

**Tin-119m Mössbauer Spectra of Trimethyltin
Phosphines Used as Ligands in Transition Metal
Carbonyl Complexes**

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SUMMARY

Tin 119m Mössbauer Quadrupole Splitting (Q.S.) data for several trimethyltin amines, phosphines, arsines, stibines and sulfides are compared with the larger values found for the transition metal carbonyl complexes of the phosphine and sulfide derivatives which reveal the polarizing effect of donor action by the adjacent group V or VI atom.

Quadrupole splittings are almost never resolved in the $^{119\text{m}}\text{Sn}$ Mössbauer spectra of organotin(IV) compounds except in cases in which the tin atom is bonded to atoms holding lone pair electrons.¹ Whether the larger electric field gradients at tin in these compounds arise primarily from electronegativity differences between the two kinds of attached groups, or from $(p \rightarrow d)\pi$ interactions has been the subject of lively

controversy. More recently it has been recognized that many organotin derivatives containing directly attached atoms with lone pairs are associated in the solid state,² and that the resolvable Q.S. may arise from distortions of the T_d geometry of the monomer unit held in such an arrangement.

A direct test of the origin of resolvable Q.S. requires monomeric organotin derivatives in which a single lone pair on a directly attached atom can be removed in bond formation. The explanation for our earlier observation of enhanced Q.S. in tricarbonyl-metal complexes of aryltin ligands is complex since direct transition metal-tin interactions may be involved,³ and trimethyltin aziridine whose Q.S. is increased by 0.7 mm/s in its BF_3 adduct is not itself monomeric.⁴ However, monomeric organotin-group V derivatives can be found whose lone pairs are sufficiently basic for complex formation.

In Table I are listed ^{119m}Sn Mössbauer data for tris-trimethyltin amine, phosphine, arsine and stibine.^{5,6} Trimethyltin derivatives of aliphatic amines generally exhibit Q.S. values smaller than 1 mm/s,^{1,4,7-8} and the splittings of the phosphines, arsines and stibines are unresolvable or tiny. However, coordination by phosphorus in transition metal carbonyl complexes gives rise to resolvable splittings with Q.S. values in the 1.1-1.3 mm/s range. This enhancement is similar to that observed on formation of the transition metal tricarbonyl complexes of aryltin ligands³ and on adduct formation of trimethyltin aziridine with BF_3 .⁴ The Q.S. value of the bis-triorganotin sulfide is also increased in the tungsten carbonyl complex. The Isomer Shift (I.S.) values of the ligands and their complexes are all within experimental error, on the other hand.

Strong (p-d)- π bonding in the group five organometallic derivatives would delocalize the lone pair and preclude further coordination in transition metal complexes, yet a large number of stable silyl, germyl, stannyl and plumbylphosphine derivatives have been prepared by the same routes used to synthesize the corresponding alkyl and arylphosphine complexes.^{5,6} The substitution of t-butyl groups in tri-t-butylphosphine by trimethylsilyl, germyl or stannyl groups does not alter sub-

Table 1
Tin-119m Mössbauer Data for Methyltin-Containing
Ligands and Their Transition Metal Carbonyl Complexes

Ligand/Complex	I.S. $\pm 0.06^{mm}/s$	Q.S. $\pm 0.12^{mm}/s$	Γ_1	Γ_2
$[(CH_3)_3Sn]_3N^a$	1.10	-	1.36	
$[(CH_3)_3Sn]_3P$	1.32	-	0.82	
$\cdot Ni(CO)_3$	1.37	1.10	1.30	1.15
$\cdot Fe(CO)_4^b$	1.36	1.32		
$[(CH_3)_3Sn]_3As$	1.30	-	1.86	
$[(CH_3)_3Sn]_3Sb$	1.35	-	1.71	
$[(CH_3)_3Sn]_2PC(CH_3)_3$	1.36	-	1.83	
$\cdot Fe(CO)_4^b$	1.36	1.22		
$\cdot Mo(CO)_5$	1.41	1.05	1.07	1.08
$\cdot Mn(CO)_4Br$	1.38	1.11	1.27	1.44
$\cdot Re(CO)_4Br$	1.37	1.24	1.29	1.26
$\{[(CH_3)_3Sn]_2P-Re(CO)_4\}_2$	1.31	1.30	1.40	1.28
$(CH_3)_3SnP(C_6H_5)_2$	1.34	0.86	0.86	1.12
$(CH_3)_3SnP[C(CH_3)_3]_2$	1.36	-	1.27	
$\cdot Ni(CO)_3$	1.39	0.97	1.16	1.23
$\cdot Fe(CO)_4^b$	1.37	1.21		
$[(C_6H_5)_3Sn]_2S^c$	1.22	1.17		
$[(CH_3)_3Sn]_2S-W(CO)_5$	1.36	2.18	1.21	1.11

Recorded at 77K vs. Ca $^{119m}SnO_3$ [New England Nuclear Corp.] by published techniques.²⁵

^aReference 7 vs. Pd(^{119m}Sn), which also reports I.S. = 1.12; Γ = 1.67 vs. $^{119m}SnO_2$.

^bReference 10 vs. Ba $^{119m}SnO_3$ at 80K.

^cReference 26 vs. $^{119m}SnO_2$ at 80K.

stantially the transition metal carbonyl infrared $\nu(\text{CO})$ frequencies as shown in a series of tricarbonylnickel complexes of silyl, germyl and stannylphosphines.⁹ Nor are the ^{57}Fe Mössbauer parameters changed significantly when trimethyltin groups are substituted in *t*-butylphosphine complexes of tetracarbonyliron.¹⁰ Likewise, the ^{119}Sn Mössbauer parameters remain nearly unaltered when a trimethylstannylphosphine is coordinated by tricarbonylnickel, tetracarbonyliron or a transition metal carbonyl halide. Thus changes introduced into either the phosphine or the transition metal carbonyl portions of the complexes are not registered in the spectroscopic parameters of the other portion. In particular, the tin-119m Mössbauer Q.S. parameter seems not to be sensitive to the nature of the transition metal carbonyl moiety, but only to coordination by the phosphorus lone pair.

If (p-d)- π interactions were responsible for the tiny Q.S. values which could be derived by fitting as doublets the broadened $^{119\text{m}}\text{Sn}$ Mössbauer resonances recorded for the phosphine ligands, then the singlet lines should sharpen on complexation. Instead, the Q.S. is increased in all cases studied. This is most straightforwardly interpreted in terms of an increase in polarity of the tin-phosphorus σ -bond on coordination. The higher effective electronegativity of the coordinated phosphorus atom then perturbs the electron distribution about the attached tin atom giving rise to an enhanced electric field gradient and the resolvable Q.S.

EXPERIMENTAL

Tris-trimethyltin amine was prepared by the lithioamination of trimethyltin chloride by lithium amide,¹¹ the phosphine¹² by the release of HCl from phosphine in the presence of triethylamine,¹³ the arsine¹⁴ by the release of trimethylchlorosilane from tris-(trimethylsilyl)arsine,¹⁵ and the stibine by the precipitation of NaCl from sodium antimonide in liquid ammonia.¹⁶ Diphenyl¹⁷ and di-*t*-butyl-(trimethyltin)phosphine¹⁸ and *t*-butyl(bis-trimethyltin)phosphine were prepared by reacting the corresponding trimethylsilylphosphines with trimethyltin chloride.^{19,20}

The nickel complexes were prepared by adding the ligand to a stoichiometric amount of tetracarbonylnickel in benzene or pentane to liberate CO. Synthesis of the molybdenum and tungsten complexes required irradiation in THF.^{9,21-23} The manganese and rhenium complexes were prepared from the pentacarbonyl bromides and the ligand.²⁴

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