# A New Route to Aryltin Compounds: Orthometallation of Schiff's Bases by Tin(IV) Halides: Crystal and Molecular Structure of *N*-Methyl-*ortho*-trichlorostannyldiphenylmethyleneamine, 2-$Cl_3SnC_6H_4C(Ph)=NMe$

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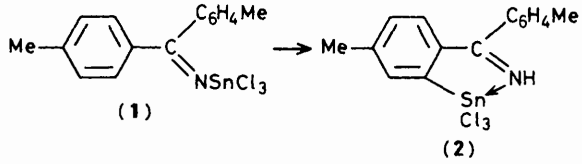
Reactions between tin(IV) halides $SnX_4$ and Schiff's bases $R'C_6H_4C(R'')=NR'''$ in boiling toluene at molar ratios of *ca.* 1 : 2 afford immonium salts $[R'C_6H_4C(R'')=NHR''']_2SnX_6$ and orthometallated materials $X_3SnC_6H_3(R')C(R'')=NR'''$, exemplified by $Cl_3SnC_6H_4C(Ph)=NMe$, the structure of which, established by an *X*-ray crystallographic study, has distorted trigonal bipyramidal metal co-ordination, with axial N → Sn and Cl–Sn bonds of length 2.284(4) and 2.401(2) Å respectively, and equatorial C–Sn and Cl–Sn bonds of lengths 2.115(3), 2.335(1), and 2.323(2) Å.

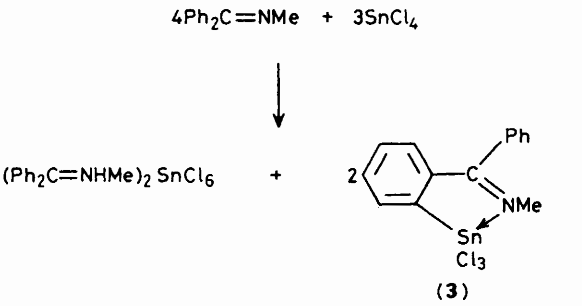
Although organotin compounds can be prepared by the action of tin, tin alloys, or occasionally tin(II) halides on organic halides, they are more usually prepared in the laboratory by the action of a Grignard or organolithium reagent on a tin(IV) halide.[1—3] Orthometallation reactions, which provide such convenient routes to a variety of aryl–transition metal compounds,[4—6] are far less common in main group organometallic chemistry, and to our knowledge have been exploited in organotin chemistry in only two ways: firstly, in the use of preformed orthometallated organometallic reagents such as $CuC_6H_4CH_2NMe_2$ to prepare related tin(IV) systems by reaction with tin(IV) halides $R_2SnBr_2$,[7—9] and secondly, in spontaneous orthometallation reactions of *N*-trichlorostannylarylmethyleneamines, aryl$C(R)=NSnCl_3$, *e.g.* reaction (1).[10]

Both of these routes suffer the disadvantage that other metallo reagents are required [the stannylamine (**1**)[10] was prepared from the lithio reagent $tolyl_2C=NLi$]. Here, we describe a new direct route to aryltin compounds that requires the use of no organometallic reagents, the reaction of Schiff's bases with tin(IV) halides, exemplified by the reaction of tin(IV) chloride with an excess of *N*-methyldiphenylmethyleneamine, $Ph_2C=NMe$ (the surplus base functions as a dehydrohalogenating reagent), reaction (2).

Exploratory experiments with various solvents and ratios of reactants have shown that reactions consistent with the stoicheiometry of equation (2) occur in good (>75%) yield when $Ph_2C=NMe$ and $SnCl_4$ interact in boiling toluene at ratios in the range 3 : 2 to 2 : 1, *i.e.* in the presence of a slight excess of the Schiff's base. The salt $(Ph_2C=NHMe)_2SnCl_6$ separates slowly as a colourless precipitate (analysing satisfactorily for $C_{28}H_{28}Cl_6N_2Sn$) even when $Ph_2C=NMe$ and $SnCl_4$ are mixed in toluene at 20 °C. Boiling for *ca.* 10 h ensures complete reaction. Removal of the insoluble hexachlorostannate by filtration leaves a clear colourless solution from which crystals analysing satisfactorily for (**3**) ($C_{14}H_{12}Cl_3NSn$) separate on cooling to −20 °C.



(1)



(2)

An *X*-ray crystallographic study of (**3**)† has established its orthometallated structure, with a distorted trigonal bipyramidal co-ordination at the metal atom, as shown in Figure 1, which also lists selected bond distances and angles. The bond lengths and angles in the $C_3NSn$ ring of (**3**) closely resemble those in the related compound (**2**):[10] both contain equatorial

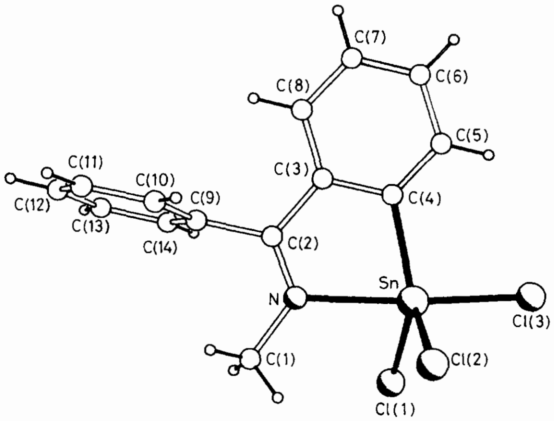


**Figure 1.** Molecular structure of 2-$Cl_3SnC_6H_4C(Ph)=NMe$, (**3**). Selected bond distances (Å) and angles (°): Sn–Cl(1), 2.335(1); Sn–Cl(2), 2.323(2); Sn–Cl(3), 2.401(2); Sn–N, 2.284(4); Sn–C(4), 2.115(3); N–C(1), 1.466(7); N–C(2), 1.273(4); C(2)–C(3), 1.485(6); C(2)–C(9), 1.494(6); C(3)–C(4), 1.392(6); Cl(1)–Sn–Cl(2), 105.4(1); Cl(1)–Sn–Cl(3), 92.0(1); Cl(2)–Sn–Cl(3), 96.7(1); Cl(1)–Sn–N, 87.0; Cl(2)–Sn–N, 90.0(1). Cl(3)–Sn–N, 173.2(1); Cl(1)–Sn–C(4), 135.9(1); Cl(2)–Sn–C(4), 115.3(1); Cl(3)–Sn–C(4), 99.1(1); N–Sn–C(4), 77.1(1); Sn–N–C(2), 112.7(3); N–C(2)–C(3), 117.9(4); C(2)–C(3)–C(4), 118.3(3); Sn–C(4)–C(3), 113.7(3).

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† *Crystal data* for (**3**): $C_{14}H_{12}Cl_3NSn$, $M = 419.3$, monoclinic, space group $P2_1/c$, $a = 11.538(2)$, $b = 13.784(2)$, $c = 11.442(2)$ Å, $\beta = 117.68(1)°$, $U = 1611.5$ Å$^3$, $Z = 4$, $F(000) = 816$, $D_c = 1.728$ g cm$^{-3}$, $\mu = 2.08$ mm$^{-1}$ for Mo-$K_\alpha$ radiation ($\lambda = 0.71069$ Å). Of 6224 reflections measured at room temperature on a Stoe-Siemens AED diffractometer with $2\theta \leqslant 50°$ and corrected for absorption, 2482 were unique with $F > 4\sigma(F)$ ($R_{int} = 0.027$). Structure solution by heavy atom methods and least-squares refinement with anisotropic non-H atoms, H atoms in calculated positions, and weighting $w^{-1} = \sigma^2(F) + 0.00029F^2$, gave $R = 0.036$, $R_w = 0.043$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Sn–C bonds of *ca.* 2.12 Å, axial Sn–N bonds of *ca.* 2.27 Å, and axial and equatorial Sn–Cl bonds of *ca.* 2.40 and 2.33 Å, respectively. Both compounds thus conform to the normal rules for trigonal bipyramidal species, in that less electronegative substituents [the aryl groups in (**2**) and (**3**)] occupy equatorial sites, and that axial bonds are normally longer than equatorial bonds. The C=N bond length of 1.273(4) Å shows that it retains fully its double bond character.

The five-membered ring in (**3**) and the benzene ring with which it shares an edge are essentially coplanar as expected (r.m.s. deviations of atoms from the mean planes of the two rings are 0.017 and 0.003 Å, and the dihedral angle between the planes is 1.7°). The dihedral angle between the two benzene rings is 80.4°, an orientation for the unsubstituted phenyl group that clearly minimises nonbonding repulsions at the expense of opportunities for conjugation with the azomethine link.

Further experiments to test the generality of the orthometallation reaction have been carried out with various other Schiff's bases B. Orthometallated products were obtained with B = 2-$MeOC_6H_4CH{=}NPh$, $Ph_2C{=}NPh$, and $PhCH{=}NR$, where R = Ph, $Bu^t$, $C_6H_4OMe$, and $C_6H_4Cl$ (the last two in low yield), together with salts $(BH)_2SnCl_6$. Adducts $B_2SnCl_4$ were also isolable when B = 2-$MeOC_6H_4CH{=}NPh$, 2-$ClC_6H_4CH{=}NPh$, $PhCH{=}NR$ (R = Ph, $Bu^t$, $C_6H_4OMe$, and $C_6H_4Cl$), or $PhCH_2CH{=}NBu^t$. Supporting structural information on the products was provided by $^1H$, $^{13}C$, and $^{119}Sn$ n.m.r. and Mössbauer studies, as will be reported elsewhere.

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## References

1 B. J. Aylett, 'Organometallic Compounds Vol. I, The Main Group Elements. Part 2, Groups IV and V,' Chapman and Hall, London, 1979.

2 A. G. Davies, and P. J. Smith, *Adv. Inorg. Chem. Radiochem.*, 1980, **23**, 1.

3 A. G. Davies and P. J. Smith, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 2, ch. 11, pp. 519—627.

4 G. W. Parshall, *Acc. Chem. Res.*, 1970, **3**, 139.

5 J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, 1976, **18**, 327.

6 M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 73.

7 G. van Koten, C. A. Schapp, and J. G. Noltes, *J. Organomet. Chem.*, 1975, **99**, 157.

8 G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, 1976, **118**, 183.

9 G. van Koten and J. G. Noltes, *J. Am. Chem. Soc.*, 1976, **98**, 5393.

10 B. W. Fitzsimmons, D. G. Othen, H. M. M. Shearer, K. Wade, and G. Whitehead, *J. Chem. Soc., Chem. Commun.*, 1977, 215.