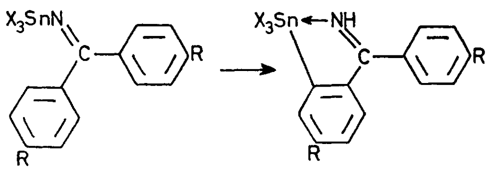
New Route to Aryltin(IV) Halides by Spontaneous Cyclometallation of Benzylideneaminotin(IV) Halides; *X*-Ray Crystal Structure of the *ortho*-Metallated Ketimine, *o*-$SnCl_3$-*p*-$MeC_6H_3C(:NH)$*p*-C_6H_4Me

By Brian Fitzsimmons
(*Chemistry Department, Birkbeck College, London* WC1E 7HX)
David G. Othen, Harrison M. M. Shearer, and Kenneth Wade*
(*Chemistry Department, Durham University, South Road, Durham* DH1 3LE
and Graham Whitehead
(*Science Department, College of Technology, Darlington*)

Summary The benzylideneaminotin(IV) halides, $SnCl_3(N:CPh_2)$, $SnCl_3[N:C(p\text{-tolyl})_2]$, $SnCl_3[N:C(p\text{-chlorophenyl})_2]$, and $SnBr_3(N:CPh_2)$ spontaneously rearrange to form the *ortho*-trihalogenostannylbenzylideneamines *o*-$SnCl_3$-*p*-$RC_6H_3C(:NH)$-*p*-C_6H_4R (R = H, Cl, or Me) (IIa—c) and *o*-$SnBr_3C_6H_4C(:NH)Ph$ (IId), the novel ring structures of which are indicated by their i.r., ^1H n.m.r., and ^{119}Sn Mössbauer spectra, and by an *X*-ray crystallographic study of the di-*p*-tolylketimine derivative *o*-$SnCl_3$-*p*-$MeC_6H_3C(:NH)$-*p*-C_6H_4Me.

We report here what are believed to be the first examples of *ortho*-metallation reactions in organotin chemistry, the surprisingly easy rearrangements of the benzylideneaminotin(IV) halides (Ia—d) affording the new tin heterocycles (IIa—d).



(I) (II)

	R	X
a,	Me	Cl
b,	H	Cl
c,	Cl	Cl
d,	H	Br

The ketiminotin(IV) halides (Ia—d) can be prepared as solid etherates $SnX_3[N:C(p\text{-}C_6H_4R)_2](Et_2O)_n$ of variable composition (*n* lies in the range 1—2), contaminated by lithium halide, from the *N*-lithioketimine and tin halide in ether [equation (1)]. These etherates dissolve in hot toluene, but cannot be recrystallised from that solvent. Instead, the solutions, when cooled, slowly deposit crystals of the *ortho*-metallated compounds (II), apparently formed by dissociation of the etherates followed by rearrangement [equation (2)]. These changes are indicated by changes in the i.r. spectra; peaks attributable to co-ordinated Et_2O disappear, a sharp absorption develops in the N–H stretching region (see Table) and the numbers, intensities, and frequencies of bands in the C=N, C=C, and Sn–X stretching regions change [*e.g.* (Ia) absorbs at 1605vs, 1560vs, and 370vw cm^{-1}, whereas (IIa) absorbs at 1610vs, 1599vs, 1582vs, 1568s, 1562sh, 1546s, 371s, and 363sh cm^{-1}). The signals due to aryl protons in the ^1H n.m.r. spectra also show the changes appropriate for *ortho*-metallation, while the five-co-ordinate state of the tin atoms of (IIa—d) is indicated by the quadrupole splittings ΔE in their Mössbauer spectra (Table).

$$LiN:C(p\text{-}C_6H_4R)_2 + SnCl_4 \xrightarrow{Et_2O} LiCl + SnCl_3[N:C(p\text{-}C_6H_4R)_2](Et_2O)_n \quad (1)$$

$$SnX_3[N:C(p\text{-}C_6H_4R)_2](Et_2O)_n \rightarrow nEt_2O + (I) \rightarrow (II) \quad (2)$$

Table

Compound (II)	ν(N–H)[a] /cm^{-1}	ΔE[b] /mm s^{-1}	δ[c]/mm s^{-1}
a	3280	1·588	0·874
b	3332	1·730	0·716
c	3324	1·440	0·764
d	3300	1·486	0·964

[a] Measured as Nujol mulls. [b] Quadrupole splitting (±0·025). [c] Chemical isomer shift (±0·025) relative to $CaSnO_3$ (Mössbauer spectra were measured with the absorbers at 78 K using a $Ca^{119m}SnO_3$ source)

The structure of (IIa) has been established from *X*-ray data (see Figure).† It crystallises from toluene as colourless monoclinic platelets with $a = 9{\cdot}298$, $b = 14{\cdot}553$, $c = 12{\cdot}982$ Å, $\beta = 107{\cdot}74°$, space group $P2_1/c$, $Z = 4$. The intensity data were collected on a Hilger and Watts four-circle diffractometer, using Zr-filtered Mo-radiation, to a limit of $\theta = 23°$. The structure was solved by means of the Patterson function and refined by full-matrix least-squares methods to $R = 0{\cdot}03$ for the 1802 reflections with net counts $\geqslant 2{\cdot}5\sigma$. Selected interatomic distances and bond angles are given in the Figure. The co-ordination about tin is distorted trigonal bipyramidal, with the nitrogen atom and one chlorine atom in the axial positions. The ring angle at tin, 76·5°, may be compared with 75·3° for ∠NSnC in the related *ortho*-metallated benzylamine, *o*-$(SnBrPh_2)C_6H_4CH_2NMe_2$ (prepared from $SnBr_2Ph_2$ and the arylcopper compound $CuC_6H_4CH_2NMe_2$),[1] and 79·4° for ∠NMnC of the metallated benzylideneaniline *o*-$[Mn(CO)_4(C_6H_4CH:NPh)]$.[2]

In other experiments, we have found that the compounds (II) can also be prepared from the tin(IV) halide and *N*-

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

trimethylsilyl ketimine [equation (3)], and that related

$$SnX_4 + SiMe_3[N:C(p\text{-}C_6H_4R)_2] \rightarrow Me_3SiX + (II) \quad (3)$$

cyclometallation reactions occur with bis- or tris-(imino)tin halides $SnCl_2[N:C(p\text{-}C_6H_4R)_2]_2$ or $SnCl[N:C(p\text{-}C_6H_4R)_2]_3$, though not with iminotin alkyls such as $SnMe_3N:CPh_2$, nor with imino-silicon or -germanium halides $MCl_3[N:C(p\text{-}C_6H_4R)_2]$ (M = Si or Ge). From these observations, noting that the cyclometallation (I) → (II) occurs progressively more readily in the sequence (Ic) < (Ib) < (Ia), and noting also that Lewis bases inhibit the rearrangement (I) → (II) [apparently significantly, we have been unable to isolate compounds (I) in unco-ordinated form], we conclude that for the *ortho*-metallation reaction to occur, the metal centre should be co-ordinatively unsaturated and highly electrophilic, properties likely to be found in other main group systems. (Recent *ortho*-metallation studies[3] have generally concerned transition metal systems, the neglect of main group systems being surprising in view of the importance of lithiation,[4] mercuration,[5] and thallation[6] reactions). We are accordingly looking for such systems, as well as exploring the scope of the tin reactions which, like the recently reported stannylation of αβ-unsaturated carbonyl compounds,[7] make a new range of mono-organotin halides directly accessible.

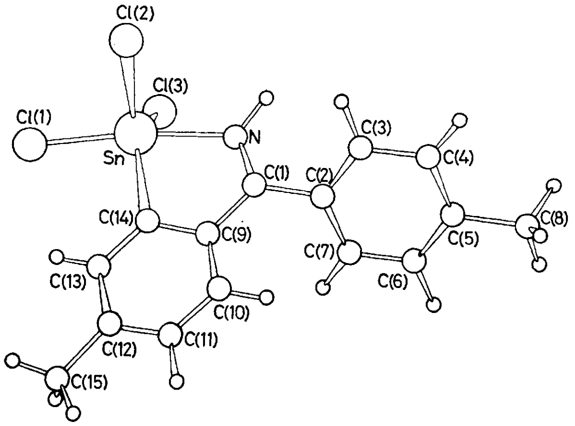


FIGURE. Structure of (IIa), $o\text{-}SnCl_3\text{-}p\text{-}MeC_6H_3C(:NH)p\text{-}C_6H_4Me$.

We thank the S.R.C. for financial support (to D.G.O.).

(*Received*, 26*th January* 1977; *Com.* 063.)

---

[1] G. van Koten, J. G. Noltes, and A. L. Spek, *J. Organometallic Chem.*, 1976, **118**, 183.

[2] R. G. Little and R. J. Doedens, *Inorg. Chem.*, 1973, **12**, 840.

[3] See, *e.g.*, G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139; F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science, London, 1973, p. 149; M. I. Bruce, 'Organometallic Chemistry,' Senior Reporters E. W. Abel and F. G. A. Stone, Specialist Periodical Reports, The Chemical Society, 1972, vol. 1, p. 282; 1973, vol. 2, p. 346; 1974, vol. 3, p. 269; B. L. Booth, *ibid.*, 1975, vol. 4, p. 268, and refs. cited therein.

[4] R. West, *Adv. Chem. Series*, 1974, **130**, 211; D. W. Slocum and D. I. Sugarman, *ibid.*, p. 222; M. D. Rausch and A. J. Sarnelli, *ibid.*, p. 248.

[5] B. C. Crosse, 'Organometallic Chemistry,' Senior Reporters E. W. Abel and F. G. A. Stone, Specialist Periodical Reports, The Chemical Society, 1972, vol. 1, p. 35; J. L. Wardell, *ibid.*, 1973, vol. 2, p. 34; 1974, vol. 3, p. 29; 1975, vol. 4, p. 25.

[6] A. McKillop and E. C. Taylor, *Chem. in Britain*, 1973, **9**, 4.

[7] J. W. Burley, R. E. Hutton, and V. Oakes, *J.C.S. Chem. Comm.*, 1976, 803.