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Tin-119 Mössbauer Spectra. I. A Study of Tertiary Phosphine Adducts of Tin Tetrachloride

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Infrared and Raman measurements have been used to demonstrate the trans stereochemistry of 10 bis-phosphine adducts of $SnCl_4$. Tin-119 Mössbauer parameters have been collected for these compounds as well as for $(PR_3)SnCl_4$ (PR_3 = $(C_6H_5)_3P$, Cy_3P) and $((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$. Isomer shifts for bis adducts are more positive than those reported previously for complexes with nitrogen, oxygen, and sulfur donors. Quadrupole splitting occurs in most cases in contrast to complexes with nitrogen donor ligands. Isomer shift and quadrupole splitting data are consistent with a weak Sn–P interaction and concentration of Sn 5s orbital character in tin–phosphorus bonds.

Introduction

There is considerable current interest in the interpretation of Mössbauer parameters for complexes of tin(IV) halides and organotin(IV) halides. Two opposing models have been proposed to explain Sn-119 quadrupole splitting. According to Greenwood and Ruddick[1] quadrupole splitting is observed only when there is an imbalance in subsidiary π interactions within the complex. Recent work has however shown this rule to be invalid for many tin(IV) compounds.[2–4] A second proposal based on the isovalent hybridization concept of Bent[5] places emphasis on asymmetry introduced by σ-bonding effects, π bonding being unimportant.[4,6] The latter model, invoking the concept of s-orbital concentration in bonds to the least electronegative ligands should theoretically allow an estimate to be made of the relative magnitudes of quadrupole splittings in complexes of the same structural type where the donor atoms differ. A considerable body of information has recently been collected for nitrogen and oxygen donor adducts[1–4] and for alkyltin halide complexes.[6,7] Information concerning tin(IV) halide and organotin(IV) halide complexes of tertiary phosphines is therefore of interest since phosphorus donors are of low electronegativity and tin(IV) is a hard acid or A class acceptor. Using Hill, Drago, and Herber's arguments[6] ΔE_q for analogous tin(IV) complexes of the type *cis*- or *trans*-SnX_4L_2 should be larger when L is the soft ligand R_3P than when L is the hard base R_3N. Moreover the basicity of phosphines can be varied considerably by changing the nature of the substituents on phosphorus. Spectra of a series of phosphine derivatives might therefore be of use in an evaluation of the effect of changing basicity of phosphorus on ΔE_q.

Tin-119 isomer shifts reflect changes in 5s-electron density at the tin nucleus and as such should be sensitive to variations in the donor abilities of ligands. Recent work[2a] has confirmed this result for oxygen donors although only a qualitative estimate of donor ability of the ligands used was available.

In this study we report isomer shift (δ) and quadrupole splitting (ΔE_q) data for a series of tertiary phosphine and diphosphine derivatives of $SnCl_4$. Since both parameters are markedly affected by structural changes,[2a,4] we have also obtained structural information from far-infrared and Raman measurements on selected compounds.

Experimental Section

Anhydrous stannic chloride was purchased from Fisher Scientific Co. The tertiary phosphines tricyclohexylphosphine (Cy_3P), diphenylethylphosphine ($C_2H_5(C_6H_5)_2P$), triethylphosphine ($(C_2H_5)_3P$), diethylphenylphosphine ($(C_2H_5)_2C_6H_5P$), tri-*n*-butylphosphine ($(n\text{-}C_4H_9)_3P$), methyldiphenylphosphine ($CH_3(C_6H_5)_2P$), dimethylphenylphosphine ($(CH_3)_2C_6H_5P$), and tri-*n*-propylphosphine ($(n\text{-}C_3H_7)_3P$) were supplied by Orgmet Inc. in sealed ampoules. The phosphines were subsequently handled only *in vacuo* or in a Vacuum Atmospheres Corp. Dri-Lab filled with an atmosphere of a 1:10 mixture of hydrogen and nitrogen continuously circulated over activated copper to remove oxygen. Triphenylphosphine was purchased from Alfa Inorganics Inc. 1,2-Bis(diphenylphosphino)ethane was prepared by a published procedure.[8] Diphenylphosphinopropyne ($(C_6H_5)_2PC\equiv CCH_3$) was prepared by the reaction of diphenylchlorophosphine with lithium propynylide in *n*-hexane.[9] Diphenylmethoxyphosphine ($(C_6H_5)_2(OCH_3)P$) was a gift from Arapahoe Chemical Co. Ltd.

Preparation of Complexes.—The syntheses of $((C_6H_5)_3P)SnCl_4$, $((C_6H_5)_3P)_2SnCl_4$, $((C_2H_5)_3P)_2SnCl_4$, $((n\text{-}C_4H_9)_3P)_2SnCl_4$, and $((n\text{-}C_3H_7)_3P)_2SnCl_4$ have been described.[3,10,11] $(Cy_3P)SnCl_4$ was prepared in the Dri-Lab by allowing 1:1 molar quantities of Cy_3P and $SnCl_4$ to react in anhydrous *n*-hexane. The white precipitate was filtered off and evacuated for 10 hr. Attempts to prepare a bis complex resulted in a mixture of $(Cy_3P)SnCl_4$ and tricyclohexylphosphine. All other bis complexes were synthesized by addition of a slight excess of phosphine in anhydrous *n*-hexane or benzene–*n*-hexane to $SnCl_4$ in *n*-hexane. The

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complexes precipitated from solution, were filtered off, washed repeatedly with *n*-hexane, and dried *in vacuo*. Microanalyses for the complexes are reported in Table I.

TABLE I

MICROANALYTICAL DATA

	% C		% H		
Complex	Calcd	Found	Calcd	Found	Mp, °C
$(Cy_3P)SnCl_4$	39.96	39.82	6.16	6.08	159–163
$((C_6H_5)_3P)SnCl_4$					114–115[a]
$((C_6H_5)_3P)_2SnCl_4$					132–134[b]
$((C_2H_5)_3P)_2SnCl_4$	29.01	28.93	6.09	6.18	150–154[c]
$((n\text{-}C_3H_7)_3P)_2SnCl_4$					157–159[d]
$((n\text{-}C_4H_9)_3P)_2SnCl_4$	43.55	43.12	8.18	8.07	132–134
$((CH_3)_2C_6H_5P)_2SnCl_4$	35.81	35.96	4.43	4.02	201–205
$(CH_3(C_6H_5)_2P)_2SnCl_4$	47.25	46.40	3.96	3.76	164–165
$((C_2H_5)_2C_6H_5P)_2SnCl_4$	40.51	39.88	5.10	4.87	142–143
$(C_2H_5(C_6H_5)_2P)_2SnCl_4$	48.81	48.32	4.39	4.21	148–153
$((CH_3O)(C_6H_5)_2P)_2SnCl_4$	45.10	45.26	3.76	3.73	98–99
$((C_6H_5)_2PC\equiv CCH_3)_2SnCl_4$	50.70	50.10	3.67	3.75	105
$((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$	47.40	46.88	3.70	3.27	207–210

[a] Literature[11] mp 115–116°. [b] Literature[11] mp 132–134°. [c] Literature[10] mp 145–150°. [d] Literature[10] mp 157–159°.

Physical Measurements.—Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Infrared measurements were made on a Beckman IR-12 spectrometer using Nujol mulls between cesium iodide plates. Spectra were calibrated with polystyrene and water vapor and are accurate to ±2 cm^{-1}. Raman spectra were recorded using a Cary 81 spectrometer fitted with an He–Ne laser. Spectra were measured as powdered solids using the 6518-Å line of carbon tetrachloride for calibration. Frequencies are accurate to ±2 cm^{-1}.

Mössbauer Spectra.—A Mössbauer drive supplied by Austin Science Associates Inc. along with control-associated electronics equipment was used for doppler shift measurements. The spectra were recorded with a Kicksort Model 701 pulse height analyzer operating on a multiscaler mode. Measurements were made with the absorber at 80°K and the $Ba^{119m}SnO_3$ source at room temperature. The doppler velocity scale was calibrated against the quadrupole splitting of a nitroprusside absorber. All isomer shift values are relative to an SnO_2 absorber. The spectral data were analyzed by the use of a hybrid analog–digital computer routine developed by the Computing Centre, University of Waterloo. Computer-simulated Lorentzian line shapes were fitted to the data. The precision of the Mössbauer parameter is estimated to be ±0.02 mm/sec.

Results and Discussion

Infrared and Raman Spectra.—Complexes of the type $(PR_3)_2SnCl_4$ have been reported for $(C_2H_5)_3P$,[10] $(n\text{-}C_3H_7)_3P$,[10] $(n\text{-}C_4H_9)_3P$,[3] $(C_6H_5)_3P$,[11] and $(CH_3)_3P$.[12] Complete Raman and infrared data for $((CH_3)_3P)_2SnCl_4$ are strongly suggestive of a trans configuration.[12] The far-infrared spectrum of $((C_6H_5)_3P)_2SnCl_4$ favors a trans geometry[11] while a dipole moment of 2.4 D indicates that $((n\text{-}C_4H_9)_3P)_2SnCl_4$ is also trans.[3] The far-infrared spectra of all the phosphine adducts of $SnCl_4$ prepared here are shown in Table II. Raman data for selected compounds are collected in Table III. In theory a trans D_{4h} configuration having one ν(M–X) mode (e_u) infrared active and two ν(M–X) modes ($a_{1g} + b_{1g}$) Raman active should be readily distinguishable from a cis C_{2v} molecule with four infrared- and Raman-active vibrations ($2\,a_1 + b_1 + b_2$). Unfortunately, the assignment of stereochemistry on the basis of far-infrared data alone may not be unambiguous and even if Raman data are also available an unequivocal structural assignment may not be possible.[13] The main difficulties are associated with detection of all four ν(M–X) modes in the cis species when one or more bands are of low intensity or are unresolved. For the bis-phosphine adducts of $SnCl_4$ however a trans geometry appears to be favored on steric grounds.[14,15] Moreover, there is now a considerable body of experimental evidence, both from X-ray studies of $((C_6H_5)_3P)_2InCl_3$,[16] $((CH_3)_3P)_2MCl_3$ (M = Al, In),[17] and $((CH_3)_3P)_2SiCl_4$[18] and from vibrational spectroscopy[12,19,20] to suggest that bis-phosphine adducts of MCl_4 (M = Si, Ge, Sn) and MCl_3 (M = Al, In) have trans-octahedral (M(IV)) or trans-trigonal-bipyramidal structures (M(III)). The far-infrared and Raman data reported here strongly support this conclusion. The infrared spectra (400–200 cm^{-1}) of $(PR_3)_2SnCl_4$ (PR_3 = $(C_6H_5)_3P$, $(C_2H_5)_3P$, $(CH_3)_2C_6H_5P$, $CH_3(C_6H_5)P$, $(C_2H_5)_2C_6H_5P$, $C_2H_5(C_6H_5)_2P$, $(C_6H_5)_2PC\equiv CCH_3$) are dominated by the occurrence of a single intense absorption between 280 and 310 cm^{-1}. The spectra of $(CH_3(C_6H_5)_2P)_2SnCl_4$ and $((C_2H_5)_2C_6H_5P)_2SnCl_4$ in this region are shown in Figure 1. These bands occur in the same spectral region as ν_3 of $SnCl_6^{2-}$ [21]

TABLE II

FAR-INFRARED SPECTRA (400–200 CM^{-1}) OF PHOSPHINE ADDUCTS OF $SnCl_4$

Complex	Freq, cm^{-1}
$(Cy_3P)SnCl_4$	350 s, 330 vs, 313 s, 300 sh
$((C_6H_5)_3P)SnCl_4$	350 s, 329 s, 290 s
$((C_6H_5)_3P)_2SnCl_4$	309 vs, 300 sh
$((C_2H_5)_3P)_2SnCl_4$	301 sh, 282 vs, 226 w
$((n\text{-}C_3H_7)_3P)_2SnCl_4$	362 w, 304 sh, 280 vs, 271 vs
$((n\text{-}C_4H_9)_3P)_2SnCl_4$	346 vw, 300 m, sh, 280 vs, 261 sh, 235 w
$((CH_3)_2C_6H_5P)_2SnCl_4$	346 w, 306 m, 281 vs
$(CH_3(C_6H_5)P)_2SnCl_4$	346 w, 291 vs, 217 w
$((C_2H_5)_2C_6H_5P)_2SnCl_4$	386 w, 346 vw, 279 vs, 273 sh
$((CH_3O)(C_6H_5)_2P)_2SnCl_4$	306 vs, 292 s, 260 w, 235 w
$(C_2H_5(C_6H_5)_2P)_2SnCl_4$	380 w, 301 s, 286 sh, 264 vw, 242 vw
$((C_6H_5)_2PC\equiv CCH_3)_2SnCl_4$	286 vw, 276 vw, 308 vs, 273 sh, 256 vw
$((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$	358 w, 336 w, 309 vs, 293 sh, s, 255 w

TABLE III

RAMAN SPECTRA (400–200 CM^{-1}) OF PHOSPHINE ADDUCTS OF $SnCl_4$

Complex	Freq, cm^{-1}
$(Cy_3P)SnCl_4$	347 m, 329 s, 320 s, 287 sh, 244 sh, 217 m
$((C_6H_5)_3P)SnCl_4$	351 m, 331 s, 296 m, 251 m
$((C_6H_5)_3P)_2SnCl_4$	279 vs, 250 w, 203 m
$((CH_3)_2C_6H_5P)_2SnCl_4$	334 w, 303 w, 268 vs, 242 w
$((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$	357 w, 311 vs, 290 sh, 267 vs, 250 m
$((C_6H_5)_2CH_3P)_2SnCl_4$	264 vs, 238 w

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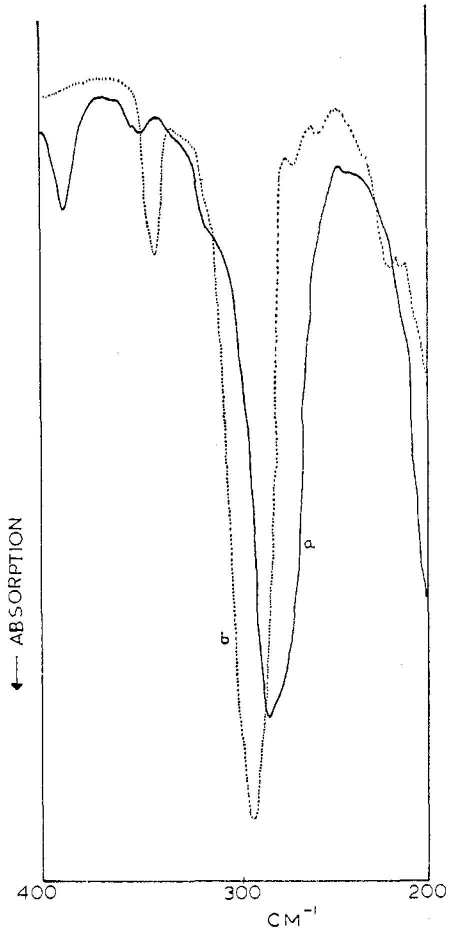

Figure 1.—Far-infrared spectra (400–200 cm^{-1}) of (a) $((C_2H_5)_2C_6H_5P)_2SnCl_4$ and (b) $(CH_3(C_6H_5)_2P)_2SnCl_4$.

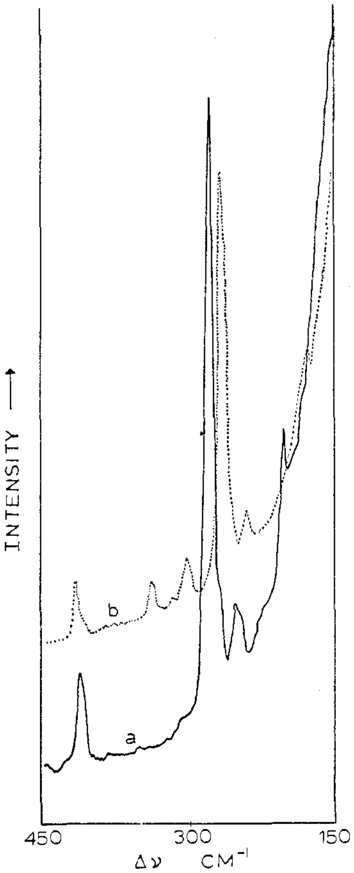

Figure 2.—Raman spectra (450–150 cm^{-1}) of (a) $((C_6H_5)_3P)_2SnCl_4$ and (b) $((CH_3)_2C_6H_5P)_2SnCl_4$.

and ν(Sn–Cl) vibrations of hexacoordinate tin complexes.[22] We therefore assign the strong band to the infrared-active e_u ν(Sn–Cl) mode of a trans-octahedral $(PR_3)_2SnCl_4$ complex. Shoulders occurring on the main absorption band may arise from solid-state splitting of the e_u mode, ligand δ(C–P–C) or δ(C–C–P) modes, or ν(Sn–^{37}Cl). For the remaining bis complexes an intense doublet is found in the ν(Sn–Cl) region. The intensities of the two components of the doublet indicate that both are due to Sn–Cl stretching modes rather than ligand modes (compare for example the ligand mode at 346 cm^{-1} and ν(Sn–Cl) at 291 cm^{-1} for $((CH_3(C_6H_5)_2P)_2SnCl_4$ (Figure 1)). However, the absorption bands do not correspond, in either frequency or intensity pattern with the spectra found for cis derivatives of $SnCl_4$.[22] We conclude that the doublet is again due to solid-state splitting of the e_u mode of *trans*-$(PR_3)_2SnCl_4$. The Raman spectra of $((C_6H_5)_3P)_2SnCl_4$ and $((CH_3)_2C_6H_5P)_2SnCl_4$ (Table III) confirm these conclusions. An intense Raman line, noncoincident with the strong infrared band and at lower frequency accompanied by a weaker line at *ca.* 30 cm^{-1} to lower frequency, appears in each case (Figure 2). This is the same type of spectrum as that found for $((CH_3)_3P)_2MCl_4$ (M = Si, Ge, Sn).[12] The strong Raman line can be assigned to the a_g ν(Sn–Cl) mode and its weaker counterpart to the b_{1g} mode of a trans D_{4h} skeleton.

Infrared data for $((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$ do not unambiguously favor the expected cis configuration with a chelating diphosphine. Only two strong bands, closely spaced, appear in the Sn–Cl stretching region compared with the four expected for a cis adduct. Moreover cis adducts usually exhibit at least one strong band due to Sn–Cl stretching above 320 cm^{-1}.[22,23] This feature is complicated however by the fact that phosphine complexes invariably exhibit ν(M–Cl) absorptions at lower frequency than the corresponding amine derivatives.[12,19,20] Furthermore a two-band infrared spectrum has been noted previously for $SnCl_4$ complexes with strongly chelating ligands.[23] Nevertheless a trans diphosphine-bridged polymeric formulation could not be eliminated with infrared data alone. The Raman spectrum is, however, considerably different from that of the trans compounds $((CH_3)_3P)_2SnCl_4$,[12] $((CH_3)_2C_6H_5P)_2SnCl_4$, and $((C_6H_5)_3P)_2SnCl_4$. Two intense Raman lines, one of which is coincident with the strong infrared absorption at 309 cm^{-1} and the other at 267 cm^{-1}, appear in the spectrum. Weaker satellites appear at 357, 290, and 250 cm^{-1}. The spectrum resembles the Raman spectra reported for cis adducts of $SnCl_4$ with chelating nitrogen ligands[24] although the

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bands are moved to lower frequency. We therefore, conclude that the Raman spectrum is indicative of cis stereochemistry for $((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$ although a detailed assignment of bands to the (2 $a_1 + b_1 + b_2$) modes expected is clearly not possible.

The monoadducts $((C_6H_5)_3P)SnCl_4$ and $(Cy_3P)SnCl_4$ are of interest in view of their possible five-coordinate structures. Rivest and coworkers[11] interpreted the far-infrared spectrum of $((C_6H_5)_3P)SnCl_4$ in terms of a dimeric halogen-bridged structure, in agreement with molecular weight measurements in dichloromethane. However, we have found that recrystallization of $((C_6H_5)_3P)SnCl_4$ or $((C_6H_5)_3P)_2SnCl_4$ affords $[(C_6H_5)_3PH]_2[SnCl_6]$ having an infrared spectrum characteristic of that of other complexes containing $SnCl_6^{2-}$.[21] The molecular weight data should therefore be treated with caution. The coincidences in the infrared and Raman spectra of $((C_6H_5)_3P)SnCl_4$ (Tables II and III) appear to rule out a centrosymmetric halogen-bridged dimeric structure.[25] The presence of three strong infrared bands and three Raman bands due to ν(Sn–Cl) argue against a C_{3v} trigonal-bipyramidal structure such as that proposed for $((CH_3)_3P)TiCl_4$ and $((CH_3)_3N)TiCl_4$ on the basis of a vibrational analysis.[27] The infrared spectrum is also inconsistent with a C_{4v} square-pyramidal structure where only two (a_1 + e) ν(Sn–Cl) modes are expected. We feel therefore that the data favor an equatorially substituted trigonal-bipyramidal or square-pyramidal structure for $((C_6H_5)_3P)SnCl_4$. A fuller analysis of the spectra does not appear justified.

The infrared spectrum of $(Cy_3P)SnCl_4$ is remarkably similar to that of $((C_6H_5)_3P)SnCl_4$. Unfortunately $(Cy_3P)SnCl_4$ is a poor scatterer; the Raman spectrum was of poor quality. The pattern of lines and intensities is such that similar structures appear likely for $((C_6H_5)_3P)SnCl_4$ and $(Cy_3P)SnCl_4$. We are currently attempting to grow single crystals of one of these adducts for X-ray work.

Mössbauer Spectra.—Sn-119 isomer shifts (δ), quadrupole splitting (ΔE_Q), and line widths at half-height Γ_1 and Γ_2 are given in Table IV.

Isomer Shifts.—Values for the bis adducts lie within the range 0.63–0.89 mm/sec. The isomer shifts are considerably more positive than for analogous complexes with oxygen,[2] nitrogen,[1,3,4] and sulfur[3] donors indicating a higher s-electron density at the tin nucleus. Indeed, it is clear from this work and previous studies[2] that the isomer shift is a sensitive probe for the strength of an interaction between tin tetrachloride and a Lewis base. In Figure 3, we have collected from recently published data[1–4] isomer shifts for various 2:1 adducts of tin tetrachloride with neutral donors to illustrate the variation in δ with donor atom. Although no attempt has been made to be comprehensive, the complexes chosen show isomer shifts typical for the particular donor involved. A decrease in isomer shift from the value of 0.80 mm/sec for $SnCl_4$ invariably occurs on complexation with N, O, or S donors. By contrast several δ values for the phosphine complexes are more positive than 0.80 mm/sec. This is an interesting result which deserves further comment. First, high positive δ values suggest a relatively weak interaction of tin(IV) with phosphorus in agreement with the predominant class (A) character of Sn(IV). In addition δ values equal to or greater than 0.80 mm/sec infer an s-electron density at the tin nucleus similar to that in $SnCl_4$ itself. For a completely covalent model a change from sp^3 hybridization in $SnCl_4$ to sp^3d^2 hybridization in L_2SnCl_4 would decrease the s character per bond from 0.25 to 0.17. Also, the ionic character of each bond formed in the octahedral species is normally greater than for tetrahedral $SnCl_4$,[28] hence reducing the Sn 5s-electron density further. Isomer shifts of comparable magnitude to $SnCl_4$ may therefore arise from one of the following effects. (a) The first is extensive Sn-P 4dπ–

TABLE IV

MÖSSBAUER PARAMETERS FOR TIN COMPLEXES

Complex	δ, mm/sec	ΔE_Q, mm/sec	Γ_1, mm/sec	Γ_2, mm/sec
$(Cy_3P)SnCl_4$	0.49	0.36	0.97	0.96
$((C_6H_5)_3P)SnCl_4$	0.59	0.42	0.71	0.74
$((C_6H_5)_3P)_2SnCl_4$	0.75		0.81	
$((C_2H_5)_3P)_2SnCl_4$	0.87	0.95	0.52	0.54
$((n\text{-}C_3H_7)_3P)_2SnCl_4$	0.89	0.95	0.78	0.73
$((n\text{-}C_4H_9)_3P)_2SnCl_4$	0.85	1.02	0.78	0.76
$((CH_3)_2C_6H_5P)_2SnCl_4$	0.85	0.97	0.68	0.68
$(CH_3(C_6H_5)_2P)_2SnCl_4$	0.81	0.58	0.66	0.64
$((C_2H_5)_2C_6H_5P)_2SnCl_4$	0.88	0.99	0.74	0.71
$(C_2H_5(C_6H_5)_2P)_2SnCl_4$	0.63	0.46	0.83	0.86
$((CH_3O)(C_6H_5)_2P)_2SnCl_4$	0.81	0.45	0.72	0.68
$((C_6H_5)_2PC{\equiv}CCH_3)_2SnCl_4$	0.77		0.89	
$((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$	0.72		0.83	

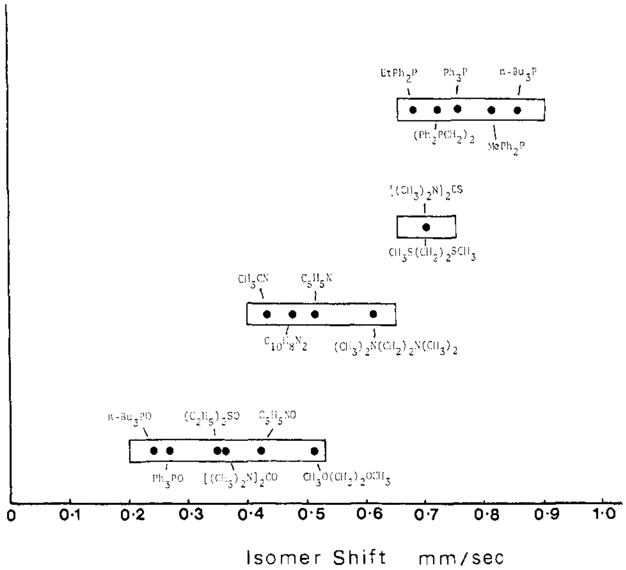

Figure 3.—Correlation table for isomer shifts (mm/sec) of L_2SnCl_4 complexes.

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[25] This does not, of course, eliminate a noncentrosymmetric dimer, but we consider such a structure unlikely in view of observations with other systems.[26a] Recent results[26b] have also shown that coincidences sometimes occur in the infrared and Raman spectra of centrosymmetric complexes.

[26] (a) R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc. A*, 1897 (1967); (b) M. J. Deveney and M. Webster, *ibid.*, *A*, 1643 (1970).

[27] I. R. Beattie and R. Collis, *ibid.*, *A*, 2960 (1969).

[28] D. Biedenkapp and A. Weiss, *Z. Naturforsch.*, **19**, 1518 (1964).

3dπ bonding in the adducts. This would deshield the Sn 5s electrons and increase δ. (b) The second is the concentration of Sn 5s-electron density in the Sn–P bonds. This would have the overall effect of leaving a greater proportion of "s"-electron density at the tin nucleus since phosphorus is considerably less electronegative than chlorine. Such an explanation presupposes a multicenter approach to the bonding in the P_2SnCl_4 skeleton in order to invoke less d-orbital contribution than in the conventional sp^3d^2 hybridization description accorded to octahedral complexes. Thus the Sn 5s and $5p_z$ orbitals could be used in bonding the two phosphorus ligands, leaving $5p_x$ and $5p_y$ to be essentially used in three-center two-electron bonds to the halides.

The evidence for π bonding involving Sn(IV) has been discussed in detail by Parish and Platt[4] and Hill, Drago, and Herber.[6] At best, π bonding to Sn(IV) is extremely weak and of secondary importance in the interpretation of Sn(IV) isomer shift and quadrupole splitting data. Further evidence that Sn–P (dπ–dπ) bonding is probably unimportant in $(PR_3)_2SnCl_4$ comes from the X-ray crystal structure of $((C_6H_5)_3P)_2InCl_3$.[16] The average In–P bond length (2.712 Å) is considerably longer than the sum of the covalent radii for phosphorus and indium(III) suggesting a weak interaction between the phosphine and the metal atom. Since tin(IV) is isoelectronic with indium(III), it seems very unlikely that π bonding between tin and phosphorus will be important in $(PR_3)_2SnCl_4$.

We therefore propose that (b) above accounts for the observed isomer shifts and quadrupole splittings. Concentration of s character in tin–phosphorus bonds and hence a consequent decrease in s character in tin–chlorine bonds of $(PR_3)_2SnCl_4$ are predictable in view of the low electronegativity of phosphorus. Moreover this conclusion derives support from several studies of the vibrational spectra of trans bis-phosphine adducts of nontransition metal halides. Thus replacement of R_3N by R_3P in L_2MX_n ($L = R_3N$ or R_3P; $n = 3$; M = Al, Ga, In; $n = 4$; M = Sn, Ge, Si) invariably results in a decrease in metal–halogen stretching frequency for the MX_n residue.[12,13,19] The correlation of decrease in stretching frequency for a bond with a decrease in s character for that bond is a phenomenon which has been adequately demonstrated.[15] Force constants derived from vibrational spectra also point to a weakening of Sn–Cl bonds on replacement of two halide ions of $SnCl_6^{2-}$ by methide ions to give *trans*-$(CH_3)_2SnCl_4^{2-}$.[29] This supports the concept of concentration of s-orbital character in Sn–C and decreased s character in Sn–Cl bonds in these complex ions.

The isomer shifts given in Table IV for the bis adducts show no marked dependence on the basicity of the phosphines $(C_2H_5)_3P$ ($pK_a = 8.69$), $(C_4H_9)_3P$ ($PK_a = 8.43$), and $(n\text{-}C_3H_7)_3P$ which give high δ values, whereas $(C_6H_5)_3P$ ($pK_a = 2.73$) and $(C_6H_5)_2PC{\equiv}CCH_3$, the least basic ligands, give rather lower isomer shifts. It seems likely that in addition to changes in basicity, structural changes resulting from packing factors and intermolecular forces may be of importance in dictating the actual magnitude of the isomer shift.

Little comment can be made on the isomer shifts of $(Cy_3P)SnCl_4$ and $((C_6H_5)_3P)SnCl_4$ since comparative data for 1:1 complexes of $SnCl_4$ are lacking. Yeats, *et al.*,[2a] have reported δ values of 0.53 and 0.41 mm/sec for $((n\text{-}C_4H_9)_3PO)SnCl_4$ and $((C_6H_5)_3PO)SnCl_4$ which are assumed to be five-coordinate monomers. The low isomer shifts for $((C_6H_5)_3P)SnCl_4$ and $(Cy_3P)SnCl_4$ (0.49–0.59 mm/sec) are rather surprising but it should be pointed out that the interaction of PR_3 with $SnCl_4$ is likely to be considerably stronger in a monomeric 1:1 adduct than in a 2:1 adduct. Moreover Cy_3P is the largest and most basic of the phosphines used in this study ($pK_a = 9.79$) and has been found to give more stable complexes with indium(III) than other phosphines.[19] A strong interaction with Sn(IV) is therefore anticipated. Alternatively the isomer shift data for $(Cy_3P)SnCl_4$ and $((C_6H_5)_3P)SnCl_4$ can be rationalized in terms of halogen-bridged dimeric structures where each tin atom is octahedrally coordinated by five halogen atoms and a phosphorus ligand. On this basis δ should be intermediate between the isomer shifts for $(PR_3)_2SnCl_4$ and $SnCl_6^{2-}$ ($\delta \approx 0.5$ mm/sec).[30]

Finally, the value found here for $((C_6H_5)_3P)_2SnCl_4$ (0.75 mm/sec) suggests that the isomer shift reported for $((C_6H_5)_3P)_2SnBr_4$ (0.63 mm/sec) may be in error. On the basis of the usual increase in s-electron density at the tin nucleus on passing from a chloride to a bromide complex, an isomer shift of *ca.* 1.00 mm/sec is expected for $((C_6H_5)_3P)_2SnBr_4$.

Quadrupole Splittings.—Considerable effort has been devoted to the interpretation of quadrupole splittings in hexacoordinated tin(IV) complexes. The current situation has been summarized recently by Yeats, *et al.*[8] These authors concluded from studies on oxo complexes of $SnCl_4$ that, in the presence of a weak interaction between donor and acceptor, steric and structural effects are mainly responsible for quadrupole splitting. Furthermore quadrupole splitting may be sensitive to cis–trans isomerism in hexacoordinated tin compounds with trans species showing the larger splittings.[31] Fortunately for the series of phosphine complexes examined discussion of factors affecting ΔE_q is not complicated by structural isomerism since the vibrational data point firmly to trans configurations for the bis adducts. With the exception of $((C_6H_5)_3P)_2SnCl_4$ and $((C_6H_5)_2PC{\equiv}CCH_3)_2SnCl_4$ (which have large line widths) all the bis-phosphine adducts show quadrupole splitting. This is the result expected on the basis of a weak Sn–P interaction. Application of the Hill, Drago, and Herber ideas[6] also predicts observable quadrupole splitting for *trans*-$(R_3P)_2SnCl_4$ due to the unequal charge densities induced in tin 5p orbitals as a result of 5s- and $5p_z$-orbital concentration in the tin–phosphorus bonds. By contrast bis adducts with the more electronegative

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(29) S. Tobias, *Inorg. Chem.*, **9**, 1296 (1970).

(30) C. A. Clausen and M. L. Good, *ibid.*, **9**, 817 (1970).

(31) B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *J. Chem. Soc. A*, 143 (1969).

donor atom nitrogen do not show quadrupole splitting.[1,2,4]

The largest ΔE_q values are found for the $(n\text{-}C_4H_9)_3P$, $(n\text{-}C_3H_7)_3P$, $(C_2H_5)_3P$, and $(C_2H_5)_2C_6H_5P$ complexes. The value for $((n\text{-}C_4H_9)_3P)_2SnCl_4$ agrees well with that previously reported.[3] For the series $((C_6H_5)_3P)_2SnCl_4$, $(C_2H_5(C_6H_5)_2P)_2SnCl_4$, and $((C_2H_5)_2C_6H_5P)_2SnCl_4$ the quadrupole splitting increases on replacement of C_6H_5 by C_2H_5. This is also the order of increasing basicity of the ligands. The same trend is observed for the series $(C_6H_5)_3P$, $CH_3(C_6H_5)_2P$, and $(CH_3)_2C_6H_5P$. There also appears to be a tendency for complexes which give the largest isomer shifts to produce larger quadrupole splittings. Other workers have noted that increasing the size of alkyl groups in a series of sulfoxide complexes produces an increase in ΔE_q and have attributed this to steric hindrance.[2] It would be interesting to have detailed X-ray data for a series such as $((C_6H_5)_3P)_2SnCl_4$, $(C_2H_5(C_6H_5)_2P)_2SnCl_4$, and $((C_2H_5)_2C_6H_5P)_2SnCl_4$ in order to ascertain whether steric effects or Sn–P bond lengths are instrumental in changing δ and ΔE_q. One further feature of interest concerns the magnitudes of quadrupole splittings in nitrogen, oxygen, and phosphorus donor complexes. As mentioned earlier bis adducts of $SnCl_4$ with nitrogen donors show no observable quadrupole splitting whereas oxo complexes exhibit splittings in the range 0.50–1.60 mm/sec.[2,3] The latter are in some cases considerably larger than the splittings observed for phosphorus donors. In conjunction with the isomer shift results presented in Figure 3, this rules out any *overall* correlation between the strength of a donor–acceptor interaction and the magnitude of a quadrupole splitting even though such a correlation may exist within a restricted series of complexes.[2a]

For $((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$, the only cis-octahedral species examined during this study, no quadrupole splitting was observed although the line width was large. This is not surprising in view of the smaller ΔE_q values associated with cis derivatives and the small splitting found for *trans*-$(CH_3(C_6H_5)_2P)_2SnCl_4$.

For $(Cy_3P)SnCl_4$ and $((C_6H_5)_3P)SnCl_4$ small quadrupole splittings were observed which are just resolvable. The splittings were measured by fitting the curve to Lorentzian line shapes in each case. ΔE_q values of similar magnitude were previously observed for the $SnCl_5^-$ ion and other five-coordinate species.[2a,21] Similarly a small quadrupole splitting might be expected for a halogen-bridged dimer.

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Notes

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The Reaction of Ligands with Pentafluorophenylmanganese Pentacarbonyl

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An extensive study of ^{19}F parameters in pentafluorophenyl derivatives has established a linear relationship between the ortho fluorine–para fluorine coupling constant (J_{24}) and para fluorine chemical shift (ϕ_p). It was suggested that this relationship or either of the parameters individually might serve as a qualitative indicator of π-electronic interactions between the pentafluorophenyl ring and its substituent, and thus indirectly of π interactions with the substituent itself.[1,2]

If the substituent on the pentafluorophenyl ring is a metal carbonyl group, carbonyl stretching frequencies should provide an alternative means of gauging π-electronic interactions, which could be compared with indications from the ^{19}F parameters. With this purpose in mind, a number of pentafluorophenylmanganese pentacarbonyl derivatives have been prepared and studied by infrared and ^{19}F nmr spectroscopy. The findings proved to be in general agreement with conclusions reached by Stewart and Treichel[3] from a comprehensive study of analogous monofluorophenyl compounds.

Experimental Section

All reactions were carried out under a nitrogen atmosphere and solid products handled with minimum exposure to air. Pentane, hexane, methylcyclohexane, benzene, toluene, and xylene were dried over sodium wire or 9.5% sodium–lead alloy; diethyl ether was obtained commercially in the anhydrous state. The ligands used in this study came from commercial sources and were allowed to react without further purification. Pentafluorophenylmanganese pentacarbonyl[4,5] was synthesized using the method of Stone, *et al.*,[4] using a more convenient preparation of pentafluorophenyllithium.[6] Yields in excess of 60% were consistently obtained.

Microanalyses were performed by Alfred Bernhardt Mikro-

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[1] M. G. Hogben and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 283 (1969).

[2] M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **91**, 291 (1969).

[3] R. P. Stewart and P. M. Treichel, *ibid.*, **92**, 2710 (1970). We are grateful to Professor Treichel for making available in advance of publication a manuscript of his very complete study.

[4] P. M. Treichel, M. A. Chaudhari, and F. G. A. Stone, *J. Organometal. Chem.*, **1**, 98 (1963).

[5] M. D. Rausch, *Inorg. Chem.*, **3**, 300 (1964).

[6] A. J. Oliver and W. A. G. Graham, *J. Organometal. Chem.*, **19**, 17 (1969).