distance [2·450(5) Å] in the present complex is longer than in *cis*-$[SnCl_4(OSeCl_2)_2]$ (2·36 and 2·41 Å),[12] *cis*-$[SnCl_4(OPCl_3)_2]$ (2·31—2·41 Å),[13] and in $[SnCl_4(MeCN)_2]$ (2·34—2·56 Å),[14] and $[SnCl_4\{NC(CH_2)_3CN\}]$ (2·35 Å),[15] for both of which structures with *cis*-nitrogen atoms have been found. In complexes having the electropositive methyl ligand present, the Sn–Cl distances are longer, as in $[SnCl_2Me_2(DMSO)_2]$ (2·51 Å), $[SnCl_2Me_2(pyO)_2]$ (2·58 Å), and $[SnClMe_2(terpy)]^+$ (2·65 Å),[11] so it would appear that the greater electropositive character of phosphorus in comparison with nitrogen and oxygen is responsible for the differences

TABLE 1

(*a*) Fractional atomic co-ordinates (×10⁴), with standard deviations in parentheses, and thermal parameters (×10³) for atoms refined with isotropic temperature factors

	x/a	y/b	z/c	U
Sn	0 *	0 *	0 *	
Cl(1)	1627(7)	−33(5)	−1766(4)	
Cl(2)	2417(7)	1223(4)	789(4)	
P	1802(7)	−1762(4)	691(4)	
C(1)	3818(26)	−1415(16)	1556(17)	55(5)
C(2)	443(28)	−2660(18)	1583(17)	63(5)
C(3)	2547(27)	−2542(18)	−483(17)	61(5)
C(4)	3405(29)	−987(19)	2673(19)	69(6)
C(5)	−1027(33)	−3360(21)	1007(21)	81(7)
C(6)	3612(32)	−3644(21)	−187(20)	79(7)
H(11) †	4678	−2148	1657	63
H(12)	4626	−788	1135	63
H(21)	1408	−3221	2008	63
H(22)	−208	−2148	2199	63
H(31)	1328	−2749	−989	63
H(32)	3442	−2020	−972	63
H(41)	4577	−783	3192	63
H(42)	2542	−254	2583	63
H(43)	2594	−1614	3105	63
H(51)	−1854	−3894	1533	63
H(52)	−2013	−2806	586	63
H(53)	−398	−3878	396	63
H(61)	4066	−4118	−903	63
H(62)	4836	−3442	301	63
H(63)	2721	−4171	285	63

* Not refined. † Hydrogen parameters were not refined and therefore no estimated standard deviations were obtained.

(*b*) Thermal parameters (×10⁴), with standard deviations in parentheses, of atoms refined with anisotropic temperature factors of the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	347(12)	417(8)	309(7)	−21(8)	31(5)	1(8)
Cl(1)	882(41)	790(33)	487(27)	157(31)	251(23)	78(31)
Cl(2)	643(37)	495(25)	708(33)	−100(22)	−226(24)	−5(23)
P	407(34)	462(24)	418(25)	−57(21)	−1(19)	−37(20)

TABLE 2

(*a*) Bond distances (Å), with standard deviations in parentheses

Sn–Cl(1)	2·445(5)	P–C(3)	1·79(2)
Sn–Cl(2)	2·455(5)	C(1)–C(4)	1·48(3)
Sn–P	2·615(5)	C(2)–C(5)	1·51(3)
P–C(1)	1·82(2)	C(3)–C(6)	1·57(3)
P–C(2)	1·82(2)		

(*b*) Valence angles (deg.), with standard deviations in parentheses

Cl(1)–Sn–Cl(2)	89·90(0·18)	Sn–P–C(3)	109·3(0·7)
Cl(1)–Sn–Cl(2′)	90·10(0·18)	C(1)–P–C(2)	103·4(0·9)
Cl(1)–Sn–P	91·18(0·18)	C(1)–P–C(3)	109·0(0·9)
Cl(1)–Sn–P′	88·82(0·18)	C(2)–P–C(3)	109·0(1·0)
Cl(2)–Sn–P	91·29(0·15)	P–C(1)–C(4)	115·4(1·4)
Cl(2)–Sn–P′	88·71(0·15)	P–C(2)–C(5)	116·2(1·6)
Sn–P–C(1)	112·3(0·6)	P–C(3)–C(6)	114·7(1·5)
Sn–P–C(2)	113·7(0·7)		

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-sized copies.)

[11] F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc.* (*A*), 1968, 3019; E. A. Blom, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc.* (*A*), 1969, 913.

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[13] C-I. Branden, *Acta Chem. Scand.*, 1963, **17**, 759.

[14] H. E. Blaydon and M. Webster, *J. Chem. Soc.* (*A*), 1969, 2443.

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in the bond lengths in the tin(IV) chloride addition complexes.* There is evidence that the presence of methyl groups in the co-ordination sphere of tin lowers the *s*-character of the Sn–Cl bonds,[16] causing them to be weakened, and since both methyl and phosphine ligands are known to have relatively high affinities for transition-metal *s*-orbitals,[17] it is reasonable to suppose that a similar effect is responsible for the Sn–Cl lengths in the tin(IV) chloride complexes.

The Sn–P distance (2·615 Å) is 0·165 Å longer than the mean of the Sn–Cl distances, and is significantly larger than the difference (0·11 Å) between the covalent radii of phosphorus (1·10 Å) and chlorine (0·99 Å). Differences in the same sense [*i.e.* l(M–Cl) $<$ l(M–P)] are found for *trans*-phosphine complexes of transition metals, but the magnitude of the difference is dependent on the metal and its oxidation-state. For square-planar Ni^{II} the difference is 0·08 Å,[18] and for platinum it is very small ($<$0·02 Å) in oxidation-state (II)[19] and larger (0·06 Å) in oxidation-state (IV).[2] Only for earlier transition-metals in higher oxidation states (W^{IV}, Re^{III}, Re^{IV}, and Os^{IV})[2] do the differences become large enough to be comparable with those for Sn^{IV}.

For the Group B metals (Table 3), the presently available results[20-22] indicate that the relatively large

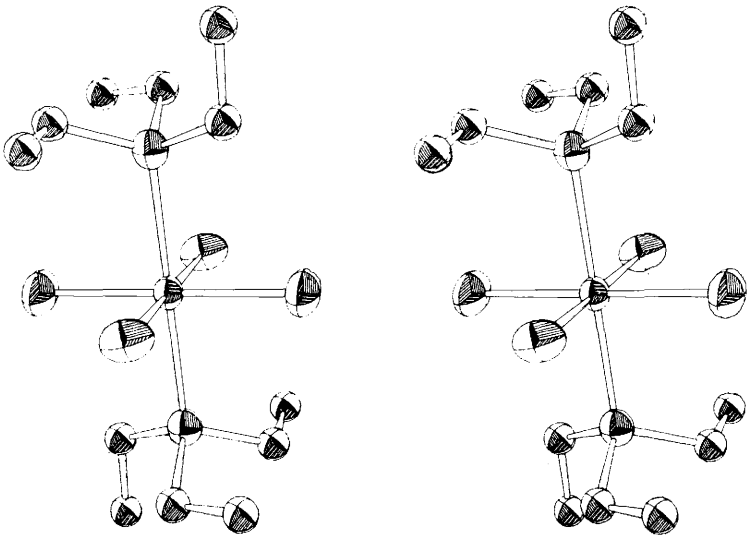

FIGURE 2 Stereoscopic pair † of perspective projections showing the anisotropic motion of the Sn, Cl, and P atoms. The thermal ellipsoids are scaled to enclose a 50% probability. The carbon atoms are shown as spheres of arbitrary radii

† These stereograms are best viewed with a stereoscope having a 12 cm focal length and a 6·5 cm separation between optical centres. They were prepared by use of ORTEP, A Fortran thermal ellipsoid plot program, P. 55, C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

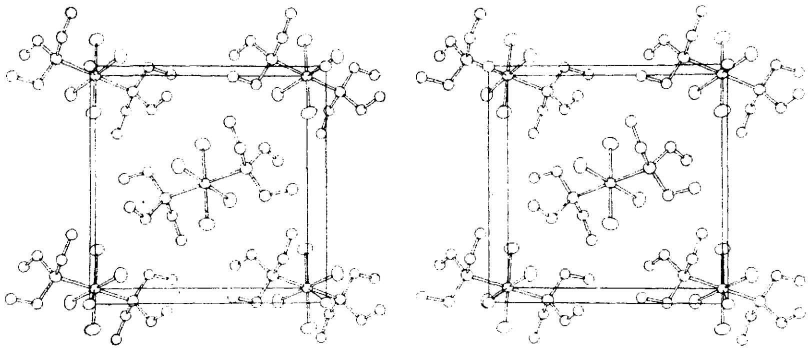

FIGURE 3 Stereogram showing the unit-cell contents as viewed down the mean *a** axis, the *c* axis points up the page and the unique monoclinic *b* axis lies across the page. The molecule is centred on the corner of the unit cell and also at the centre of the cell. For clarity only the Sn atoms of the molecules centred on the top corners are shown ‡

‡ See footnote to Figure 2.

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* DMSO = dimethyl sulphoxide, pyO = pyridine oxide, and terpy = terpyridyl.

[16] J. C. Hill, R. S. Drago, and R. H. Herber, *J. Amer. Chem.* 1969, **91**, 1644; R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 1296.

[17] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

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[20] A. F. Cameron, K. P. Forrest, and G. Ferguson, *J. Chem. Soc.* (*A*), 1971, 1286.

[21] G. G. Mather and A. Pidcock, *J.C.S. Dalton*, 1973, 560; J. Bennett, P. Coggon, A. T. McPhail, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2094.

[22] M. V. Veidis and G. D. Palenik, *Chem. Comm.*, 1969, 586.

difference in the M–P and M–Cl lengths is present in the higher and lower oxidation-states and that the difference undergoes rapid changes for oxidation-state (II) as the electron configuration changes from d^8 to d^{10}, reversing the trend in the results across the transition-metal series. Until recently, this difference between the Group VIII metals and the Group B metals would probably have been attributed to the availability of d_π electrons for back-donation to phosphorus in the complexes of the Group VIII metals, but the evidence now clearly indicates that π-bonding between alkylphosphines and, for example, platinum(II) is probably very weak indeed.[23] It seems probable that an explanation in terms of the changes of energy and form of the metal σ-orbitals should be sought, and it would be of interest to extend the calculations of Mason and Randaccio [24] to complexes of Group B metals. It is possible that one factor which tends to lead to relatively weak phosphorus to Group B metal bonding is the absence or very small degree of participation of metal d_σ orbitals. Also, apart from any specific effect this would have on the binding energy of phosphorus ligands, the availability of only *s*- and *p*-orbitals in the valence shell of Group B metals can be expected to lower the total metal–ligand binding energy in octahedral complexes compared with that in complexes of transition-metals, and the generally weaker bonds which result will show greater changes in length in response to steric effects than do transition-metal complexes. A combination of effects of this sort would seem to be necessary to explain the very long bonds to phosphorus in the trigonal bipyramidal complex [$InCl_3(Ph_3P)_2$].[22]

TABLE 3

Metal–phosphorus and –chlorine distances (Å) in complexes of Group B metal chlorides

Complex	Mean l(M–P)	 l(M–Cl)	Δ [a]
$CdCl_2(Ph_3P)_2$ [b]	2·63	2·47	0·16
$Hg[(RO)_2PO]_2$ [b]	2·41	2·30 [d]	0·11
$InCl_3(Ph_3P)_2$ [c]	2·71	2·38	0·33
$SnCl_4(Et_3P)_2$ [e]	2·61	2·45	0·16

[a] Δ is l(M–P) minus l(M–Cl). [b] Ref. 20. [c] Ref. 21. [d] Length in octahedral complexes of $HgCl_2$. [e] Ref. 22.

N.m.r. Coupling Constants.—Metal–phosphorus coupling constants are determined in part by the *s* component of the metal–phosphorus bond and results for the ^{117}Sn–^{31}P and ^{119}Sn–^{31}P coupling constants in *trans*-[$SnCl_4Y_2$] (Y = Et_3P or Et_2PhP) have been reported very recently.[6] The approximate MO expression for the Fermi contact contribution to ^1J(M–P) involves a variety of terms in addition to the *s* component of the bond,[1] and since these are of rather uncertain magnitude, it is not possible to determine directly from the coupling constants whether, as was suggested in the discussion of the bond lengths, the phosphine ligands induce a high *s*-contribution in the tin orbitals forming the Sn–P bonds. Some indication may, however, be obtainable by a calculation of ^1J(Sn–P) from an expression of the type in equation (1).[25] Here the ratio of the indirect coupling constants ^2J(MCH) in four-co-ordinate compounds are used to correct ^1J(Pt–P) in *trans*-[$PtCl_4(Et_3P)_2$] (1474 Hz) [25] for differences between tin and platinum magnetogyric ratios, excitation energies, and valence-state *s*-electron densities at the metal nuclei. The use of values of ^2J(MCH) for this purpose is justified, apart from the availability of the data, on the grounds that the methyl ligands are considered to have high affinities for metal *s*-orbitals in both tin compounds [16] and platinum complexes,[17] and it has also been shown that there is a linear relationship between ^2J(PtCH) in *trans*-[Pt(Me)XP_2] and ^1J(Pt–P) for the phosphonate ligand in *trans*-[Pt{$(PhO)_2PO$}XP_2].[26] There exists a measure of choice in the values of ^2J(MCH), as they depend significantly on the other ligands attached to the metal. We have selected $^2J(^{119}$SnCH) in $MeSnCl_3$ (100 Hz) [27] and ^2J(PtCH) in *trans*-[Pt(Me)ClP_2] (85 Hz),[17] because in platinum(II) compounds the coupling constants are sensitive to the nature of the *trans*-ligand and the co-ordination number of the complex. The value of ^2J(SnCH) is larger in $MeSnCl_3$ than the other methyltin chlorides, so use of other values would give smaller values of $^1J(^{119}$Sn–P) from equation (1). Insertion of the numerical values leads to an estimate of 1734 Hz for $^1J(^{119}$Sn–P) in *trans*-[$SnCl_4(Et_3P)_2$], and this is to be compared with the experimental result of 2383 Hz.[6] As the Pt–P bonds in *trans*-[$PtCl_4(Et_3P)_2$] have a significantly greater share of the platinum 6*s*-orbital than do the Pt–Cl bonds,[23,24] the result that ^1J(Sn–P) is even greater than the value calculated from equation (1), supports the suggestion that there is a large tin 5*s*-component in the Sn–P bonds, provided that the estimate from equation (1) is not too imprecise.

$$^1J(\text{Sn–P}) \simeq [^2J(\text{SnCH})/^2J(\text{PtCH})] \cdot {}^1J(\text{Pt–P}) \qquad (1)$$

Some tests of expressions of the type of equation (1) can be made with results for rhodium and mercury compounds. The magnitude of ^2J(RhCH) in *trans*-[$RhCl_2(CH_3)(CO)(Me_2PhP)_2$], in which the methyl group is *trans* to chloride, can be estimated from equation (2), the value of ^1J(M–P) for the mutually *trans* phosphines in *mer*-[$RhCl_3(Et_3P)_3$] (83·8 Hz),[28] in *trans*-[$PtCl_2(Et_3P)_2$] (2400 Hz),[1] and the value of ^2J(PtCH) given earlier. The calculation gives an estimate of 3·0 Hz for ^2J(RhCH) which compares reasonably well with the value 2·1 Hz

$$^2J(\text{RhCH}) \simeq [^1J(\text{Rh–P})/^1J(\text{Pt–P})] \cdot {}^2J(\text{PtCH}) \qquad (2)$$

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[28] B. E. Mann, C. Masters, and B. L. Shaw, *J.C.S. Dalton*, 1972, 704.

reported for *trans*-[$RhCl_2(Me)(CO)(Me_2PhP)_2$].[29] Alternatively, the ratio of the M–P couplings in equation (2) can be calculated from the results for square-planar compounds, *viz.* [$RhCl(CO)(Et_3P)_2$] ^1J(Rh–P) 116·1 Hz,[30] and *trans*-[$PtCl_2(Et_3P)_2$ (2400 Hz),[1] and the value of ^2J(PtCH) 67 Hz for the octahedral complex *trans*-[$PtCl_3(Me)(Me_2PhP)_2$] in which the methyl group is *trans* to chloride.[31] In this instance, the calculated value of ^2J(RhCH) is 3·2 Hz, and other available results permit a third estimate of 2·7 Hz to be made by use of values of ^1J(M–P) for phosphines *trans* to chloride in Rh^{III} (ref. 28) and Pt^{IV}.[1] Comparable results are available for approximately diagonal mercury(II) compounds, where ^2J(HgCH) in MeHgCl may be estimated from ^2J(PtCH) in *trans*-[$PtCl(Me)(Et_3P)_2$] (85 Hz) [17] by use of equation (3) and the values of coupling constants ^1J(M–P) in [$HgCl\{(EtO)_2PO\}$] (12,670 Hz) [21] and *trans*-[$PtCl\{(MeO)_2PO\}(Bu_3P)_2$] (5238 Hz) [26] or in [$Hg\{(EtO)_2PO\}$] (7500 Hz) [21] and *trans*-[$Pt\{(EtO)_2PO\}_2(Et_3P)_2$] (3243 Hz).[26] The estimated values are 206 Hz and 197 Hz, both of which are in satisfactory agreement with the experimental value of 215 Hz.[32] Thus the estimation procedures [equations (1)—(3)] appear to have some value when results are available for complexes of suitable

$$^2J(\mathrm{HgCH}) \simeq [^1J(\mathrm{Hg{-}P})/^1J(\mathrm{Pt{-}P})] \,.\, ^2J(\mathrm{PtCH}) \quad (3)$$

oxidation-state, co-ordination number, and stereochemistry, but the method may not be useful when the metal–ligand bonds have very dissimilar characters. As already noted, for the heavy transition-metals, methyl- and phosphorus-donor ligands have several characteristics in common, and values of ^2J(MCH) and ^1J(M–P) appear to be particularly closely related.

The availability of bond-length measurements permits discussion of another aspect of metal–phosphorus n.m.r. coupling constants ^1J(M–P). These coupling constants increase with increasing phenyl substitution in the phosphines $R_nPh_{3-n}P$ for complexes of H^+, W^0, Rh^I, and Pt^{II},[1,30,33] but they decrease for the Group B metal complexes of Cd^{II},[34] Hg^{II},[1] and Sn^{IV}.[6] Changes in the valence-state *s* wavefunction at the phosphorus nucleus and the *s* character of the phosphorus lone-pair are expected to cause an increase of ^1J(P–M) with an increasing phenyl substitution,[1] and the results showing the opposite trend are for complexes where *X*-ray structure analysis indicates that the metal–phosphorus bonds are relatively weak (Table 3). For weak metal–phosphorus bonds the steric effects of phenyl groups on phosphorus may cause the effect of bond-lengthening on ^1J(M–P) to outweigh the changes in the *s* orbitals on phosphorus. In addition, differences in the basicities of the phosphines may well lead to greater changes of M–P bond length for the complexes of the Group B metals.

It has also been shown that ^2J(PSnP′) in *trans*-[$SnCl_4(Et_3P)(Et_2PhP)$] is much smaller than values found for *trans*-phosphines in complexes of transition-metal chlorides.[6] Although the approximate MO expression for the indirect couplings contains several terms that could differ for the transition and Group B metals,[1] the result is not surprising in view of the long Sn–P bonds found for *trans*-[$SnCl_4(Et_3P)_2$]. The indirect coupling constants are related to coefficients of the phosphorus *s*-orbitals in the M–P σ-orbitals of the complex, and these coefficients will decrease with increase of M–P bond length. The result for ^2J(PSnP′) is certainly not inconsistent with the inference of large tin 5*s*-contributions to Sn–P bonding, since the coefficients of the metal orbitals do not enter the expression for ^2J(PMP′).

Mössbauer Parameters.—The earlier discussion has provided support for a model for the bonding in *trans*-[$SnCl_4P_2$] which is, in extreme form, the utilization of tin 5*s*- and one 5*p*-orbital for bonds to phosphorus, with the remaining two 5*p*-orbitals used for three-centre bonding to four chlorine atoms. Support for this model has been obtained previously from Mössbauer parameters.[5] The isomer shift in phosphine adducts of $SnCl_4$ indicates an *s*-electron density at the tin nucleus similar to that in $SnCl_4$ and greater than that in complexes with nitrogen- or oxygen-atom donors.[5] The longer Sn–Cl bonds in the phosphine complexes indicate greater ionic character in the Sn–Cl bonds which thereby make a smaller contribution to the metal *s*-density, so the interaction between tin and the less-electronegative phosphorus atoms must be associated with considerable tin 5*s*-character. In addition, the quadrupole splittings in the Mössbauer spectra of the phosphine complexes are consistent with the bonding model,[5,35] since this involves substantially greater occupation of the 5*p* orbitals used in bonding to phosphorus compared with those used for chlorine.

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