One-pot synthesis of a novel tridentate tin(IV) ligand; syntheses and structures of [$Bu^nSn(NC_5H_4$-*C,N*$)_3MBr$] (M = Li, Cu)

Michael A. Beswick, Clemens J. Belle, Maxwell K. Davies, Malcolm A. Halcrow, Paul R. Raithby, Alexander Steiner and Dominic S. Wright*

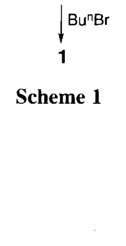
University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW

During the reaction of [$Sn(C_5H_5)_2$] with 2-lithiopyridine, further reaction of the [Bu^nBr] byproduct leads to the formation of [$Bu^nSn(NC_5H_4$-*C,N*$)_3LiBr$]·0.5thf 1, interaction of the tris(pyridyl)tin(IV) ligand of which, with $CuCl_2$, produces [$Bu^nSn(NC_5H_4$-*C,N*$)_3CuBr$]·0.5thf 2

We recently showed that nucleophilic addition occurs when group 14 metallocenes {[$E(C_5H_5)$], E = Sn, Pb} are treated with the weak $C_5H_5^-$ nucleophile, producing mononuclear and extended anions containing $E(C_5H_5)_3$ units.[1] With more potent nucleophiles, substitution of the C_5H_5 ligands occurs, producing a variety of tin(II) and lead(II) metallo-organic complexes.[1b,2] As illustrated by the formation of [$E\{N{=}C(Bu^t)Ph\}_3$]$^-$ anions in the reactions of [$E(C_5H_5)_2$] with [$LiN{=}C(Bu^t)Ph$],[2a,d] such nucleophilic substitution reactions furnish a simple halide-free method by which a range of triorgano-group 14 metal anions can be prepared, these anions being potential tripodal ligands to various metals.[3] However, so far the general application of tris(imino)–group 14 anions as a tripodal ligands has proved unsuccessful due to ligand-transfer reactions.[4] This finding has prompted us to investigate more robust p-block metal ligand systems.

We report here the simple one-pot synthesis of [$Bu^nSn(NC_5H_4$-*C,N*$)_3LiBr$]·0.5thf **1** from the reaction of [$Sn(C_5H_5)_2$] with 2-lithiopyridine (generated *in situ* from the reaction of 2-bromopyridine with Bu^nLi).† The most obvious route to **1** is that of nucleophilic displacement of the byproduct Bu^nBr with the intermediate triorganostannate (Scheme 1). However, oxidative addition of Bu^nBr to tin(II) intermediates cannot be ruled out. The reaction of **1** with $CuCl_2$ (1 : 2 equiv.) results in the unexpected formation of [$Bu^nSn(NC_5H_4$-*C,N*$)_3CuBr$]·0.5thf **2**, the excess tris(pyridyl)tin(IV) ligand presumably being involved in the reduction of Cu^{II} to Cu^I.[5]

Low-temperature X-ray studies of **1** and **2**‡ show them to have similar ion-contacted structures, [$Bu^nSn(NC_5H_4$-*C,N*$)_3MBr$]·0.5thf (M = Li **1**, Cu **2**) (Fig. 1), resulting from the chelation of the Li–Br and Cu–Br monomer units by the donor N atoms of the tin(IV) tris(pyridyl) ligand [$Bu^nSn(NC_5H_4$-*C,N*$)_3$]. The C_{py}–Sn–C_{py} angles in **1** and **2** [av. 101.3 and 102.0°, respectively] are considerably more acute than the bridgehead angles observed in coordination compounds of [$XC(NC_5H_4$-*C,N*$)_3$] (X = H, OH) (*ca.* 111°).[6] In the latter, the C_{py}–C–C_{py} angles are insensitive to the ionic radii of the coordinated metal atoms and it is likely that the more acute angles found in [$Bu^nSn(NC_5H_4$-*C,N*$)_3$] can be simply ascribed to the contraction brought about by the greater polarity of the Sn–C bond (VSEPR). Overall, the bond lengths and angles within the [$Bu^nSn(NC_5H_4$-*C,N*$)_3$] units of **1** and **2** are similar. However, in contrast to the symmetrical coordination of the Li^+ cation of **1** [in which the N–Li bonds (*av.* 2.08 Å) are all *ca.* 4° out of the planes of their associated pyridine rings], there is a more marked distortion in the geometry of the Cu^+ ion of **2**. One of the Cu–N bonds [Cu–N(2) 2.09(1) Å] is longer than the other two [*av.* 2.05 Å] and *ca.* 16° out of the plane of its associated pyridine ring (*cf. ca.* 3° for the other Cu–N bonds with respect to their pyridine rings).



Scheme 1

Although complexes containing a range of tris(pyridyl) ligands ([ENC_5H_4-*C,N*$)_3$], E = C–H, C–OH, N, P, As) have been investigated,[6,7] these are the first structural characterisations of complexes containing a p-block metal bridgehead. One feature of this new ligand system is its greater reactivity compared to other [$E(NC_5H_4$-*C,N*$)_3$] ligands and the ability for reduction of the metal to accompany ligand complexation. This is witnessed in the synthesis of **2** which can be compared to the formation of [$Cu\{HC(NC_5H_4$-*C,N*$)_3\}_2$]$^{2+}$ from [$HC(NC_5H_4$-*C,N*$)_3$] and $CuCl_2$.[6h] Electrochemical studies give further insights into the formation and stability of **2**. The cyclic voltammogram in thf shows that the copper(II) species generated on oxidation is highly unstable and decomposes

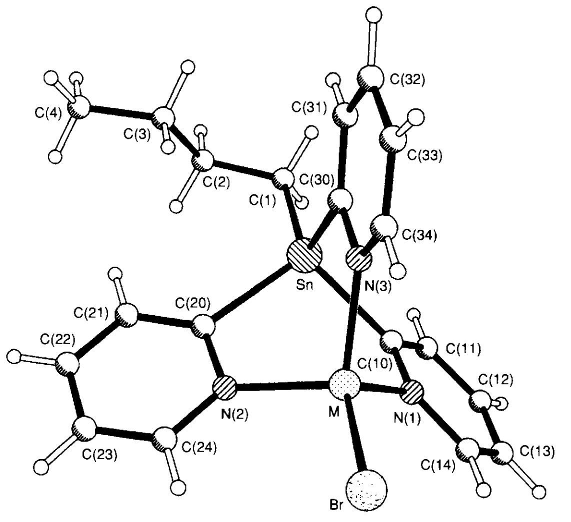


Fig. 1 Structures of **1** and **2**. Hydrogen atoms and the lattice-bound thf molecule have been omitted for clarity. Key bond lengths (Å) and angles (°): **1**, Sn–C(1) 2.144(4), Sn–C(10) 2.162(4), Sn–C(20) 2.171(4), Sn–C(30) 2.155(4), av. C$\stackrel{\cdots}{-}$C(py) 1.38, av. C$\stackrel{\cdots}{-}$N(py) 1.35, av. Li–N 2.08, Li–Br 2.435(6), Sn···Li 3.263(6); av. C(1)–Sn–C(py) 116.8, C(10)–Sn–C(20) 101.5(1), C(10)–Sn–C(30) 103.31(1), C(20)–Sn–C(30) 99.2(1), av. N–Li–N 101.0, av. N–Li–Br 116.9, av. Sn(1)–C(py)–N(py) 113.2, av. C(py)–N(py)–Li 119.7, Sn···Li–Br 173.9; **2**, Sn–C(1) 2.15(2), Sn–C(10) 2.15(1), Sn–C(20) 2.19(1), Sn–C(30) 2.14(1), av. C$\stackrel{\cdots}{-}$C(py) 1.37, av. C$\stackrel{\cdots}{-}$N(py) 1.36, av. Cu–N 2.06, Cu–Br 2.402(2), Sn···Cu 3.206(2), av. C(1)–Sn–C(py) 116.1, C(10)–Sn–C(20) 102.5(5), C(10)–Sn–C(30) 104.4(5), C(20)–Sn–C(30) 99.2(5), av. N–Cu–N 103.1, av. N–Cu–Br 115.2, av. Sn–C(py)–N(py) 112.8, av. C(py)–N(py)–Cu 118.2, Sn···Cu–Br 173.3.

immediately on formation, presumably by reaction with the coordinated $[\mathrm{Bu^nSn(NC_5H_4}\text{-}C,N)_3]$ ligand. Furthermore, the coordination of $\mathrm{Cu^I}$ by the $[\mathrm{Bu^nSn(C_5H_4}\text{-}C,N)_3]$ ligand causes a marked change in the chemistry of the tin(IV) centre, which is more resistant to reduction in **2** than in **1**.§ This may reflect an increase in electron density of the Sn centre. The latter and the shortness of the Cu–Br bond in **2** {2.402(2) Å, *cf.* 2.5–2.6 Å in $[(\mathrm{pyridyl})_3\mathrm{CuBr}]$ derivatives[8*a*,*b*] and 2.481(5) Å in $[(\mathrm{Ph_3P})_3\mathrm{CuBr}]$[8*c*]} provide an indication of the acceptor behaviour of the $[\mathrm{Bu^nSn(NC_5H_3}\text{-}C,N)_3]$ ligand.

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Footnotes

† *Syntheses*: **1**; $\mathrm{Bu^nLi}$ (1.90 ml, 1.6 mol $\mathrm{dm^{-3}}$ in hexanes, 3.0 mmol) was added dropwise to a stirred solution of 2-bromopyridine (0.47 g, 3.0 mmol) in thf (20 ml) at −78 °C. The resulting mixture was stirred at −78 °C (1 h), giving a deep red solution, before adding $[\mathrm{Sn(C_5H_5)_2}]$ (0.25 g in 1 ml thf, 1.0 mmol). After further stirring at −78 °C (1 h), the solution was filtered (Celite, porosity 3). Reduction of the yellow–green filtrate to *ca.* 8 ml *in vacuo* gave a yellow precipitate, which was gently warmed into solution. Storage at 5 °C (24 h) produced a crop of yellow crystalline blocks of **1**; yield 0.35 g (65%) (scaling the reaction to 50 mmol gives a similar yield); decomp. *ca.* 190 °C; IR (Nujol), $\nu_{\mathrm{max}}/\mathrm{cm^{-1}}$ 1547m, 1556w $[\nu(\mathrm{C{\doteq}N})]$, other bands at 1260m, 1152m, 1041m, 999m, 803m, 762m, 722m; ^{1}H NMR [400.14 MHz, $(\mathrm{CD_3})_2\mathrm{SO}$, +25 °C], 8.72 [d, 3 H, py C(6)–H], 7.68 [m, 6 H, py C(4,6)–H], 7.32 [m, 3 H, py C(3)–H], 3.60 (m, 2 H, thf), 1.74 (m, 2 H, thf), 1.66 [m, 2 H, C(1)–H, $\mathrm{Bu^n}$], 1.58 [m, 2 H, C(2)–H, $\mathrm{Bu^n}$], 1.32 [m, 2 H, C(3)–H, $\mathrm{Bu^n}$], 0.78 [t, 3 H, C(4)–H, $\mathrm{Bu^n}$]; ^{13}C NMR [100.61 MHz, $(\mathrm{CD_3})_2\mathrm{SO}$, +25 °C], 171.1 [py C(2)], 150.7, 134.4, 133.2, 133.2, 123.2 [py C(3)–C(6)], 67.1 ($\mathrm{CH_2}$, thf), 28.1 ($\mathrm{CH_2}$, $\mathrm{Bu^n}$, 26.4 ($\mathrm{CH_2}$, $\mathrm{Bu^n}$), 25.2 ($\mathrm{CH_2}$, thf), 13.5 ($\mathrm{CH_3}$, $\mathrm{Bu^n}$), 11.3 ($\mathrm{CH_2}$, $\mathrm{Bu^n}$); satisfactory elemental analysis.

2; Anhydrous $\mathrm{CuCl_2}$ (0.27 g, 2.0 mmol) was added to a stirred solution of **1** (2.13 g, 4.0 mmol) in thf (30 ml) at 20 °C. The bright yellow solution produced was filtered to remove the faint cloudiness and the filtrate was reduced to *ca.* 20 ml, whereupon a yellow precipitate was formed. The solid was heated back into solution and storage at 20 °C gave a crop of large hexagonal plates of **2**; yield 0.62 g (53%) [reaction of **1** with CuBr (1 : 1) gave the same product in similar yield]; decomp. *ca.* 125 °C; IR (Nujol), $\nu_{\mathrm{max}}/\mathrm{cm^{-1}}$ 1573m, 1552w $[\nu(\mathrm{C{\doteq}N})]$, additional bands similar to **1**; ^{1}H NMR (400.14 MHz, $[^2\mathrm{H_8}]$thf, +25 °C), 8.90 [d, 3 H, py C(6)–H], 7.66 [m, 6 H, py C(4,6)–H], 7.24 [m, 3 H, py C(3)–H], 3.62 (m, 2 H, thf), 2.25 (m, 2 H, C(1)–H, $\mathrm{Bu^n}$], 1.80 [m, 2 H, C(2)–H, $\mathrm{Bu^n}$], 1.74 (m, 2 H, thf), 1.67 [m, 2 H, C(3)–H, $\mathrm{Bu^n}$], 1.09 [t, 3 H, C(4)–H, $\mathrm{Bu^n}$]; ^{13}C NMR (100.61 MHz, $[^2\mathrm{H_8}]$thf, +25 °C), 170.6 [py C(2)], 152.1, 134.9, 133.8, 124.1 [py C(3)–C(6)], 29.8 ($\mathrm{CH_2}$, $\mathrm{Bu^n}$), 28.5 ($\mathrm{CH_2}$, $\mathrm{Bu^n}$), 14.0 ($\mathrm{CH_3}$, $\mathrm{Bu^n}$), 11.2 ($\mathrm{CH_2}$, $\mathrm{Bu^n}$); satisfactory elemental analysis.

‡ *Crystal data*: **1**; $\mathrm{C_{21}H_{25}BrLiN_3O_{0.05}Sn}$, $M = 532.98$, monoclinic, space group $C2/c$, $a = 17.838(4)$, $b = 8.562(2)$, $c = 29.731(7)$ Å, $\beta = 100.47(2)°$, $U = 4665(2)$ Å^3, $Z = 8$, $D_c = 1.586$ Mg m^{-3}, $\lambda = 0.71073$ Å, $T = 153(2)$ K, $\mu(\text{Mo-K}\alpha) = 2.946$ mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly cooled crystal[9] of dimensions 0.3 × 0.3 × 0.3 mm by the θ–ω method ($4.17 < \theta < 22.49°$). Of a total of 2907 collected reflections, 2900 were independent. The structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1\ [F > 4\sigma(F)] = 0.025$ and $wR2 = 0.062$ (all data); largest peak and hole in the final difference map 0.457 and −0.320 e Å^{-3}.

2; $\mathrm{C_{21}H_{25}BrCuN_3O_{0.5}Sn}$, $M = 589.58$, monoclinic, space group $C2/c$, $a = 17.760(4)$, $b = 8.510(2)$, $c = 29.666(6)$ Å, $\beta = 100.74(2)°$, $U = 4405(2)$ Å^3, $Z = 8$, $D_c = 1.778$ Mg m^{-3}, $\lambda = 0.71073$ Å, $T = 153(2)$ K, $\mu(\text{Mo-K}\alpha) = 3.927$ mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly cooled crystal[9] of dimensions 0.3 × 0.2 × 0.2 mm by the θ–ω method ($4.02 \leqslant \theta \leqslant 22.52°$). Of a total of 3358 collected reflections, 2864 were independent. The structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1[F > 4\sigma(F)] = 0.070$ and $wR2 = 0.239$ (all data); largest peak and hole in the final difference map 2.354 and −1.87 e Å^{-3}.

§ The cyclic voltammogram (CV) of **1** in thf–0.5 mol dm^{-3} $\mathrm{NBu^n{}_4PF_6}$ (298 K) at a double Pt electrode shows, in addition to oxidations arising from free $\mathrm{Br^-}$, an irreversible one-electron reduction [$E_{\mathrm{pc}} = -1.83$ V *vs.* $\mathrm{F_c\text{–}F_c^+}$). This probably involves formation of an $\mathrm{R_3Sn\cdot}$ radical, presumably generated by the cleavage of a weaker Sn–pyridyl bond of the $[\mathrm{Bu^nSn(NC_5H_4}\text{-}C,N)_3]$ ligand.[11] The CV of **2** under the same conditions shows a broad irreversible $\mathrm{Cu^I\text{–}Cu^{II}}$ oxidation ($E_{\mathrm{pa}} = -0.04$ V) which contains at least three low-potential shoulders. Addition of excess $\mathrm{NBu^n{}_4Br}$ to **2** simplifies the CV, with only a single irreversible oxidation now being observed ($E_{\mathrm{pa}} = -0.14$ V) which is irreversible at all scan rates. An extremely broad irreversible reduction ($E_{\mathrm{p}} = -2.20$ V), with an associated desorption spike, could be assigned to a $\mathrm{Cu^I\text{–}Cu^0}$ couple. No Sn-based reduction is observed below the solvent limit ($E_{\mathrm{pc}} = -2.6$ V) for **2**.

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