

Novel poly(methimazoly)borate complexes of niobium(v) and tantalum(v)

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The reactions of $[\text{MCl}_4(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Nb}, \text{Ta}$) with $\text{Ph}_3\text{Sn}\{\text{HB}(\text{mt})_3\}$ ($\text{mt} = \text{methimazoly}$) provide structurally characterised complexes of the new chlorobis(methimazoly)borate ligand, $[\text{MCl}_3(\eta\text{-C}_5\text{H}_5)\{\kappa^2\text{-S}, \text{S}'\text{-HCIB}(\text{mt})_2\}]$.

The hard and soft acid and base (HSAB) description of metal–ligand interactions provides a useful conceptual framework. However, it can also discourage the exploration of areas of chemistry that might be expected to involve an HSAB mismatch of ligand donors and metals. It might thus be argued that the comparative under-development of the chemistry of early transition metals ligated by sulfur donors is due in part to preconceived perceptions of lability and instability. A second contributing factor however, is perhaps the somewhat limited range of sulfur-based ligands for which the lability can be curtailed through chelation. One such group of ligands which might show promise in this respect are the poly(methimazoly)borates (Fig. 1). The anionic ligands $\text{H}_x\text{B}(\text{mt})_{4-x}$ introduced by the groups of Reglinski ($x = 1$)¹ and Parkin ($x = 2$)² present either three or two soft sulfur donors, the superlative basicity of which has been quantified through IR spectroscopy.^{3,4} The π -basicity of these ligands is potentially a useful feature for coordination to early transition metals with low d-occupancies. Further intrigue is offered by the possibility of 3-centre, 2-electron B–H–metal interactions ($\kappa^3\text{-H}, \text{S}, \text{S}'$) for both $\text{H}_2\text{B}(\text{mt})_2$ ⁵ and more surprisingly $\text{HB}(\text{mt})_3$ chelates.⁶ Such interactions have been implicated for the B–H activation of the $\text{HB}(\text{mt})_3$ ligand in complexes of ruthenium, osmium, rhodium and platinum leading to metallaboratranes (Fig. 1(c)).^{6,7} A simplistic bonding description for such cage structures^{7c} would suggest that the key feature, a metal–boron dative bond, will not arise for octahedral metal centres with configurations less than d^8 . We have

therefore begun a general investigation of the coordination and organometallic chemistry of these ligands, based on the early transition metals with lower d-occupancies. In this paper we report the first examples of poly(methimazoly)borate ligands coordinated to group 5 metals.

Our treatment of either $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$ or $\text{Na}[\text{HB}(\text{mt})_3]$ with the halides M_2Cl_{10} ($\text{M} = \text{Nb}, \text{Ta}$) has so far led to intractable mixtures of as yet unidentified products. We presume that the complexity of these reactions might be traced to either redox and/or ligand cleavage reactions (Hmt is observed in the product mixture) due to the highly electrophilic nature of the M^{V} centres. Working on this assumption and being aware that similar complications had been noted for the synthesis of poly(pyrazoly)borate complexes of niobium and tantalum⁸ we turned our attention to the potential use of organotin derivatives as $\text{H}_x\text{B}(\text{mt})_{4-x}$ transfer agents. Organotin pyrazolyborates have found success in this respect⁹ and a small number of organotin derivatives of the $\text{HB}(\text{mt})_3$ ligand have been reported.¹⁰ For our studies we prepared the compound $\text{Ph}_3\text{Sn}\{\text{HB}(\text{mt})_3\}$ (**1**) via the reaction of $\text{Na}[\text{HB}(\text{mt})_3]$ with chlorotriphenylstannane (Scheme 1). Compound **1** has been recently reported and characterised on the basis of spectroscopic data,^{10†} to which we now contribute structural data.‡ The results of this study are summarised in Fig. 2 and demonstrate that the $\text{HB}(\text{mt})_3$ ligand adopts a monodentate coordination to four-coordinate tin. This mode of coordination leaves two potential donor sites pendant, a feature we suspected might offer kinetic advantages in any transfer processes.

Unfortunately, the reactions of **1** with M_2Cl_{10} also proved to be complex and have not yet yielded simple metathesis derivatives. Accordingly, the less electrophilic complexes $[\text{MCl}_4(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Nb}, \text{Ta}$) were investigated. Treating a solution of $[\text{TaCl}_4(\eta\text{-C}_5\text{H}_5)]$ in tetrahydrofuran with one equivalent of **1** led to the formation and isolation of an orange compound appearing to contain both the borate and cyclopentadienyl ligands. However, spectroscopic and analytical data† were not consistent with the anticipated product $[\text{TaCl}_3(\eta\text{-C}_5\text{H}_5)\{\text{HB}(\text{mt})_3\}]$. Most notably,

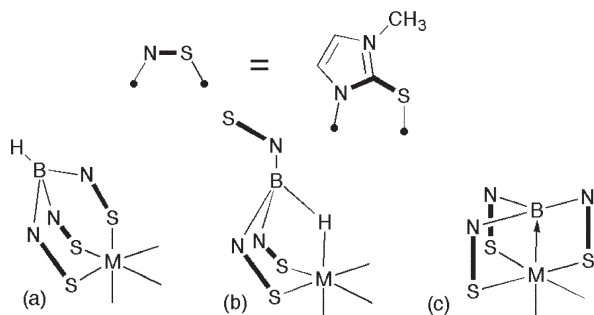
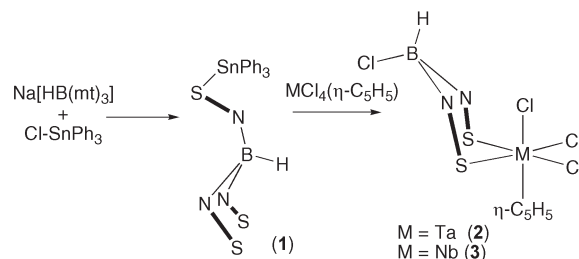


Fig. 1 Tris(methimazoly)borate and metallaboratrane coordination: (a) $\kappa^3\text{-S}, \text{S}', \text{S}''$; (b) $\kappa^3\text{-H}, \text{S}, \text{S}'$; (c) $\kappa^4\text{-B}, \text{S}, \text{S}', \text{S}''$.



Scheme 1 Synthesis of 1–3.

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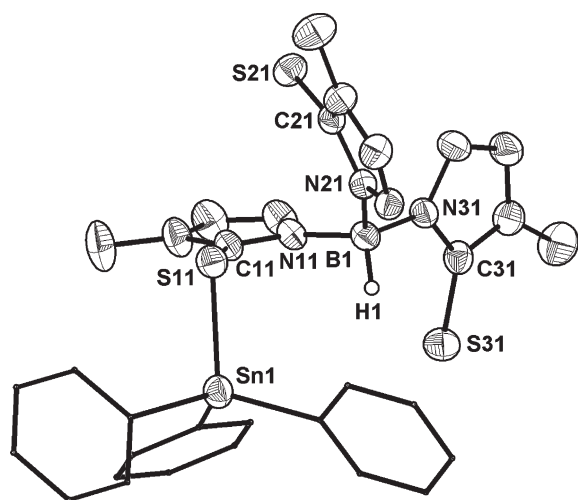


Fig. 2 Molecular structure of **1**; hydrogen atoms attached to carbon omitted and phenyl groups simplified, 50% displacement ellipsoids. Selected bond lengths (Å) and angles (°): Sn1–S11 2.457(1), S11–C11 1.740(3), S21–C21 1.690(3), S31–C31 1.690(3); Sn1–S11–C11 99.8(1).

there was no signature for the B–H functional group in either infrared or NMR spectra. In a similar manner, the corresponding niobium complex was obtained and showed comparable spectroscopic data.† The formulation of the complexes was eventually established on the basis of crystallographic studies of both the niobium and tantalum examples.‡ Fig. 3 depicts the molecular geometry of the niobium complex whilst an alternative view of the similar but not isomorphous tantalum complex is depicted in Fig. 4. Both crystal structures reveal that the complexes are in fact $[\text{MCl}_3(\eta\text{-C}_5\text{H}_5)\{\text{HCIB}(\text{mt})_2\}]$ ($\text{M} = \text{Nb}$ **2**, Ta **3**) which bear the novel chlorobis(methimazolyl)borate ligand in a bidentate $\kappa^2\text{-S,S}'$ mode. The possibility of either a B–H–M or B–Cl–M interaction

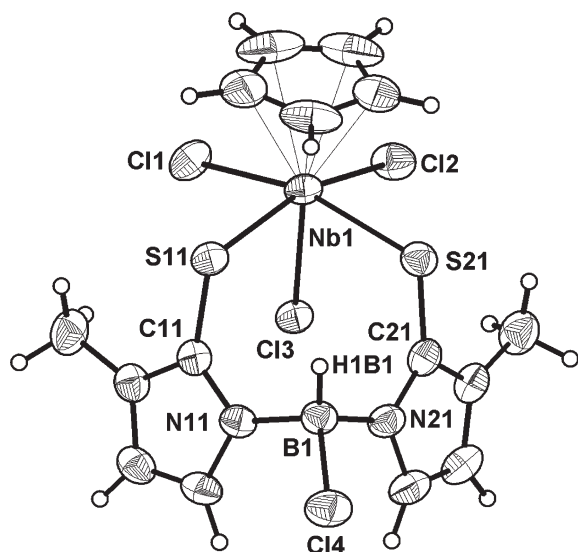


Fig. 3 Molecular structure of **2**; 50% displacement ellipsoids. Selected bond lengths (Å) and angles (°): Nb1–S11 2.5137(13), Nb–S21 2.5537(10), Nb–Cl1 2.4881(9), Nb–Cl2 2.4485(11), Nb–Cl3 2.4430(8), B1–Cl4 1.869(4); S11–Nb1–S21 88.09(3), Cl1–Nb–Cl2 87.59(4), Cl1–Nb1–S11 90.33(4), Cl2–Nb–S21 88.71(3).

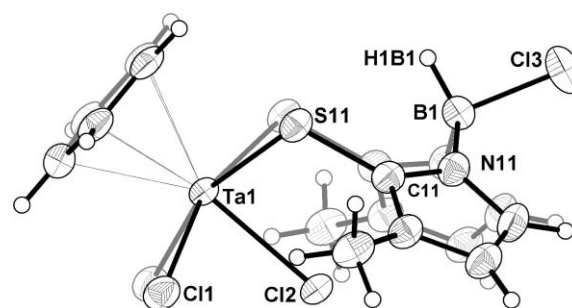


Fig. 4 Molecular geometry of **3**; 50% displacement ellipsoids; symmetry generated atoms in grey. Selected bond lengths (Å) and angles (°): Ta1–S11 2.5477(13), Ta–Cl1 2.4469(11), Ta–Cl2 2.4472(16), B1–Cl3 1.862(7); S1–Ta1–S1' 88.29(6), Cl1–Ta–Cl1' 87.19(6), Cl1–Ta1–S11 89.63(5), Cl2–Ta–S11 83.22(3), Cl1–Ta1–Cl2 79.35(4).

to allow the metals to attain 18-electron configurations is presumably sterically precluded.

The formation of compounds **2** and **3** involve cleavage of one methimazolyl group from the $\text{HB}(\text{mt})_3$ ligand and transfer of chloride from tantalum or niobium to boron with the presumed elimination of $\text{Ph}_3\text{Sn}(\text{mt})$. Two mechanistic possibilities suggest themselves: Were the initial target complexes $[\text{MCl}_3(\eta\text{-C}_5\text{H}_5)\{\kappa^2\text{-HB}(\text{mt})_3\}]$ formed, one might envisage a subsequent reaction with ClSnPh_3 to abstract a pendant 'mt' group from boron. Alternatively, and we suspect more probably, elimination of $\text{Ph}_3\text{Sn}(\text{mt})$ might occur directly from an intermediate mono- or bidentate adduct of $\text{Ph}_3\text{Sn}\{\text{HB}(\text{mt})_3\}$ to generate a complex of the borane $\text{HB}(\text{mt})_2$ which abstracts a halide from the metal centre. The ultimate position of the chloride exo to the metal whereby steric effects are minimised may be arrived at *via* dissociation/recoordination of the labile mt group. We have recently obtained an iridium complex of the $\text{HB}(\text{mt})_2$ borane supporting its intermediacy.¹¹

Whilst we have not yet been successful in deploying the organotin compound **1** as a simple $\text{HB}(\text{mt})_3$ transfer reagent for group 5 metals, the isolation of the complexes **2** and **3** has resulted in the identification of the novel chlorobis(methimazolyl)borate chelate.

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Notes and references

† *Characterisation data:* for **2**: Yield 11%. ^1H NMR (CD_2Cl_2 , 25 °C, 300 MHz): δ_{H} 3.69 (s, 3 H, NCH_3), 4.04 (s, 6 H, NMe), 6.72 (s, 5 H, C_5H_5), 7.47, 7.26 (d \times 2, 1 H \times 2, $\text{NCH}=\text{CH}$). For **3**: Yield 13%. ^1H NMR (CD_2Cl_2 , 25 °C, 300 MHz): δ_{H} 4.07 (s, 6 H, NMe), 6.71 (s, 5 H, C_5H_5), 7.19, 7.49 (d \times 2, 1 H \times 2, $\text{NCH}=\text{CH}$).

‡ *Crystal data:* for **1**: $\text{C}_{30}\text{H}_{31}\text{BN}_6\text{Sn}\cdot\text{CH}_2\text{Cl}_2$, $M = 786.21$, triclinic, $P\bar{1}$, $a = 9.180(2)$, $b = 10.140(2)$, $c = 21.540(4)$ Å, $\alpha = 96.09(3)$, $\beta = 98.22(3)$, $\gamma = 114.39(3)^\circ$, $V = 1776.8(6)$, Å³, $Z = 2$, $D_c = 1.47$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.08$ mm⁻¹, $T = 200(2)$ K, colourless prism; 8125 independent measured reflections, F^2 refinement, $R_1 = 0.038$, $wR_2 = 0.098$, 6587 independent observed absorption-corrected reflections [$|F_o| > 2\sigma(F_o)$], $2\theta_{\text{max}} = 55^\circ$, 400 parameters. CCDC 243423. For **2**: $0.5\text{C}_6\text{H}_{12}\cdot\text{C}_{13}\text{H}_{16}\text{BCl}_4\text{N}_4\text{NbS}_2\cdot 0.5\text{C}_6\text{H}_{12}$, $M = 580.01$, monoclinic, $C2/c$, $a = 25.983(5)$, $b = 10.429(5)$, $c = 16.715(5)$ Å, $\beta = 109.247(5)^\circ$, $V = 4276(3)$, Å³, $Z = 4$, $D_c = 1.802$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.27$ mm⁻¹,

$T = 200(2)$ K, red prism; 4905 independent measured reflections, F^2 refinement, $R_1 = 0.038$, $wR_2 = 0.096$, 4095 independent observed absorption-corrected reflections [$|F_o| > 2\sigma(|F_o|)$, $2\theta_{\max} = 55^\circ$], 259 parameters. CCDC 252476. For **3**: $C_{13}H_{16}BCl_4N_4S_2Ta$, $M = 312.99$, orthorhombic, $Pnma$, $a = 11.343(5)$, $b = 12.087(5)$, $c = 13.837(5)$ Å, $V = 1897.1(13)$, Å³, $Z = 8$, $D_c = 2.192$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 6.58$ mm⁻¹, $T = 200(2)$ K, orange prism; 2270 independent measured reflections, F^2 refinement, $R_1 = 0.032$, $wR_2 = 0.078$, 2055 independent observed absorption-corrected reflections [$|F_o| > 2\sigma(|F_o|)$, $2\theta_{\max} = 55^\circ$], 125 parameters. CCDC 252477. See <http://www.rsc.org/suppdata/cc/b4/b415852k/> for crystallographic data in .cif or other electronic format.

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