Novel redox properties of $HB(3\text{-}Bu^tpz)_3^-$ as shown by its reaction with In^{III} and Sn^{IV}

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The novel redox properties of $HB(3\text{-}Bu^tpz)_3^-$ are demonstrated by the isolation and structural characterisation of $[In_2I_3\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_2(5\text{-}Bu^tpz)\}(\eta^1\text{-}5\text{-}Bu^tpzH)]$ 1, a novel In–In bonded species, and $Sn_2(Ph)_6$ 2, on reaction with In^{III} and Sn^{IV}, respectively.

In previous publications we have reported the synthesis and X-ray crystal structures of $[In\{HB(3,5\text{-}Me_2pz)_3\}_2]I$ and $[In\{MeGa(pz)_3\}_2]InI_4$,[1] $[In\{HB(3\text{-}Phpz)_3\}]$,[2] and $[In\{HB(3\text{-}Bu^tpz)_3\}]$.[3] In each case synthesis was achieved by reacting InI with the potassium salt of the appropriate ligand. We have now extended this work to include the reaction of indium(III) and tin(IV) with the above ligands. We report here the results of the reaction of InI_3 and $SnPh_3Cl$ with $KHB(3\text{-}Bu^tpz)_3$ in detail, because of their unprecedented course.

During the reaction of InI_3 with $KHB(3\text{-}Bu^tpz)_3$, in thf at room temperature, finely divided In metal precipitated and subsequent work up of the reaction mixture produced X-ray quality crystals of **1**.†

Elemental analysis, ^1H, ^{13}C NMR and mass spectra of **1** were recorded. NMR evidence for Bu^tpzH in addition to $HB(Bu^tpz)_3^-$, a peak at *m/z* 1116 in the FAB^+ mass spectrum and the formation of In metal in the course of the reaction indicated that **1** was not a 'simple In^{III} complex'. To elucidate the structure of **1** an X-ray crystallographic study was undertaken. The structure is shown in Fig. 1.‡ The structure of **1** is entirely consistent with the analytical, NMR and mass spectral data. In **1** the negative charges on the three iodides and the $HB(Bu^tpz)_3^-$ require a total charge of plus four on the two In cations. Since the starting material was InI_3 this leads to the ineluctable conclusion that partial reduction of In^{III} has taken place.

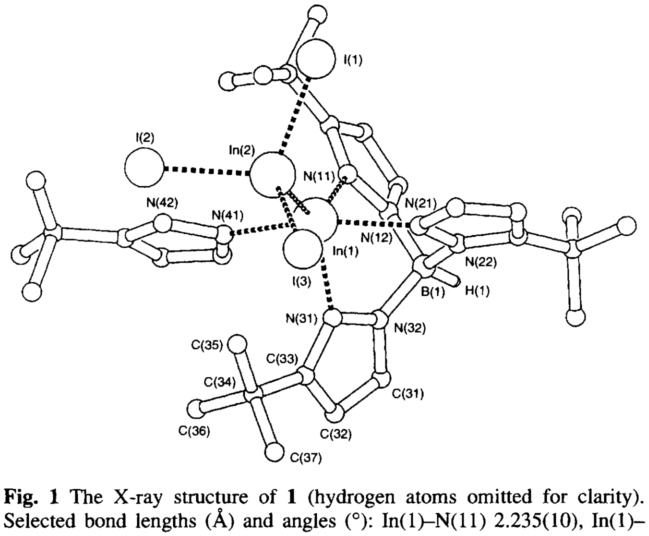

Fig. 1 The X-ray structure of **1** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): In(1)–N(11) 2.235(10), In(1)–N(21) 2.267(11), In(1)–N(31) 2.234(11), In(1)–N(41) 2.420(11), In(2)–I(1) 2.718(4), In(2)–I(2) 2.740(3), In(2)–I(3) 2.705(2), In(1)–In(2) 2.748(4), In(1)–In(2)–I(1) 114.5, In(1)–In(2)–I(2) 109.9, In(1)–In(2)–I(3) 112.8.

We offer the following as a possible route to the formation of **1**. $HB(3\text{-}Bu^tpz)_3^-$ coordinates to In^{III} and reduces it to In^I, accompanied by a breakdown of the $HB(3\text{-}Bu^tpz)_3^-$ to give Bu^tpzH as one of the products. The In^I is then stabilised by coordination with unreacted $HB(3\text{-}Bu^tpz)_3^-$. Adduct formation then occurs between the stereochemically active lone pair of the In^I complex and InI_3. The increase in steric crowding, on the already hindered In^I complex, by the approach of InI_3 could facilitate the rearrangement $In\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ to $In\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_2(5\text{-}Bu^tpz)\}$.[4] This would ease the steric constraint on the In^I lone pair and assist adduct formation. It is envisaged that this sequence would take place in a concerted fashion. Support for this mechanism comes from the In–I bond angles in **1**, which are similar to those in, for example, $InI_3(PPh_3)$,[5] (In–I 2.677 Å, P–In–I 115°), and from our synthesis and X-ray structural determination of $[In\{HB(3\text{-}Phpz)_3\}]$ and $[In\{HB(3\text{-}Bu^tpz)_3\}]$§ which demonstrate that air- and solution-stable monomeric In^I complexes exist.[2,3]

From a formulation of **1** as an In^{III}–In^I adduct it is apparent that reduction of some of the In^{III} starting material has taken place and it is claimed that the source of this reducing power is $HB(3\text{-}Bu^tpz)_3^-$. This is a feature of the coordination chemistry of $HB(3\text{-}Bu^tpz)_3^-$ which has received little attention and which we consider to be of considerable significance. $KHB(3,5\text{-}Me_2pz)_3$ with InI_3 gives the structurally characterised six-coordinate In^{III} complex $[\{HB(3,5\text{-}Me_2pz)\}InI_2(3,5\text{-}Me_2pzH)]$.[3]

In an attempt to support the above claim the room-temperature reaction of $SnPh_3Cl$ with $KHB(3\text{-}Bu^tPz)_3$ in thf was carried out. This led to rapid formation of KCl and subsequent work up of the filtered solution produced air-stable block like crystals of **2**.† Elemental analysis, ^1H, ^{13}C, ^{119}Sn NMR and mass spectra of **2** all indicated the formulation Sn_2Ph_6, the crystal structure of which is known.[6] However, since the method used here for the synthesis of Sn_2Ph_6 is unusual, confirmation that the product was indeed Sn_2Ph_6 was sought through crystal-structure analysis.

A speculative mechanism for the formation of Sn_2Ph_6 is that reaction of $KHB(3\text{-}Bu^tpz)_3$ and $SnPh_3Cl$ takes place to give, transiently, $[\{HB(3\text{-}Bu^tpz)_3\}SnPh_3]$. However, because of the reducing properties of the coordinated $HB(3\text{-}Bu^tpz)_3^-$ ligand-mediated reduction of the Sn^{IV} takes place to give, for example, $SnPh_3\cdot$ which then undergoes dimerisation to Sn_2Ph_6. $KHB(pz)_3$ and $KHB(3,5\text{-}Me_2pz)_3$ with SnI_4 give the six-coordinate Sn^{IV} complexes $[\{HB(pz)_3\}SnI_3]$ and $[\{HB(3,5\text{-}Me_2pz)_3\}SnI_3]$.[7] These ligands with $SnPh_3Cl$ give the six-coordinate Sn^{IV} complexes $[\{HB(pz)_3\}SnPh_3]$ and $[\{HB(3,5\text{-}Me_2pz)_3\}SnPh_3]$.[7] All four complexes have been characterised structurally by X-ray crystallography.[7]

Because $HB(3\text{-}Phpz)_3^-$ like $HB(3\text{-}Bu^tpz)_3^-$ is able to stabilise In^I, and in the case of $HB(3\text{-}Bu^tpz)_3^-$ this stabilisation is thought to be related to its reducing properties, we are currently investigating the reaction of $HB(3\text{-}Phpz)_3^-$ with In^{III} and Sn^{IV}; and both ligands with other main-group compounds.

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Footnotes

† *Syntheses*: all manipulations were performed under argon using standard Schlenk techniques and all solvents dried prior to use.

1, addition of a solution of InI_3 (2.63 g, 5.30 mmol) in 20 cm^3 of thf to a solution of potassium hydrotris(3′-*tert*-butylpyrazolyl)borate (2.23 g, 5.30 mmol) in 60 cm^3 of thf with rapid stirring led to immediate opacity of the reaction mixture. After 18 h the reaction mixture was filtered to give a pale yellow filtrate and grey residue. On slow evaporation under reduced pressure the filtrate gave solvent dependent crystals, yield 0.52 g (18%), which were of X-ray quality. Anal. Calc. for $C_{28}H_{45}BI_3In_2N_8$: C, 30.15; H, 4.12; N, 10.04. Found C, 34.74; H, 4.85; N, 10.81%. ^{1}H NMR (250 MHz, CD_2Cl_2) δ 10.44 (s, 1 H, NH), 7.41 (d, 2 H, H5), 7.21 (d, 1 H, H3), 6.28 (d, 1 H, H4), 6.05 (d, 2 H, H4), 5.24 (d, 1 H, H4), 1.17 [s, 9 H, $C(CH_3)_3$], 1.15 [s, 9 H, $C(CH_3)_3$], 1.12 [s, 18 H, $C(CH_3)_3$].

2, a slurry of potassium hydrotris (3′-*tert*-butylpyrazolyl)borate (1.5 g, 3.57 mmol) and $SnPh_3Cl$ (1.35 g, 3.57 mmol) in 60 cm^3 of thf was stirred for 5 d. The thf was removed *in vacuo* and the resulting white residue treated with 60 cm^3 CH_2Cl_2 and filtered to remove KCl (0.21 g). The filtrate was reduced in volume to *ca.* 20 cm^3 and left standing at −30 °C for *ca.* four weeks after which time the X-ray quality crystals that had formed were filtered off, yield 1.92 g (77%). Anal. Calc. for $C_{36}H_{30}Sn_2$: C, 61.77; H, 4.32. Found C, 61.69; H, 4.21%.

‡ *Crystal data*: **1**; $C_{28}H_{45}BI_3In_2N_8$, M = 1114.87, monoclinic, space group $P2_1/n$, a = 13.03(3), b = 23.20(2), c = 15.270(3) Å, β = 104.,06(4)°, U = 4479(10) Å^3, Z = 4, D_c = 1.641 Mg m^{-3}, $F(000)$ = 2124, λ = 0.71069 Å, T = 293 K, μ(Mo-Kα) = 9.353 cm^{-1}. Absorption correction with DIFABS. Data were collected on a Delft Instruments FAST TV area detector diffractometer. Of a total of 15 103 collected reflections 6567 were unique. The structure was solved by direct methods. Refinement was by full-matrix least squares on F^2, final R indices [$(I > 2\sigma(I)$], R_1 = 0.0649, wR_2 = 0.1742.

For [In{HB(3-Bu^{t}pz)$_3$}]; a later determination of the X-ray crystallographic structure of this compound[8] has recently been re-evaluated[9] and is in essential agreement with our earlier findings[3] *viz.* $C_{21}H_{34}BInN_6$, M = 496.17, orthorhombic, space group $Cmc2_1$, a = 15.885(1), b = 15.121(2), c = 9.838(2) Å, U = 2363.06 Å^3, Z = 4, D_c = 1.395 Mg m^{-3}, $F(000)$ = 1024, λ = 0.71067 Å, T = 150 K, μ(Mo-Kα) = 9.844 cm^{-1}. Absorption correction with DIFABS. Data were collected on a Delft Instruments FAST TV area detector diffractometer. Of a total of 6087 collected reflections, 3105 were unique. The structure was solved by Patterson methods and refined by full-matrix least squares to R_1 = 0.030 and R_w = 0.035 [$F_o > 3\sigma(F_o)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/146.

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