Studies in Mössbauer Spectroscopy. Part VI.[1] Tin-119 Spectra of Some Trichlorostannyl Transition-metal Complexes

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The ^{119}Sn-Mössbauer data for some trichlorostannyl complexes of iron(II), ruthenium(II), rhodium(I), iridium(III), platinum(II), copper(I), silver(I), and gold(I) are reported and discussed in terms of the nature of the tin–metal bond. Previously suggested configurations for complexes of the type $(Ph_3P)_2Pt(X)SnCl_3$ (X = Cl and H) have been confirmed by i.r. data, and it has been shown that the red complexes previously thought to contain the *trans*-$[PtCl_2(SnCl_3)_2]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$ anions have identical Mössbauer and i.r. parameters; it seems likely that the latter formulation is correct. The isomer shifts of all the complexes have been correlated with the Sn–Cl stretching frequencies.

TRICHLOROSTANNYL derivatives of many transition metals are known, but most data are available for metal carbonyl and cyclopentadienyl–carbonyl complexes. ^{119}Sn-Mössbauer data have been reported for several trichlorostannyl complexes, and for many related derivatives.[2,3] Although all these compounds are formally derived from the tin(II) species $SnCl_3^-$, the isomer shifts indicate that the tin is definitely four-covalent.[4-6] We now report the Mössbauer parameters for trichlorostannyl derivatives of a range of metals from Groups VIII and IB, the majority of which involve ligands other than carbonyl or cyclopentadienyl groups. In some cases, previously suggested stereochemistries have been confirmed by i.r. measurements.

RESULTS AND DISCUSSION

Platinum Complexes.—Phosphine complexes. A few phosphine-containing trichlorostannyl complexes have been reported. Orange and white isomers of composition $(Ph_3P)_2Pt(Cl)SnCl_3$ have been assigned *cis*- and *trans*-geometry respectively on the basis that the reaction between *cis*-$(Ph_3P)_2PtCl_2$ and $SnCl_2$ gives the orange form first and substitution is expected to be stereospecific; the white (*trans*) isomer was assumed to be formed by slow isomerisation.[7] Similarly, the product

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[1] Part V, R. V. Parish and P. J. Rowbotham, *Chem. Phys. Letters*, 1971, **11**, 137.

[2] R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, 101.

[3] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, in the press.

[4] D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, 1969, **8**, 1771.

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

[6] G. M. Bancroft and K. D. Butler, *J.C.S. Dalton*, 1972, 1209.

[7] M. C. Baird, *J. Inorg. Nuclear Chem.*, 1967, **29**, 367.

obtained from treating *trans*-$(Ph_3P)_2PtHCl$ with stannous chloride was assumed to have the *trans*-configuration.[8] The ^1H n.m.r. spectrum of the corresponding triethylphosphine complex confirms the *trans*-geometry in this case also.[9] A derivative of platinum(IV), $(Ph_3P)_2PtCl_2(SnCl_3)_2$, has also been claimed.[7]

We have examined complexes of each of these types, data for which are in Table 1. Far-i.r. spectra for the two forms of $(Ph_3P)_2Pt(Cl)SnCl_3$ are not inconsistent with the *cis*- and *trans*-formulations suggested previously. Baird reported[7] that the isomers gave similar spectra in the region 300—350 cm^{-1}, with bands at 341, 325, and 315 cm^{-1} of which the first two were attributed to Sn–Cl stretching and the last to Pt–Cl stretching. We find that the two spectra are different in this region; we therefore assign the common bands as ν(Sn–Cl). In addition, the orange (*cis*) isomer has a band at 275 cm^{-1}, which is in the range normally associated with chlorine *trans* to a tertiary phosphine. In this isomer, the Pt–P mode also appears to be split. The white (*trans*) isomer has a single Pt–P band and an additional band at 339 cm^{-1} which we tentatively assign as the stretching of Pt–Cl with chlorine *trans* to $SnCl_3$. It has recently been shown that the *trans*-influence of the groups MCl_3 is considerably less than those of MR_3 (M = Si, Ge; R = Me, Ph), as measured by the change (*ca.* 30 cm^{-1}) in the *trans*-metal–chlorine stretching frequency.[10] A value of 339 cm^{-1} for ν(Pt–Cl) would be consistent with the same trend for M = Sn, since *trans*-$L_2Pt(Cl)SnMe_3$ has bands at 278 cm^{-1} (L = Et_3P)[11] or 296 cm^{-1} (L = Ph_3P).[12] On this basis, the $SnCl_3$ group has one of the lowest *trans*-influences known, which is in line with the weak σ-donor properties suggested for this ligand.[9]

TABLE 1

Spectroscopic and analytical data for platinum phosphine complexes

	δ	Δ	ν(Pt–P)	ν(Pt–Cl)	ν(Sn–Cl)			
	mm s^{-1}		cm^{-1}	cm^{-1}	cm^{-1}	C(%)[a]	H(%)[a]	Cl(%)[a]
trans-$(Ph_3P)_2Pt(Cl)SnCl_3$	1·84	2·07	418	339	320, 311, 290	44·4 (44·1)	3·3 (3·1)	14·8 (14·5)
cis-$(Ph_3P)_2Pt(Cl)SnCl_3$			417, 422	257	319, 310, 288	45·0 (44·1)	3·2 (3·1)	15·2 (14·5)
trans-$(Ph_3P)_2Pt(H)SnCl_3$	1·94	1·98	420	—	324, 298	47·1 (45·7)	3·7 (3·3)	11·2 (11·3)
trans-$(Et_3P)_2Pt(H)SnCl_3$	2·02	1·89				21·9 (21·9)	4·8 (4·7)	15·8 (16·2)
$(Ph_3P)_2PtCl_2(SnCl_3)_2$	1·69	1·94	420	—	335, 320	34·9 (34·8)	2·7 (2·4)	22·2 (22·9)

[a] Calculated values in parentheses.

Two values are reported[7,8] for the Pt–H stretching frequency of $(Ph_3P)_2Pt(H)SnCl_3$, *viz.*, 2056 and 2100 cm^{-1}; our value, 2096 cm^{-1}, is close to the higher of these. It has been suggested[8] that there may be *cis*- and *trans*-forms of this complex. On the argument used above, the *trans*-influence of $SnCl_3$ is considerably less than that of Ph_3P, so that the higher-frequency form obtained here is the *trans*-isomer. The frequency is very similar to that for $(Et_3P)_2Pt(H)SnCl_3$ (2105 cm^{-1}), which is known from n.m.r. evidence to have the *trans*-configuration.[13] We have also measured the n.m.r. spectrum of this complex, which agrees with the previous report. The hydride resonance (τ 19·4) shows coupling to platinum (142 Hz) but that to the phosphorus nuclei is not resolved, suggesting rapid exchange presumably by reversible elimination of $SnCl_2$.

The Mössbauer spectra of these complexes are all quite similar and show little dependence on substitution at platinum. [Unfortunately it was not possible to obtain a good spectrum of *cis*-$(Ph_3P)_2Pt(Cl)SnCl_3$ owing to equipment failure, but the results were clearly very similar to those for the *trans* form.] The isomer shifts for the hydride complexes are slightly higher than that for the chloro-complex, which would be consistent with reduced donation from the $SnCl_3^-$ ligand when the *trans*-ligand has a high *trans*-influence, *i.e.*, H–Pt: is a better donor to tin than Cl–Pt:. There seems to be an inverse relationship between isomer shift and quadrupole splitting, which is also found in other series of complexes and is discussed below.

Chloro-complexes. Complexes containing platinum and tin have been used for many years in colorimetric analysis, but it is only recently that the species involved have been isolated. It is, however, still not clear what the constitution of the species is. Cramer *et al.* isolated compounds of composition $(Ph_3PMe)_2[PtCl_2(SnCl_3)_2]$ (yellow) and $(Ph_3PMe)_3[Pt(SnCl_3)_5]$ (red)[14] and preliminary *X*-ray data indicated that the latter contained a trigonal-bipyramidal $PtSn_5$-group.[15] Young *et al.*[16] found that freshly mixed solutions of platinum(II) and tin(II) (Pt : Sn = 1 : 2) were red but became yellow on standing (10—15 min). From fresh and aged solutions red and yellow salts were obtained which appeared to have the same constitution, and were formulated as containing the *trans* (red) and *cis* (yellow) forms of $[PtCl_2(SnCl_3)_2]^{2-}$. The geometries were assigned on the presumed higher *trans*-effect of $SnCl_3^-$ than Cl^-. The yellow and red species appeared to be in equilibrium in solution and the concentration of the red form increased with increasing Sn : Pt ratio. However, precipitation from red solutions cooled to 200 K gave yellow solids

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[8] J. C. Bailar and H. Itatani, *Inorg. Chem.*, 1965, **4**, 1618.

[9] R. D. Cramer, R. V. Lindsey, G. W. Parshall, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658.

[10] R. N. Haszeldine, R. V. Parish, and J. H. Setchfield, to be submitted.

[11] D. J. Cardin, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1970, 2594.

[12] M. Akhtar and H. C. Clark, *J. Organometallic Chem.*, 1970, **22**, 233.

[13] R. V. Lindsey, G. W. Parshall, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658.

[14] R. D. Cramer, E. L. Jenner, R. V. Lindsey, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1691.

[15] R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658.

[16] J. E. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1964, 5176.

which, even after careful washing, turned red on warming. This apparent thermal isomerisation was attributed to traces of occluded tin(II), although no foreign species could be detected by *X*-ray diffraction. When the triphenylmethylphosphonium cation was used, red solutions always yielded orange salts which were thought to be mixtures of the isomers. Solutions containing Sn : Pt ratios greater than 2 : 1 yielded red salts which frequently contained more than two moles of tin per mole of platinum, up to a limiting ratio of 5 : 1. The *X*-ray powder patterns of these materials were all the same, were identical to that of Cramer's $[Pt(SnCl_3)_5]$ complex, and showed no lines due to other tin or platinum compounds. It thus seemed that three species existed, *viz.*, yellow $[PtCl_2(SnCl_3)_2]^{2-}$, red $[PtCl_2(SnCl_3)_2]^{2-}$, and red $[Pt(SnCl_3)_5]^{3-}$.

We have prepared complexes of each of these types. Aged (15 min) solutions of tin(II) chloride and tetrachloroplatinate(II) ion (2 : 1) in hydrochloric acid gave reproducible, well defined yellow salts analysing as $(cation)_2[PtCl_2(SnCl_3)_2]$. The far-i.r. spectrum of the tetraethylammonium salt shows well resolved bands at 352, 337, 306, and 280 cm^{-1}, which is not inconsistent with a *cis*-planar configuration for the anion, the higher-frequency band again being assumed to be a Pt–Cl stretching mode of chlorine *trans* to $SnCl_3$ (see below). Precipitation from freshly mixed solutions (Pt : Sn = 2 : 1) gave red or orange products (depending on the cation), visually very similar to those obtained from solutions containing 5 : 1 Sn : Pt. None of the red products gave consistent analyses, but the figures were always closer to those expected for $[Pt(SnCl_3)_5]^{3-}$ salts than for $[PtCl_2(SnCl_3)_2]^{2-}$ salts. The far-i.r. spectra of tetramethylammonium salts obtained by both routes were identical, consisting of an unresolved series of bands with maximum absorption at 330 cm^{-1}, as reported by Adams and Chandler.[17]

The red complexes from either preparation become yellow on cooling and regain their colour on warming to room temperature, and the cycle can apparently be traversed any number of times. The colour change begins at *ca.* 260 K and is complete at *ca.* 215 K, but there does not seem to be any sharp transition temperature. Isomerisation in the solid state does not seem likely and the Mössbauer spectra, measured at 80 K (Table 2), show that these complexes are different from the yellow complexes. It is also apparent, in agreement with the i.r. and *X*-ray data, that the two series of red salts are indistinguishable. The orange salts (*i.e.*, those with Ph_3PBz and Ph_4As cations) do not appear to be mixtures. Spectra of the two orange triphenylbenzylphosphonium salts were also obtained at 4·2 K. The spectra were again indistinguishable, and neither showed indications of any additional components; in particular, no absorption was found in the 3—4 mm s^{-1} region which could be attributed to tin(II) species.

TABLE 2

Mössbauer and analytical data for platinum chloro-complexes

	Yellow (2 : 1) [a]			Red (2 : 1) [a]			Red (5 : 1) [a]			Cl(%) calc.	
Cation	δ (mm s^{-1})	Δ (mm s^{-1})	Cl(%)	δ (mm s^{-1})	Δ (mm s^{-1})	Cl(%)	δ (mm s^{-1})	Δ (mm s^{-1})	Cl(%)	2 : 1	5 : 1
Me_4N	1·70	2·13	32·5 [b]	1·65	1·73	33·7 [c]	1·63	1·79	33·3 [d]	32·8 [e]	34·5 [f]
	1·70	2·08 [g, i]		1·80	1·61 [h, i]		1·66	2·10 [g]			
Et_4N	1·61	2·01	27·8	1·69	1·78	29·8	1·74	1·72	30·0	28·0	30·2
				1·56	1·61 [h, i]		1·64	1·53 [h]			
Ph_3PCH_2Ph	1·84	2·21	20·2	1·69	1·75	21·4	1·72	1·74	21·4	20·0	21·4
Ph_4As	1·67	2·18	18·5	1·75	1·69	20·5	1·69	1·82	20·0	18·0	20·7

[a] Ratios refer to Sn : Pt in the solution from which the salts were precipitated. [b] C, 11·3; H, 2·9%. [c] C, 8·7; H, 2·5%. [d] C, 8·9; H, 2·5%. [e] C, 11·1; H, 2·8%. [f] C, 9·3; H, 2·3%. [g] V. I. Baranovskii, V. P. Sergeev, and B. E. Dzevitskii, *Doklady Akad Nauk S.S.S.R., Chem. Phys. Sect.*, 1969, **184**, 632. [h] Ref. 4. [i] Assumed to be the red form on the basis of the quadrupole splitting.

It is thus apparent that only two species exist, one of which is the yellow *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$. The identity of the red anion is still somewhat uncertain, but we feel that the $[Pt(SnCl_3)_5]^{3-}$ formulation is the better for the following reasons. (i) The preliminary *X*-ray examination suggested a trigonal-bipyramidal $PtSn_5$ unit.[15] Refinement of these data was complicated by the size of the anion, but we understand that examination of a simpler salt is intended.[18] (ii) Our analytical data for the red compounds are always close to those required for the 5 : 1 formulation and are significantly different from those for the 2 : 1 formulation. (iii) The yellow compound is converted into the red form in the presence of tin(II) to an extent which depends on the concentration of tin.[16] The position of a simple isomerisation equilibrium would not depend on tin concentration, although the rate of attainment of equilibrium could be so dependent. Above Sn : Pt = 5 : 1 the red species is the only one present, according to u.v. spectroscopic measurements, and this result is confirmed by Mössbauer measurements on frozen solutions.[19] A single tin-containing species is present for Sn : Pt up to 5 : 1, beyond which ratio free stannous chloride was detected. (iv) In the solid red compounds no tin(II) species other than the platinum complex was observed even at 4·2 K, and no extra component was detected by Young's *X*-ray measurements.[16] (v) On the basis of the data for the phosphine complexes, it seems unlikely that a

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[17] D. M. Adams and P. J. Chandler, *Chem. and Ind.*, 1965, 269.

[18] R. D. Cramer, personal communication.

[19] G. V. Novikov, V. A. Trukhtanov, A. P. Krushch, A. E. Shilov, and V. I. Goldanskii, *Doklady Akad. Nauk S.S.S.R., Phys. Chem. Sect.* (English Translation), 1969, **189**, 822.

change in quadrupole splitting as great as 0·3 mm s^{-1} would result simply from a change in geometry. It is therefore probable that the red species is $[Pt(SnCl_3)_5]^{3-}$, although it is curious that this should be the first complex formed in solutions for which Sn : Pt is only 2 : 1.

Copper(I), *Silver*(I), *and Gold*(I) *Complexes*.—The complexes $(Ph_3P)_3MSnCl_3$ (M = Cu, Ag, or Au) were first prepared by Dilts and Johnson [20] who suggested on the basis of i.r. data (Sn–Cl stretching frequencies) that M–Sn bonds were involved. The Mössbauer data (Table 3) indicate clearly that the complexes do not contain isolated $SnCl_3^-$ ions; the isomer shifts are considerably lower than expected for tin(II) chloride species,[21] and show that the tin is four-covalent. The values are substantially higher than those for other trichlorostannyl metal complexes which, with the exception of some rhodium(I) derivatives discussed below, all have isomer shifts in the range 1·5—1·9 mm s^{-1}.[2] The high values for the copper, silver, and gold complexes are presumably related to the relatively high co-ordination number for these metals. Gold(I) and silver(I) are normally two-co-ordinate. On an electroneutrality basis, the higher co-ordination numbers observed here (all the phosphine molecules being assumed to be co-ordinated) would require less donation from each ligand than for a lower co-ordination number. The M–Sn bond is then expected to be quite polar with relatively high electron density on the tin atom. The quadrupole splittings do not entirely support this view, however; the values suggest that Sn–M donation (from the tin 5*p*-orbital) is greatest for the gold(I) complex.

TABLE 3

Spectroscopic and analytical data for other trichlorostannyl complexes

	δ	Δ	ν(Sn–Cl)	C(%)	H(%)
	mm s^{-1}		cm^{-1}		
$(Ph_3P)_3CuSnCl_3$	2·46	1·88	209, 280	58·1 (60·3) [a]	4·2 (4·2) [a]
$(Ph_3P)_3AgSnCl_3$	2·54	1·69	308, 281	56·8 (57·9) [b]	4·0 (4·1) [b]
$(Ph_3P)_3AuSnCl_3$	2·44	1·58	302, 280	51·5 (53·6)	4·0 (3·8)
$(Ph_3P)_2C_7H_8RhSnCl_3$	2·41	1·83	298, 275	54·9 (54·7)	4·3 (4·0)
$(Ph_3As)_2C_7H_8RhSnCl_3$	2·28	1·89	302, 287, 278	50·0 (50·0)	4·0 (3·7)
$(Ph_3Sb)_2C_7H_8RhSnCl_3$	2·15	2·04	308, 290	45·6 (45·8)	3·5 (3·4)
$(C_7H_8)_2RhSnCl_3$	2·16	1·72	313, 292, 273	33·1 (32·8)	3·4 (3·2)
$(Ph_3P)_3RhSnCl_3$	2·10	1·91	308, 286, 277	56·7 (58·2)	4·2 (4·1)
	1·78 [c]	1·73 [c]			
$(Et_4N)_2[Rh(CO)Cl_2SnCl_3]$	1·77	1·93	312	28·1 (27·9)	5·7 (5·8)
$(Et_4N)_2[Rh(CO)Cl(SnCl_3)_2]$	1·74	2·15	310	21·6 (21·9)	4·7 (4·6)
$(Et_4N)_2[Rh(CO)(SnCl_3)_3]$	1·68	2·25	323, 312	17·8 (18·0)	3·7 (3·8)
$(Me_4N)_4[Rh_2Cl_2(SnCl_3)_4]$	1·70	1·85	333, 315	12·4 (13·4)	3·1 (3·4)
	1·90 [c]	1·62 [c]			
$(Ph_3PCH_2Ph)_4[Rh_2Cl_2(SnCl_3)_4]$	1·67	1·90	329, 318	43·2 (46·5)	3·5 (3·4)
$(Me_4N)_2[RuCl_2(SnCl_3)_2]$	1·84	1·93	310, 290	12·9 (12·8)	3·5 (3·2)
	1·93 [c]	1·64 [c]			
$(Ph_3PH)_2[RuCl_2(SnCl_3)_2]$	1·83	1·97	315	39·8 (37·6)	3·0 (2·8)
	1·94 [d]	2·04 [d]			
$(Me_4N)_4[Ir_2Cl_6(SnCl_3)_4]$	1·67	1·94	328, 315	10·2 (10·7)	3·0 (2·7)
$(Ph_3PH)_4[Ir_2Cl_6(SnCl_3)_4]$	1·72	2·01		36·5 (33·9)	2·9 (2·5)
$(diars)_2Fe(Cl)SnCl_3$	1·98	1·81	315, 286	27·2 (27·1)	3·8 (3·6) [e]
$Cs[SnCl_3]$	3·40	1·22	304, 258		

[a] Cl, 10·2 (9·9)%. Cl, 9·3 (9·5)%. [c] Ref. 4. [d] See note *g* of Table 2. [e] Cl, 16·1 (16·0)%.

Rhodium(I) *Complexes*.—Two types of rhodium(I) complex have been studied, in which the rhodium is either four- or five-co-ordinate. The isomer shifts of the five-co-ordinate complexes are all higher than those for the four-co-ordinate complexes. This difference is presumably related to the co-ordination number of the rhodium as discussed above. The electron density on the rhodium atom would increase for the larger co-ordination number unless the degree of donation from the ligands were reduced. The i.r. data also suggest greater Sn–Rh interaction in the four-co-ordinate derivatives (higher Sn–Cl stretching frequencies).

The quadrupole splittings of the complexes $L_2(C_7H_8)RhSnCl_3$ support this interpretation, since the splitting increases as L becomes softer, $Ph_3P < Ph_3As < Ph_3Sb$. As L becomes a better donor, less donation is required from the lone pair on the $SnCl_3^-$ ion. The Sn–Cl bonds are polar in the sense $Sn^{\delta+}–Cl^{\delta-}$, so that increasing electron density in the (5*p* part of the) lone pair will increase the electric-field gradient at the tin nucleus. In this series the trend in isomer shift is in the opposite sense (*cf.* the platinum complexes). This trend could result in part from increased shielding by the rising 5*p* population, but could also indicate some rehybridisation of the Rh–Sn bond to involve more (Sn)5*p*-character and less (Sn)5*s*-character as L varies from Ph_3P to Ph_3Sb. The change in quadrupole splitting is consistent with rehybridisation of this type.

The four-co-ordinate complex $(Ph_3P)_3RhSnCl_3$ also has a high isomer shift relative to the other four-co-ordinate complexes. The structure of this compound is presumably similar to that of $(Ph_3P)_3RhCl$ in which steric interactions between the bulky phosphine ligands force a distortion from the expected square-planar geometry.[22] Steric crowding would be greater in the trichlorostannyl

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[20] J. A. Dilts and M. P. Johnson, *Inorg. Chem.*, 1966, **5**, 2079.

[21] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 287.

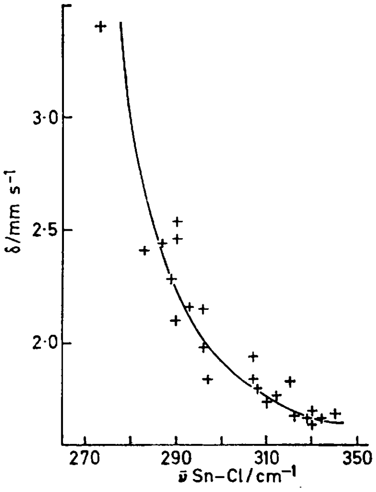
[22] P. B. Hitchcock, M. McPartlin, and R. Mason, *Chem. Comm.*, 1969, 1367.

complex and could well result in a weakening of the Rh–Sn bond.

For the series of complexes $[Rh(CO)Cl_{3-n}(SnCl_3)_n]^{2-}$ (n = 1—3) there is an inverse trend in isomer shift and quadrupole splitting similar to, but smaller than, that found for $L_2(C_7H_8)RhSnCl_3$. Presumably a similar electroneutrality argument can be applied, less Sn–Rh donation being required as the number of soft (Sn) ligands increases.

Ruthenium(II) *and Iridium*(III) *Complexes*.—The Mössbauer parameters for the ruthenium(II) and iridium(III) complexes are very similar to those for the square-planar rhodium(I) complexes. The nature of the tin-metal bond is thus hardly affected by change in the formal oxidation state of the metal.

Iron(II) *Complex*.—The complex $(diars)_2FeCl_2$ (diars = *o*-phenylenebisdimethylarsine) reacts in acetone solution with stannous chloride to give the blue-green complex $(diars)_2Fe(Cl)SnCl_3$. No indication was obtained of the formation of a bistrichlorostannyl complex even in the presence of a large excess of tin(II) chloride. The Mössbauer parameters of this complex are very similar to those of other low-spin iron(II) trichlorostannyl complexes.[6] These data again clearly indicate that the $SnCl_3$ group is co-ordinated, in contrast to the bisdiphenylphosphinoethane complex $[(dppe)_2CoCl]SnCl_3$.[23]



Isomer shift *vs.* weighted average Sn–Cl streching frequency, $[(A_1) + 2(E)]/3$

Correlation with Infrared Data.—An $SnCl_3$ unit of C_{3v} symmetry is expected to give rise to two i.r.-active Sn–Cl stretching modes. Shriver and Johnson [24] have correlated the frequencies of these modes in metal complexes of some of the types considered above with the electron affinity of the gaseous transition-metal ion of charge corresponding to the formal oxidation state. Despite the inadequacy of the latter parameter, a general correlation was found, the frequency increasing with increasing charge on the transition-metal ion. That is, as the metal becomes a better acceptor, the $SnCl_3^-$ ligand donates more charge, the tin atom becomes more positive, and the Sn–Cl bond is strengthened. The Mössbauer isomer shift is also a measure of the charge on the tin atom and a similar correlation might be expected. We have therefore measured the far-i.r. spectra of the complexes (Table 3) and in the Figure the weighted mean frequency is plotted against isomer shift. [Use of the weighted mean allows inclusion of complexes for which the individual modes are not resolved. We have assumed that the higher-frequency band corresponds to the A_1 mode.] There is a reasonable correlation which includes both the free $SnCl_3^-$ ion and those complexes of relatively high co-ordination number which appeared to give high isomer shifts. Both parameters can therefore be related to the nature of the M–Sn bond. On the basis of this correlation, the Sn–Cl stretching frequencies of $(Me_4N)_2[PtCl_2(SnCl_3)_2]$ are at 337, 306, and 280 cm⁻¹; if only the last two figures are used, a much higher isomer shift would be expected. The remaining band in this region (352 cm⁻¹) must therefore be a Pt–Cl stretching frequency.

EXPERIMENTAL

Mössbauer spectra were measured with the apparatus described previously,[25] a ^{119m}Sn–Pd source being used at room temperature and samples cooled to liquid-nitrogen temperature. The spectra at 4·2 K were obtained from the P.C.M.U., Harwell. Isomer shifts are quoted relative to stannic oxide at room temperature.

The rhodium, iridium, ruthenium, platinum, and gold complexes were prepared by literature methods.[7,16,20,26] We were unable to obtain the complexes $(Ph_3P)_3MSnCl_3$ (M = Cu or Ag) by the reported method [19] but the modification given below was satisfactory. Analytical data are in the Tables.

Trichlorostannyltris(*triphenylphosphine*)*copper*(I).—A solution of the complex $(Ph_3P)_3CuCl$ (2·29 g, 3·0 mmol) in dichloromethane (30 ml) was stirred with anhydrous tin(II) chloride (0·84 g, 4·5 mmol) and triphenylphosphine (0·70 g, 2·6 mmol) for 1 h. Acetone (50 ml) was added to the resulting clear solution which was then concentrated to half bulk under reduced pressure. White crystals of the product were formed. Trichlorostannyltris(triphenylphosphine)-silver(I) was prepared similarly, but no additional triphenylphosphine was used.

Chloro(*trichlorostannyl*)*bis*-(*o-phenylenebisdimethylarsine*)-*iron*(II).—The complex $(diars)_2FeCl_2$ (0·2 g, 0·31 mmol) and anhydrous tin(II) chloride (0·05 g, 0·27 mmol) were warmed in acetone (5 ml) for a few minutes. On cooling, blue-green *crystals* of $(diars)_2Fe(Cl)SnCl_3$ formed, which were washed with ether and dried; m.p. 180—185° (decomp.).

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