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Niobium and Tantalum Tris(methimazolyl)borate Complexes $[M(=NC_6H_3{}^iPr_2\text{-}2,6)Cl_2\{HB(mt)_3\}]$ ($M = Nb, Ta$; mt = Methimazolyl)

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The first early transition metal tris(methimazolyl)borate complexes $[M(=NR)Cl_2\{HB(mt)_3\}]$ ($M = Nb, Ta$; $R = C_6H_3{}^iPr_2\text{-}2,6$; mt = methimazolyl) have been obtained from the reactions of $[Nb(=NR)Cl_3(DME)]$ or $[Ta(=NR)Cl_3(THF)_2]$ (DME = dimethyl ether; THF = tetrahydrofuran) with $Na[HB(mt)_3]$ and structurally characterized, illustrating that the $HB(mt)_3$ ligand can indeed be compatible with "hard" metals in high oxidation states.

The coordination chemistry of the bis- and tris(methimazolyl)borate ligands, $H_xB(mt)_{4-x}$ (mt = methimazolyl; $x = 2$,[1] 1[2]), has attracted increasing attention. Investigations have, however, been concerned primarily with the lighter (3d) transition metals of groups 9−12 in low oxidation states. One impetus for this focus has been the supposition that methimazolyl donors mimic in some respects the sulfur donors that support the active sites of metalloenzymes, a principle that has been extensively explored by the groups of Parkin,[1,3] Vahrenkamp,[4] and Rabinovich.[5] Our own work has, in contrast, been concerned with these ligands in an organometallic context,[6] including the facility with which they can lead to metallaboratranes via B−H activation processes.[7,8]

In the case of the $HB(mt)_3$ ligand, studies have also been motivated by a perceived analogy between this anionic, potentially multidentate sulfur-donor ligand (Figure 1a) and Trofimenko's more familiar tris(pyrazolyl)borate ligand (Figure 1b).[9] However, limitations to the analogy have begun to emerge: the "soft" sulfur donors and requisite larger chelate ring size afford notable differences in structural and chemical properties in comparison to poly(pyrazolyl)borates. The geometric strain attending tripodal coordination of the ligand (local C_3 $HB(mt)_3M$ symmetry compared to local C_{3v} $HB(pz)_3M$ symmetry) might be expected to confer increased lability on the complexes, and mt-dissociative fluxional processes have been documented.[6] In addition to these geometric considerations, the electronic nature of the sulfur (mt) vs nitrogen (pz) donors provides a second point of distinction, though investigations have focused on "soft" metals, for which this might be less apparent. The $HB(mt)_3$ ligand possesses ideal donor properties for late transition

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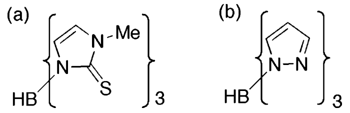

Figure 1. (a) Hydrotris(methimazolyl)borate and (b) hydrotris(pyrazolyl)borate ligands.

metals, according to “soft acid/soft base” compatibility. However, their use with “hard”, high-valent transition metals has not been investigated, possibly reflecting a perceived hard and soft acids and bases (HSAB) mismatch of donor/acceptor properties. Indeed, the chemistry of hard early transition metals, especially from group 5, ligated by soft sulfur donors has generally lagged behind the more mature chemistry of such metals with hard (O, N) donors, being limited in the main to thiolato, sulfido, and dithiocarbamato derivatives.[10] We reasoned that a situation might be contrived for early transition metals wherein chelated sulfur donors might offer the useful property of hemilability, more widely studied in the context of tethered hard donors in association with soft metals. Toward this end, we have investigated the synthesis of group 5 complexes of the $HB(mt)_3$ ligand with, until now, a notable lack of success: The reactions of MCl_5 (M $=$ Nb, Ta) with $Na[HB(mt)_3]$ provide intractable mixtures, while that of $Ph_3Sn(mt)_3BH$ with $[MCl_4(\eta\text{-}C_5H_5)]$ provided the novel chlorobis(methimazolyl)borate complexes $[MCl_3\{ClHB(mt)_2\}(\eta\text{-}C_5H_5)]$.[11] We attribute the problems encountered not to any inherent instability of early-transition-metal $HB(mt)_3$ complexes but rather to synthetic hurdles associated with the extreme electrophilicity and Lewis acidity of metal precursors that result in redox and $HB(mt)_3$ hydrolysis/cleavage processes. Toward this end, the imido complexes $[M({=}NR)Cl_3L_2]$ [R $=$ $C_6H_3{}^iPr_2$-2,6; ML_2 $=$ Nb(DME),[12] $Ta(THF)_2$ [13], where DME $=$ dimethyl ether and THF $=$ tetrahydrofuran], in which the d^0 metal is “π-loaded” and sterically shielded, present themselves as potential M^V substrates of reduced electrophilicity.

Treating solutions of $[Nb({=}NR)Cl_3(DME)]$[12] or $[Ta({=}NR)Cl_3(THF)_2]$[13] in THF with $Na[HB(mt)_3]$ at -78 °C results in the formation of the octahedral complexes $[M({=}NR)Cl_2\{HB(mt)_3\}]$ (M $=$ Nb (**1**),[14] Ta (**2**)[15]). The reactions may also be carried out at room temperature; however, this somewhat compromises the yields obtained. The formulations follow from a combination of spectroscopic and elemental microanalytical data and were confirmed by crystallographic studies of **1**$\cdot CH_2Cl_2$ and **2**$\cdot$THF.[16] The spectroscopic characterization of both **1** and **2** reveals a feature of note. The ^1H NMR spectrum displays three sets of resonances for the aromatic and NCH_3 groups of the methimazolyl heterocycles, indicating that all three are in different chemical environments. This can be attributed to the intrinsic chirality in the twisted bicyclo[3.3.3] C_3 $HB(mt)_3M$ cages, by analogy with the alkylidyne complexes $[W(\equiv CR)(CO)_2\{HB(mt)_3\}]$.[6] Thus, at ambient temperatures, the cages of **1** and **2** do not undergo racemization. Variable-temperature NMR studies reveal a modest broadening of these resonances (C_6D_6, 80 °C) but no coalescence behavior. Two processes have been discussed for $HB(mt)_3M$ racemization: untwisting through a strained local C_{3v} $HB(mt)_3M$ transition state or, alternatively, an mt-dissociative route via a stereochemically fluxional five-coordinate intermediate. In the case of $[W(\equiv CR)(CO)_2\{HB(mt)_3\}]$, the dependence upon the electronic rather than steric nature of R (C_6H_4Me-4 vs N^iPr_2) was taken as indicative of the latter process, a corollary of the superlative trans influence and trans effect of alkylidyne ligands. The trans influence of the imido ligands in **1** and **2** is equivocal (vide infra), and the electrophilicity of the M^V metal centers may well discourage mt dissociation.

The complexes **1** and **2** were structurally characterized, given that structural data for imido complexes of these metals with sulfur donors are currently limited to those for the

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(14) A solution of $[Nb(NC_6H_3{}^iPr_2\text{-}2,6)Cl_3(DME)]$ (0.20 g, 0.43 mmol) in THF (10 mL) was cooled (dry ice/propanone) and then treated with $Na[HB(mt)_3]$ (0.16 g, 0.43 mol). The mixture was stirred overnight to provide a pink suspension that turned orange when allowed to warm to room temperature. The white solid (NaCl) was removed from the orange solution by filtration, and the filtrate was concentrated under reduced pressure to 3 mL and diluted with hexane to provide a crude product that was recrystallized from a mixture of CH_2Cl_2 and hexane to provide red crystals. Yield: 0.16 g (56%). Data for **1**: ^1H NMR (C_6D_6, 25 °C) δ_H 7.14 (d, 2 H, $H^{3,5}(C_6H_3)$, $^3J_{HH} = 7.8$ Hz), 6.96 (t, 1 H, $H^4(C_6H_3)$, $^3J_{HH} = 7.8$ Hz), 6.46, 6.32, 6.31, 5.90, 5.84, 5.61 (d $\times$ 6, 1 H $\times$ 6, NCH$=$CHN, $^3J_{HH} = 2.1$ Hz), 5.16 (h, 2 H, C*H*Me), 3.36, 3.01, 2.78 (s $\times$ 3, 3 H $\times$ 3, NCH_3), 1.55, 1.42 (d $\times$ 2, 3 H $\times$ 2, CCH_3, $^3J_{HH} = 6.6$ Hz), 1.25 (d, 6 H, CCH_3, $^3J_{HH} = 6.6$ Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ_C 148.4 (N_2CS), 127.3, 125.9, 124.9, 124.3, 123.8, 121.9 ($=NC_6H_3$), 122.7 (2 C), 122.3 (1 C), 120.5, 120.4, 120.3 (NCH$=$CHN), 35.3, 34.8, 27.9 (NCH_3), 28.0, 26.3, 24.4 ($CHMe_2$). Anal. Calcd for $C_{24}H_{35}BCl_2N_7S_3Nb\cdot CH_2Cl_2$: C, 38.63; H, 4.80; N, 12.61 (CH_2Cl_2 confirmed by ^1H NMR integration and crystallography). Found: C, 38.32; H, 4.48; N, 11.95.

(15) A solution of $[Ta(NC_6H_3{}^iPr_2\text{-}2,6)Cl_3(THF)_2]$ (0.20 g, 0.35 mmol) in THF (10 mL) was cooled (dry ice/propanone) and then treated with $Na[HB(mt)_3]$ (0.126 g, 0.34 mol). The mixture was stirred overnight and then allowed to warm slowly to room temperature. The white solid (NaCl) was removed from the orange solution by filtration, and the filtrate was concentrated under reduced pressure to 3 mL and diluted with an equal amount of hexane. Cooling (-25 °C) provided orange crystals. Yield: 0.15 g (61%). Data for **2**: ^1H NMR (C_6H_6) δ_H 7.31 (d, 2 H, $H^{3,5}(C_6H_3)$, $^3J_{HH} = 7.8$ Hz), 6.90 (t, 1 H, $H^4(C_6H_3)$, $^3J_{HH} = 7.8$ Hz), 6.45, 6.34, 6.32 (d $\times$ 3, 1 H $\times$ 3, NCH$=$CH, $^3J_{HH} = 1.8$ Hz), 5.81 (s br, 2 H, NCH$=$CH, $^3J_{HH}$ not resolved), 5.59 (d, 1 H, NCH$=$CH, $^3J_{HH} = 1$ Hz), 5.12 (h, 2 H, CHMe, $^3J_{HH} = 6.9$ Hz), 3.34, 3.03, 2.84 (s $\times$ 3, 3 H $\times$ 3, NCH_3), 1.60, 1.49 (d $\times$ 2, 6 H $\times$ 2, CCH_3, $^3J_{HH} = 6.9$ Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ_C 148.3 (N_2CS), 124.7, 124.5, 124.0, 122.5, 121.8 ($=NC_6H_3$), 122.0 (3 C), 122.7 (2 C), 120.4 (NCH$=$CHN), 35.4 (NCH_3), 27.6, 26.5, 24.6 ($CHMe_2$). Anal. Calcd for $C_{24}H_{35}BCl_2N_7S_3Ta\cdot 1.5CH_2Cl_2$: C, 33.74; H, 4.22; N, 10.80 (CH_2Cl_2 confirmed by ^1H NMR integration). Found: C, 33.88; H, 4.01; N, 10.82.

(16) (a) Crystal data for **1**$\cdot CH_2Cl_2$: $C_{25}H_{35}BCl_4N_7NbS_3$, $M_w = 775.30$, triclinic, $P\bar{1}$ (No. 2), $a = 9.6970(19)$ Å, $b = 13.235(3)$ Å, $c = 14.971(3)$ Å, $\alpha = 93.74(3)°$, $\beta = 96.90(3)°$, $\gamma = 107.50(3)°$, $V = 1808.7(6)$ Å^3, $Z = 2$, $D_{calcd} = 1.424$ mg m^{-3}, μ(Mo Kα) $= 0.828$ mm^{-1}, $T = 200(2)$ K, 7791 independent reflections. F^2 refinement, $R = 0.045$, $wR = 0.0904$ for 7791 reflections [$I > 2\sigma(I)$, $2\theta_{max} = 54°$], 381 parameters, CCDC 268935. (b) Crystal data for **2**$\cdot$THF: $C_{28}H_{41}BCl_2N_7OTaS_3$, $M_w = 850.53$, orthorhombic, *Pnma*, $a = 18.799(4)$ Å, $b = 14.606(3)$ Å, $c = 12.791(3)$ Å, $V = 3512(1)$ Å^3, $Z = 4$, $D_x = 1.799$ mg m^{-3}, μ(Mo Kα) $= 1.089$ mm^{-1}, $T = 200(2)$ K, 5114 independent reflections. F^2 refinement, $R = 0.039$, $wR = 0.036$ for 5114 reflections [$I > 2\sigma(I)$, $2\theta_{max} = 50°$], 341 parameters. N.B.: Satisfactory refinement of the structural model was achieved with the application of nonstandard procedures and required the inclusion of constraints and restraints upon the geometry of the imido substituent and methimazolyl rings. Details of nonstandard refinement protocols are discussed in the CIF data provided in the Supporting Information (CCDC 272892).

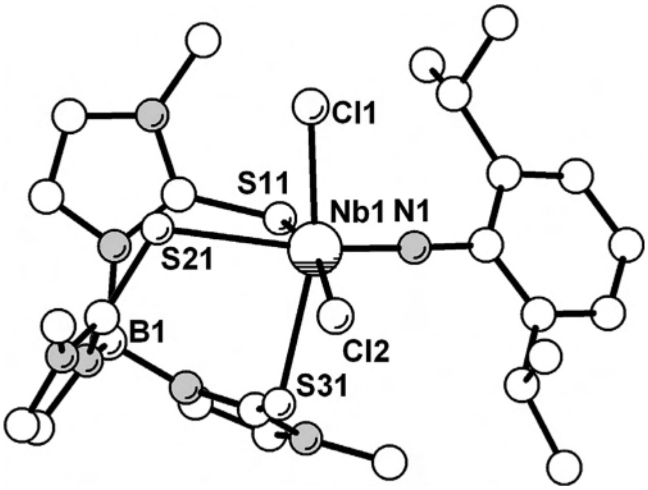

Figure 2. Molecular geometry of **1**. Selected bond lengths (Å) and angles (deg): Nb1−N1, 1.784(3); Nb1−Cl1, 2.4738(13); Nb1−Cl2, 2.5250(13); Nb1−S11, 2.5446(14); Nb1−S21, 2.7099(10); Nb1−S31, 2.6930(12); N1−Nb1−Cl1, 97.21(9); N1−Nb1−Cl2, 101.97(9); Cl1−Nb1−S11, 94.69(4); Cl2−Nb1−S31, 73.88(4); Cl1−Nb1−S21, 77.93(4); Cl2−Nb1−S21, 90.33(4).

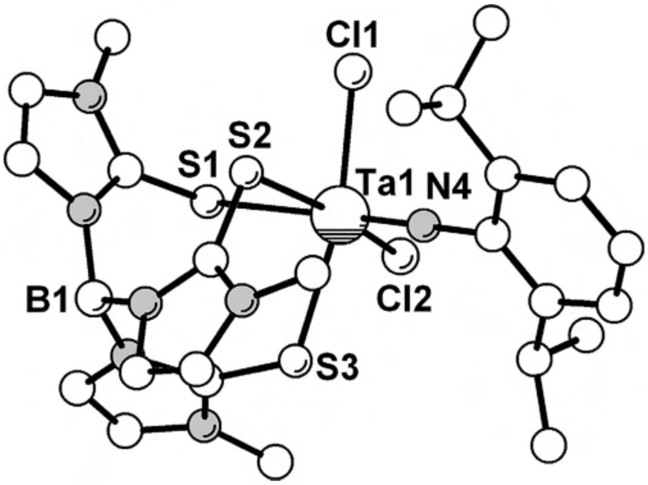

Figure 3. Molecular geometry of **2**. Selected bond lengths (Å) and angles (deg): Ta1−Cl1, 2.402(2); Ta1−Cl2, 2.402(2); Ta1−N4, 1.768(8); Ta1−S1, 2.725(3); Ta1−S2, 2.529(2); Ta1−S3, 2.529(2); Cl1−Ta1−N4, 98.0(3); Cl2−Ta1−N4, 101.1(3); Cl1−Ta1−S1, 83.1(1); Cl2−Ta1−S1, 80.6(1); Cl1−Ta1−S2, 85.6(2); Cl2−Ta1−S3, 88.3(2).

binuclear thioether adducts $[M_2({=}NPh)_2Cl_6(SMe_2)_2]$.[17,18] The results of crystallographic analyses of **1**·CH_2Cl_2 and **2**·THF are summarized in Figures 2 and 3, respectively. Superficially, the gross molecular geometries appear similar; however, closer inspection reveals subtle differences. Typical of octahedral imido complexes,[17] both show the metal displaced from the equatorial mean plane toward the imido nitrogen, with all N−M−Cl angles being obtuse in both structures. However, in the case of **1**, there is a deformation of one mt arm *toward* the imido [N1−Nb1−S11 = 81.89(9)° compared to N1−Nb1−S31 = 99.60(9)°]. In **2**, however, this disparity is absent, with both Ta−S vectors being essentially orthogonal to the imido ligand [N4−Ta1−S2 = 91.9(3)° and N4−Ta1−S3 = 92.8(3)°]. Inter-sulfur "bite" angles for **1** and **2** lie in the narrow range 86.0−90.3°, while in both structures, the inter-chloride angles are slightly obtuse [100.02(4) and 94.6(1)°, respectively]. The M−Cl and M═N bond lengths are unremarkable for these metals, and so interest is focused on the geometry of the HB(mt)$_3$ chelate. In the case of **2**, it could be argued that there is a clear imido trans influence such that the Ta−S1 bond is elongated (65σ) relative to the equatorial Ta1−S2 and Ta1−S3 bonds. However, for **1**, it is the equatorial Nb1−S11 bond length that is significantly shorter than either Nb1−S21 (138σ) or Nb−S31 (114σ). Such dramatic differences in analogous complexes suggest that M−S binding in HB(mt)$_3$M cages must be particularly flexible and that structural data should not be overinterpreted.

The isolation of the complexes **1** and **2** illustrates that there is nothing intrinsically unstable as far as complexes of the HB(mt)$_3$ ligand with hard, early-transition-metal centers in high formal oxidation states are concerned. Accordingly, we anticipate that their use should become far more widespread than might have been expected based solely on the HSAB perspective.

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Supporting Information Available: Full details of the crystal structure determination of **1**·CH_2Cl_2 (CCDC 268935) and **2**·THF (CCDC 272892) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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