

# Dihydrobis(methimazolyl)borate and methimazolyl complexes of titanium

Anthony F. Hill\* and Matthew K. Smith

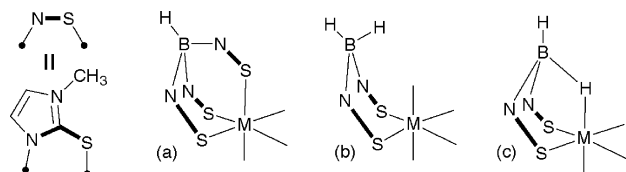
Received 19th September 2005, Accepted 6th October 2005

First published as an Advance Article on the web 27th October 2005

DOI: 10.1039/b513251g

The first poly(methimazolyl)borato complex of group 4,  $[\text{Ti}(\text{=NCMe}_3)\{\text{H}_2\text{B}(\text{mt})_2\}_2]$  ( $\text{mt}$  = methimazolyl), results from the reaction of  $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$  with  $[\text{Ti}(\text{=NCMe}_3)\text{Cl}_2(\text{py})_3]$  and features both  $\kappa^2\text{-S,S'}$  and  $\kappa^3\text{-H,S,S'}$  coordination of  $\text{H}_2\text{B}(\text{mt})_2$  ligands coincident within the same molecule.

The poly(methimazolyl)borate ligands  $\text{H}_n\text{B}(\text{mt})_{4-n}$  ( $\text{mt}$  = methimazolyl, Scheme 1) present themselves as 'soft' analogues of the more familiar poly(pyrazolyl)borates. Reglinski's  $\text{HB}(\text{mt})_3$  ligand<sup>1</sup> in general functions as a simple tridentate  $\kappa^3\text{-S,S',S''}$  facially coordinating ligand. Examples of  $\kappa^3\text{-H,S,S'}$  coordination have also been encountered involving three-centre–two-electron ( $3c\text{-}2e$ )  $\text{B-H-M}$  interactions<sup>2</sup> and these are implicated in the formation of metallaboratranes.<sup>2,3</sup>

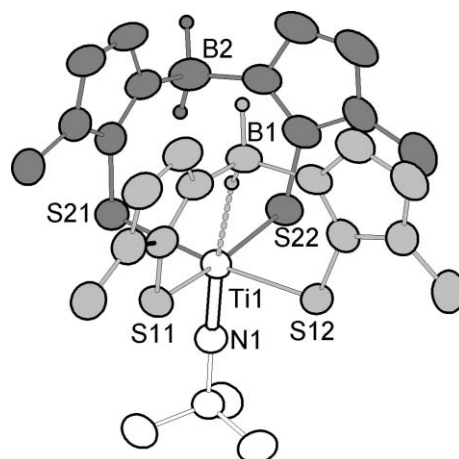


**Scheme 1** Poly(methimazolyl)borate coordination: (a)  $\kappa^3\text{-S,S',S''}$ ; (b)  $\kappa^2\text{-S,S'}$ ; (c)  $\kappa^3\text{-H,S,S'}$ .

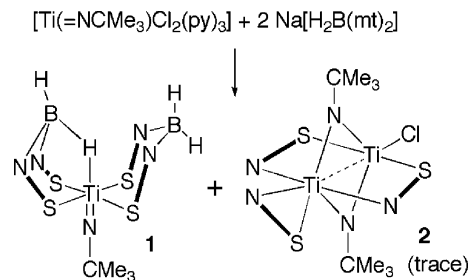
This type of coordination has also been observed for Parkin's bis(methimazolyl)borate ligand<sup>4</sup>  $\text{H}_2\text{B}(\text{mt})_2$ , when coordinated to molybdenum,<sup>5</sup> rhenium<sup>6</sup> and platinum<sup>7</sup> centres. The affinity of these ligands for soft late transition metals in low oxidation states is to be expected from simple hard and soft acid and bases (HSAB) considerations. We have therefore turned our attention to seemingly less appropriate metals on the assumption that the ambivalence of hard metals towards sulfur donors might be overcome at least in part through the entropic advantages offered by methimazolylborate chelation. A further point is that of the wide class of facially tridentate ligands,  $\text{H}_n\text{B}(\text{mt})_{4-n}$  have been shown to be exceptionally  $\pi$ -basic.<sup>8</sup> This feature might be traced to a strong  $\pi$ -donor role for sulfur in which case coordination to high oxidation state metal centres might actually be favourable. Herein we report the first reactions of  $\text{H}_n\text{B}(\text{mt})_{4-n}$  salts with high oxidation state titanium complexes.

Our initial investigations of the reactions of  $\text{TiCl}_4$  or  $[\text{TiCl}_4(\text{thf})_2]$  with  $\text{Na}[\text{HB}(\text{mt})_3]$  or  $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$  were spectacularly unsuccessful, providing intractable mixtures of unidentified compounds, none of which appeared to be the desired simple complexes  $[\text{TiCl}_x\{\text{H}_n\text{B}(\text{mt})_{4-n}\}_{4-x}]$ . Although our attempts were not exhaustive, we are inclined to suspect that both redox processes and ligand

cleavage reactions interfere with the simple halide metathesis. These problems might be traced to the potent Lewis acidity of the  $\text{Ti}^{\text{IV}}$  reagents. We have recently found that similar synthetic hurdles in the chemistry of niobium(v) and tantalum(v) may be overcome by the inclusion of a  $\pi$ -basic imido co-ligand to reduce the electrophilicity of the metal centre thereby allowing the isolation of the complexes  $[\text{M}(\text{=NC}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{Cl}_2\{\text{HB}(\text{mt})_3\}]$ .<sup>9</sup> We now find that a similar approach meets with success in the chemistry of  $\text{Ti}^{\text{IV}}$ : treating Mountford's versatile imido complex  $[\text{Ti}(\text{=NCMe}_3)\text{Cl}_2(\text{py})_3]$ <sup>10</sup> with two equivalents of  $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$  results in the formation of the complex  $[\text{Ti}(\text{=NCMe}_3)\{\text{H}_2\text{B}(\text{mt})_2\}_2]$  (**1**; Fig. 1, Scheme 2).<sup>†</sup> The putative intermediate  $[\text{Ti}(\text{=NCMe}_3)\text{Cl}(\text{py})\{\text{H}_2\text{B}(\text{mt})_2\}]$  is not observed even when a deficiency of  $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$  is employed, suggesting it reacts more rapidly with  $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$  than does the precursor.



**Fig. 1** Molecular structure of **1** (40% displacement ellipsoids; methimazolyl hydrogen atoms omitted;  $\kappa^2\text{-S,S'}$ - $\text{H}_2\text{B}(\text{mt})_2$  in dark gray;  $\kappa^3\text{-H,S,S'}$ - $\text{H}_2\text{B}(\text{mt})_2$  in light grey). Selected bond lengths (Å) and angles (°):  $\text{Ti1-N1}$  1.696(6),  $\text{Ti1-S12}$  2.509(2),  $\text{Ti1-S11}$  2.514(2),  $\text{Ti1-S22}$  2.515(2),  $\text{Ti1-S21}$  2.516(2),  $\text{B1H-Ti}$  2.09(3),  $\text{B(1)-Ti}$  3.124(8);  $\text{N1-Ti1-S12}$  91.4(2),  $\text{N1-Ti1-S11}$  93.9(2),  $\text{S12-Ti1-S11}$  84.57(8),  $\text{N1-Ti1-S22}$  96.5(2),  $\text{N1-Ti1-S21}$  98.7(2),  $\text{S22-Ti1-S21}$  92.64(8),  $\text{C1-N1-Ti1}$  175.9(5).

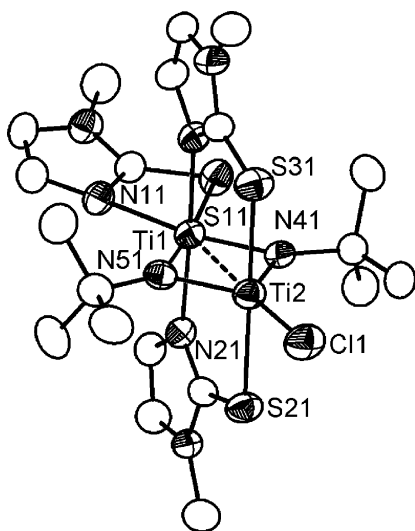


**Scheme 2** Synthesis of **1** and **2**.

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, A.C.T., Australia. E-mail: a.hill@anu.edu.au; Fax: (+61) 2 6125 3216; Tel: (+61) 2 6125 8577

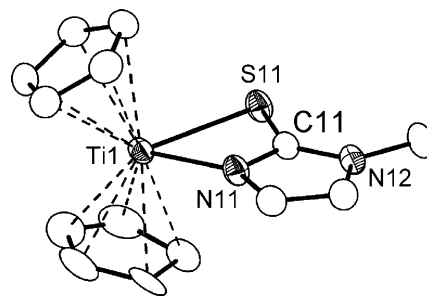
The molecular geometry of **1** is depicted in Fig. 1 and whilst the low precision of the structural model† precludes detailed discussion, the overall topology reveals an interesting bonding scenario: The two  $\text{H}_2\text{B}(\text{mt})_2$  ligands adopt different modes of coordination within the same molecule to provide a collar of sulfur  $\pi$ -donors, with the imido ligand on one side, *trans* to one  $3c-2e$  B–H–Ti interaction. In principle the electron deficient  $d^0\text{-Ti}^{\text{IV}}$  centre might be expected to accommodate two such B–H–Ti interactions, however any tendency for this is presumably outweighed by the heavy  $\pi$ -loading and issues of attendant steric factors and ring strain. Furthermore, the  $\kappa^3\text{-H}_2\text{B}(\text{mt})_2$  ligand (light grey) fits snugly into a cleft provided by the alternate  $\kappa^2\text{-H}_2\text{B}(\text{mt})_2$  ligand (dark grey).

A second trace product, **2**, was isolated from the reaction, and whilst this was only obtained in sufficient quantities for crystallographic identification,† the molecular geometry is presented in Fig. 2 as it illustrates some features of note. The compound is the binuclear bis(imido) complex  $[\text{Ti}_2(\mu\text{-NCMe}_3)_2(\mu\text{-mt})_2(\kappa^2\text{-mt})\text{Cl}]$  (**2**) which apparently arises from the degradation of the  $\text{H}_2\text{B}(\text{mt})_2$  pro-ligand salt. The  $\text{Ti}_2(\text{NCMe}_3)_2$  core is a comparatively recurrent feature of the chemistry of Mountford's complex,<sup>11</sup> and whilst no examples have involved sulfur based ligands, the topology is somewhat reminiscent of Cotton's formamidinate derivative  $[\text{Ti}_2(\mu\text{-NPh})_2(\mu\text{-PhNCHNPh})_2(\kappa^2\text{-PhNCHNCPh})_2]$ .<sup>12</sup> The bridging mode of mt coordination in which the Ti–Ti vector is effectively coplanar with the mt heterocycles is unprecedented and presumably reflects the ( $\sigma + \pi$ ) donor role for this heterocycle bound to  $d^0\text{-Ti}^{\text{IV}}$ . The Ti1–Ti2 separation (2.7335(16) Å) is remarkably short for a  $\text{Ti}^{\text{IV}}\text{-Ti}^{\text{IV}}$  'non-bond' with only the oxo-bridged complexes  $[\text{Ti}_2(\mu\text{-O})_2\text{Cl}_2\{\text{C}_5\text{H}_2(\text{SiMe}_3)_2\}_2]$  (2.707 Å)<sup>13</sup> and  $[\text{Ti}_2(\mu\text{-O})_2(\mu\text{-H}_2\text{CC}_5\text{Me}_4)(\text{C}_5\text{Me}_3)_2]$  (2.725 Å)<sup>14</sup> having shorter associations.



**Fig. 2** Molecular structure of **2** (40% displacement ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ti1–N51 1.895(4), Ti1–N41 1.897(4), Ti1–N21 2.153(4), Ti1–N11 2.181(4), Ti1–S11 2.6141(18), Ti1–C11 2.710(5), Ti1–Ti2 2.7335(16), C11–Ti2 2.3409(17), Ti2–N 51 1.869(4), Ti2–N41 1.877(4), Ti2–S31 2.4704(16), Ti2–S21 2.4738(16); N51–Ti1–N41 86.36(16), N51–Ti1–N21 87.35(15), N41–Ti1–N21 90.63(15), N51–Ti2–N41 87.68(16), N51–Ti2–C11 138.22(13), N41–Ti2–C11 134.07(13), N51–Ti2–S31 90.09(11), N41–Ti2–S31 92.13(11).

Given the absence of the methimazolyl ligand from early transition metal chemistry, other than **2**, we have investigated the reaction of Hmt with  $[\text{Ti}^{\text{IV}}\text{Bu}_2(\eta\text{-C}_5\text{H}_5)_2]$ .<sup>15</sup> Rather than the anticipated  $\text{Ti}^{\text{IV}}$  complexes  $[\text{TiH}(\text{mt})(\eta\text{-C}_5\text{H}_5)_2]$  or  $[\text{Ti}(\text{mt})_2(\eta\text{-C}_5\text{H}_5)_2]$ , we find that *inter alia* the major product is the blue  $\text{Ti}^{\text{III}}$  methimazolyl complex  $[\text{Ti}(\kappa^2\text{-mt})(\eta\text{-C}_5\text{H}_5)_2]$  (**3**; Fig. 3)† in which the methimazolyl ligand adopts a bidentate coordination mode through both nitrogen and sulfur. Structural data are not available for mt complexes of early transition metals, however relative to the more familiar pyridinethiolato ligand bound to titanium,<sup>16</sup> the methimazolyl chelate bite angle in **3** is some  $10^\circ$  wider, with longer Ti–S and comparable Ti–N bond lengths. Relative to **2**, the chelated mt in **3** has shorter Ti–N and longer Ti–S bond lengths subtending an increased N–Ti–S bite angle.



**Fig. 3** Molecular structure of **3** (40% displacement ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ti1–N11 2.226(2), Ti1–S11 2.499(2), S11–C11 1.809(2), N11–C11 1.272(2); C11–S11–Ti1 75.64(7), C11–N11–Ti1 97.13(13).

## Notes and references

† **1**:  $^1\text{H}$  NMR data for **1**: ( $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ):  $\delta_{\text{H}}$  0.99 (s, 9 H,  $\text{CCH}_3$ ), 3.32, 3.33 (s  $\times$  2, 6 H  $\times$  2,  $\text{NCH}_3$ ), 6.67, 6.68, 6.97, 6.98 (d  $\times$  4, 2 H  $\times$  4,  $\text{NCH}=\text{CH}$ ,  $J_{\text{HH}} = 1.8$  Hz). Crystal data for  $\text{C}_{20}\text{H}_{33}\text{N}_8\text{S}_4\text{Ti}$  **1**,  $M_r = 597.31$ , monoclinic, space group  $P2_1/c$ ,  $a = 16.540(3)$ ,  $b = 9.2900(19)$ ,  $c = 18.924(4)$  Å,  $\beta = 94.27(3)^\circ$ ,  $V = 2899.7(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 200(2)$  K, yellow prism,  $D_c = 1.368$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.611$  mm<sup>-1</sup>, 6611 independent reflections,  $F$  refinement,  $R = 0.107$ ,  $wR = 0.248$  for 4009 independent absorption corrected reflections [ $I > 2\sigma(I)$ ,  $2\theta \leq 55^\circ$ ], 346 parameters. CCDC reference number 283377. Crystal data for  $\text{C}_{20}\text{H}_{33}\text{N}_8\text{S}_4\text{Ti}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$  **2**,  $M_r = 655.44$ , tetragonal, space group  $P4_32_1$ ,  $a = 12.981(5)$ ,  $b = 12.981(5)$ ,  $c = 36.183(5)$  Å,  $V = 6097(3)$  Å<sup>3</sup>,  $Z = 8$ , red hexagon,  $D_c = 1.428$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.930$  mm<sup>-1</sup>,  $T = 200(2)$  K, 3097 independent reflections,  $F$  refinement,  $R = 0.0315$ ,  $wR = 0.0772$  for 2756 independent absorption corrected reflections [ $I > 2\sigma(I)$ ,  $2\theta = 41.2^\circ$ ], 331 parameters, CCDC reference number 283376. Crystal data for  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{STi}$  **3**:  $M_r = 291.24$ , monoclinic, space group  $P2_1/a$ ,  $a = 13.730(3)$ ,  $b = 7.9000(16)$ ,  $c = 12.780(3)$  Å,  $\beta = 103.24(3)^\circ$ ,  $V = 1349.4(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 200(2)$  K, blue prism,  $D_c = 1.434$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.771$  mm<sup>-1</sup>, 3749 independent reflections.  $F$  refinement,  $R = 0.0459$ ,  $wR = 0.114$  for 2837 independent absorption corrected reflections [ $I > 2\sigma(I)$ ,  $2\theta \leq 55^\circ$ ], 184 parameters CCDC reference number 283378. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513251g

- M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer and A. R. Kennedy, *Chem. Commun.*, 1996, 1975.
- M. R. St, J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Organometallics*, 2003, **22**, 4446.
- A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**, 2759; M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, *Organometallics*, 2004, **23**, 913; I. R. Crossley and A. F. Hill, *Organometallics*, 2004, **23**, 5656; I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2005, **24**, 1062; I. R. Crossley, M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2005, 221.

- 
- 4 C. Kimblin, T. Hascall and G. Parkin, *Inorg. Chem.*, 1997, **36**, 5680; C. Kimblin, B. M. Bridgewater, T. Hascall and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 2000, 891.
- 5 M. R. St.-J. Foreman, A. F. Hill, N. Tshabang, A. J. P. White and D. J. Williams, *Organometallics*, 2003, **22**, 5593; R. J. Abernethy, A. F. Hill, H. Neumann and A. C. Willis, *Inorg. Chim. Acta*, 2005, **358**, 1605; M. R. St.-J. Foreman, A. F. Hill, N. Tshabang and M. K. Smith, *Organometallics*, 2005, **24**, 5224.
- 6 R. Garcia, A. Domingos, A. Paulo, I. Santos and R. Alberto, *Inorg. Chem.*, 2002, **41**, 2422; R. Garcia, A. Paulo, A. Domingos and I. Santos, *J. Organomet. Chem.*, 2001, **632**, 41.
- 7 I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2005, **24**, 4889.
- 8 M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, *Organometallics*, 2003, **22**, 3831.
- 9 A. F. Hill and M. K. Smith, *Chem. Commun.*, 2005, 1920; A. F. Hill, A. D. Rae and M. K. Smith, *Inorg. Chem.*, 2005, **44**, 7316.
- 10 A. J. Blake, P. E. Collier, S. C. Dunn, W.-S. Li, P. Mountford and O. V. Shishkin, *J. Chem. Soc., Dalton Trans.*, 1997, 1549.
- 11 P. J. Stewart, A. J. Blake and P. Mountford, *Inorg. Chem.*, 1997, **36**, 3616; P. J. Stewart, A. J. Blake and P. Mountford, *J. Organomet. Chem.*, 1998, **564**, 209.
- 12 F. A. Cotton and W. A. Wojtczak, *Polyhedron*, 1994, **13**, 1337.
- 13 J. Okuda and E. Herdtweck, *Inorg. Chem.*, 1991, **30**, 1516.
- 14 F. Bottomley, I. J. B. Lin and P. S. White, *J. Am. Chem. Soc.*, 1981, **103**, 703.
- 15 A. F. Hill, H. D. Hönig and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 3031.
- 16 Y. Nakayama, K. Miyamoto, N. Ueyama and A. Nakamura, *Chem. Lett.*, 1991, 391.