Organometallic Tantalum Tris(methimazolyl)borato Complexes: [Ta(η^2-RC≡CR)Cl_2{HB(mt)$_3$}] (R = Ph, Et; mt = methimazolyl)

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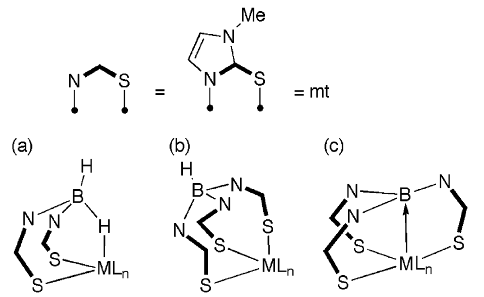
Summary: The reactions of Na[HB(mt)$_3$] (mt = methimazolyl) with [Ta(η^2-RC≡CR)Cl_3(dme)] (R = Ph, Et) provide the structurally characterized complexes [Ta(η^2-RC≡CR)Cl_2{HB(mt)$_3$}], the first examples of organometallic tris(methimazolyl)borato derivatives of group 5. The intrinsic chirality of the HB(mt)$_3$ ligand is expressed in a skewing of the alkyne orientation.

Introduction

The majority of studies involving the poly(methimazolyl)borates "$H_xB(mt)_{4-x}$" (mt = methimazolyl, Chart 1), discovered by Reglinski ($x = 1$)[1] and Parkin ($x = 2$),[2] fall into three strands of research: bioinorganic, organometallic, and metallaboratrane chemistry. By far the greatest attention has been directed toward possible relevance to the modeling of sulfur-ligated active sites in metalloenzymes.[1−5] A perceived analogy with Trofimenko's poly(pyrazolyl)borates[6] has led to their growing popularity as co-ligands in organotransition metal chemistry,[7−10] although one recurrent feature to emerge is their facile conversion to metallaboratranes (Chart 1c),[11−15] a possibility not (apparently) available to poly(pyrazolyl)borates. All these studies have in common that they are limited to late transition metals (groups

Chart 1. (a) Dihydrobis(methimazolyl)borato, (b) Hydrotris(methimazolyl)borato, and (c) Tris(methimazolyl)borane ("metallaboratrane") Complexes



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6−12) in low oxidation states (0−II), with the bioinorganic chemistry being naturally focused upon first-row metals. We have recently extended the coordination chemistry of poly(methimazolyl)borate ligands to the early transition metals titanium,[16] zirconium,[17] niobium,[18] and tantalum[18] in their highest oxidation states, i.e., situations where metallaboratrane formation is precluded by the zero d-occupancy. Furthermore, Parkin has recently reported the zirconium complex $[ZrCl_2(\eta\text{-}C_5H_5)\{HB(mt)_3\}]$ and demonstrated modest catalytic activity for ethene polymerization.[19] Thus it is beginning to emerge that these ligands may also be compatible with high oxidation state "hard" metal centers.

We have been eager to broaden the scope of organometallic poly(methimazolyl)borate chemistry, primarily with a view to understanding the factors that facilitate or deter metallaboratrane formation. The unique feature of metallaboratranes is a transannular metal−boron dative interaction within a methimazolyl-butressed cage. We have shown that this is readily achievable for metals from groups 8−10 with *formal* metal oxidation states of 0−II, valencies of 2−4, and d^8 or d^{10} electronic configurations.[20] While the $HB(mt)_3$ ligand would appear ideally suited to late low-valent transition metals on the basis of simple hard and soft acid and base (HSAB) arguments, it is less clear that it could serve as an effective ligand for early "harder" transition metal centers, in particular for situations where the metal is in a moderately high oxidation state. Herein we report the first hydrotris(methimazolyl)borato organotantalum complexes.

Results and Discussion

An early indication that problems might be encountered was provided by our unsuccessful attempts to introduce the $HB(mt)_3$ ligand into the coordination sphere of pentavalent niobium and tantalum. The reaction of $Na[HB(mt)_3]$ with M_2Cl_{10} (M = Nb, Ta) has so far provided only intractable mixtures, while that of $[MCl_4(\eta\text{-}C_5H_5)]$ with $[SnPh_3\{HB(mt)_3\}]$ resulted in fragmentation of the proligand (presumably to provide Ph_3Sn-mt) and formation of complexes of the novel chlorobis(methimazolyl)borato ligand, $[MCl_3(\eta\text{-}C_5H_5)\{ClHB(mt)_2\}]$ (M = Nb, Ta).[21] The same complexes were identified among the mixture obtained when $Na[HB(mt)_3]$ was employed. We attribute these outcomes to the high electrophilicity of the M^V centers in the chosen substrates that favors both redox processes and Lewis acid mediated ligand degradation. Accordingly, we have sought an alternative route to tantalum complexes of the $HB(mt)_3$ ligand based on precursors in which the metal has been reduced prior to $HB(mt)_3$ introduction, a strategy that has met with success.

Complexes of the form $[M(\eta\text{-}RC{\equiv}CR)Cl_3(ether)_2]$ (M = Nb, Ta) are readily available via the reduction of M_2Cl_{10} in ethereal solvent in the presence of a variety of alkynes,[22] and they have proven useful lead compounds in the development of poly(pyrazolyl)borate chemistry of formally trivalent[23] tantalum, primarily by the groups of Templeton and Etienne.[24] Given that simple dithiocarbamato derivatives of niobium(III) have also originated from these reagents,[24g] they appeared suitable substrates for the introduction of poly(methimazolyl)borato ligands. Superficially, poly(methimazolyl)borates might be viewed as hybrids of dithiocarbamates and poly(pyrazolyl)borates. Treating solutions of $[Ta(RC{\equiv}CR)Cl_3(dme)]$[22] in thf with $Na[HB(mt)_3]$ at −78 °C results in the formation of the chiral octahedral complexes $[Ta(\eta^2\text{-}RC{\equiv}CR)Cl_2\{HB(mt)_3\}]$ (R = Ph, **1**; Et, **2**). The formulations follow from a combination of spectroscopic and elemental microanalytical data. At ambient temperatures both **1** and **2** give rise to a single resonance for the alkyne carbon nuclei (δ_C = 240.6 (**1**), 246.2 (**2**) ppm; 75.4 MHz), indicating rapid alkyne rotation. Variable-temperature ^1H NMR studies on complex **1** indicate, however, that the chiral $HB(mt)_3Ta$ cage is rigid with three methimazolyl environments being observed, as noted previously for the alkylidyne complexes $[W({\equiv}CR)(CO)_2\{HB(mt)_3\}]$ (R = C_6H_4Me-4, N^iPr_2).[7a] In the case of these alkylidyne complexes, the temperature at which inversion of the cage is observed was found to be dependent on the nature of the alkylidyne substituent, an observation taken to suggest that fluxionality might occur via dissociation of one methimazolyl arm. In the case of the alkyne complexes however, simple coalescence of the methimazolyl signals was not observed. The associated signals begin to broaden at 60 °C; however by 80 °C there are signs of the onset of decomposition. The steric profile of the $HB(mt)_3$ ligand is less intrusive upon the inner coordination sphere than that of the more familiar $HB(pzMe_2)_3$ ligand, and the origins of alkyne rotation barriers in the complexes $[Nb(\eta\text{-}RC{\equiv}CR)Cl_2\{HB(pzMe_2)_3\}]$ have been attributed primarily to steric factors (vide infra).[24a] Thus for both **1** and **2**, we envisage a low-energy rotation barrier for alkyne rotation, while the barrier to cage inversion is sufficiently high such that decomposition competes.

The complexes **1** and **2** were structurally characterized,[26] and the results of crystallographic analyses of their dichloromethane solvates $\mathbf{1}\cdot(CH_2Cl_2)_3$ and $\mathbf{2}\cdot(CH_2Cl_2)_2$ are summarized in Figures 1 and 2, respectively, confirming in the solid state the composition and ground-state geometry. The structure of **2** was determined with a higher precision than that of **1** due primarily to poorly modeled lattice solvent in the former. The four-electron ($\sigma+\pi$ donor) nature of the alkyne coordination[25] is manifest in short Ta−C separations (**1**: 2.060(9), 2.117(9); **2**: 2.056(5), 2.084(5), Å) accompanied by somewhat long alkyne C≡C bond lengths. In each case the Ta−C bond distal to the $HB(mt)_3$ ligand is significantly shorter than that which is proximal to the scorpionate. These geometric parameters conform to the copious structural data available for mononuclear tantalum alkyne complexes.[26−33] Selected germane examples for which ^{13}C NMR

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[20] Although referred to on occasion, the formal oxidation states and d-configurations of metallaboratranes being open to debate are thus of questionable utility. We recommend use of the unambiguous $(M{\rightarrow}B)^n$ notation in which "n" refers to the *total* number of d electrons, including the electron pair associated with the metal−boron dative bond: Hill, A. F. *Organometallics* **2006**, *25*, 4741.

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[23] Inasmuch as oxidation states have any meaning in covalent organotransition metal chemistry, we shall consider the alkyne to act as a neutral ligand. This is an arbitrary choice in that the chemistry of alkynes bound to "trivalent" tantalum often involves behavior more suggestive of an alkene-1,2-diyl coordinated to pentavalent tantalum.

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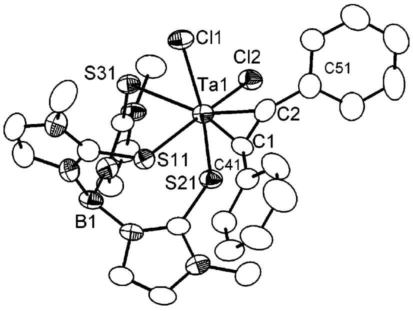

Figure 1. Molecular geometry of **1** in a crystal of **1**·$(CH_2Cl_2)_3$ (50% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted). Distances (Å) and angles (deg): Ta1−C2 2.060(9), Ta1−C1 2.117(9), Ta1−Cl1 2.400(2), Ta1−Cl2 2.445(2), Ta1−S11 2.464(2), Ta1−S21 2.533(2), Ta1−S31 2.736(2), C1−C2 1.304(13), C2−Ta1−C1 36.4(3), Cl1−Ta1−Cl2 95.00(8), Cl1−Ta1−S11 94.73(8), Cl1−Ta1−S21 159.51(8), Cl2−Ta1−S21 75.67(8), S11−Ta1−S21 90.62(7), Cl1−Ta1−S31 74.95(7), Cl2−Ta1−S31 84.30(7), S11−Ta1−S31 84.99(7), S21−Ta1−S31 85.87(7), C2−C1−C41 137.0(9), C2−C1−Ta1 69.4(5), C41−C1−Ta1 152.6(7), C1−C2−C51 140.0(9), C1−C2−Ta1 74.2(6), C51−C2−Ta1 145.7(7).

data are also available are collated in Table S1 (Supporting Information). The complexes are ordered first according to the number of valence electrons (*n*VE) provided by the metal and co-ligands and second according to the chemical shift, δ_C, of the alkyne carbon. This latter parameter is considered a reliable indicator of the “four-electron” nature of alkyne binding;[25] for example, the single two-electron alkyne example $[Ta(MeC\equiv CMe)\{C(=CH_2)CN\}(C_5H_5)_2]$[33] has these resonances shifted significantly upfield (mean value 134 ppm) from the 12VE examples (mean values 222−256 ppm). It should however be noted that this parameter appears far more responsive in some cases to the alkyne substituent than to variations in metal co-ligands. From the table it can be seen that of the complexes in which the alkyne is bound to a 12VE center, there is a remarkably narrow spread of *mean* Ta−C bond lengths (2.050−2.089 Å) that fall within the region typical of tantalum−carbon multiple bonding. The alkyne bond lengths in **1** (1.304(13) Å) and **2** (1.315(7) Å) also fall within the range for such complexes (1.30−1.34 Å), being significantly elongated relative to the free alkyne (1.211 Å for PhC≡CPh[34]).

In both **1** and **2** a substantial *trans* influence is exerted by the alkyne ligand such that the Ta−S bond *trans* to the alkyne is lengthened; however it is noteworthy that in both structures the Ta atom is displaced from the equatorial SSClCl donor plane toward the alkyne with all angles between *cis* ligands and either S31 (**1**) or S(11) (**2**) being acute.

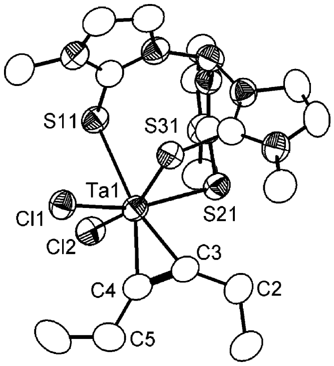

Figure 2. Molecular geometry of **2** in a crystal of **2**·$(CH_2Cl_2)_2$ (50% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted). Distances (Å) and angles (deg): Ta1−C4 2.056(5), Ta1−C3 2.084(5), Ta1−Cl2 2.4180(13), Ta1−Cl1 2.4234(12), Ta1−S21 2.4739(13), Ta1−S31 2.6071(13), Ta1−S11 2.7149(14) C2−C3 1.495(7), C3−C4 1.315(7), C4−C5 1.492(8), C4−Ta1−C3 37.05(19), Cl2−Ta1−Cl1 100.42(5), Cl2−Ta1−S21 93.62(4), Cl1−Ta1−S31 76.00(4), S21−Ta1−S31 86.71(4), Cl2−Ta1−S11 72.93(4), Cl1−Ta1−S11 85.04(4), S21−Ta1−S11 87.26(4), S31−Ta1 S11 88.45(4), C4−C3−C2 139.6(5), C4−C3−Ta1 70.3(3), C2−C3−Ta1 150.1(4), C3−C4−Ta1 72.6(3), C5−C4−Ta1 148.3(4).

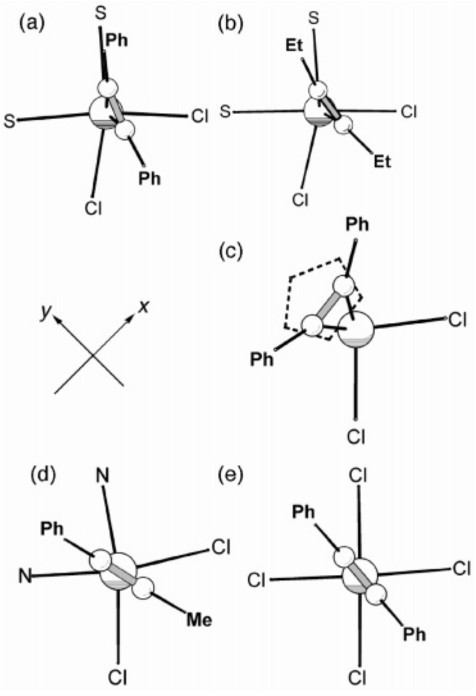

Figure 3. Alkyne orientations with respect to coordinate system from ref 24a, viewed along “*z*”: (a) **1**; (b) **2**; (c) $[Ta(PhC\equiv CPh)Cl_2(\eta\text{-}C_5Me_5)]$;[29] (d) $[TaCl_2(MeC\equiv CPh)Cl_2\{HB(pzMe_2\text{-}3,5)_3\}]$;[24f] (e) $[pyH][Ta(PhC\equiv CPhCl_4(py)]$.[35] (c−e) Coordinates from CCDC.[26]

For octahedral d^2-Ta^{III}Cl$_2$ alkyne complexes, the alkyne is generally found to align in such a way as to bisect the planes defined by the remaining five ligands.[22,24,29,35] Templeton and Etienne have interpreted this in terms of an MO scheme based on a coordinate system in which the “*z*” axis bisects the alkyne midpoint. This frame of reference presents a pair of metal fragment dπ orbitals (d_{xz}, d_{yz}) for interaction with the occupied π-dative and empty π-retrodative orbitals of the alkyne C≡C bond. This *combination* of metal dπ orbitals available for

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(26) Cambridge Crystallographic Data Centre, Conquest, Version 1.7, November 2006 release.

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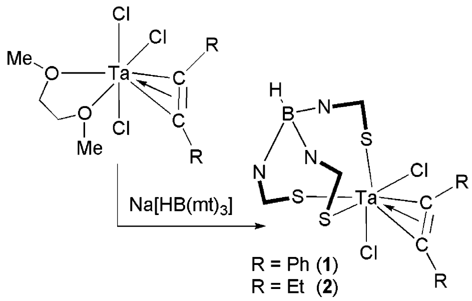
Scheme 1. Synthesis of Hydrotris(methimazolyl)borato Alkyne Complexes



interaction with the alkyne has essentially axial symmetry about z. Thus, the net π interactions are retained throughout alkyne rotation, thereby contributing little to the alkyne rotation barriers and ground-state geometric preferences, leading to the inference that rotation barriers derive primarily from steric effects.[24a] Such interligand steric effects are especially exaggerated in the case of the complex $[TaCl_2(\eta^2\text{-}MeC{\equiv}CPh)Cl_2\{HB(pzMe_2\text{-}3,5)_3\}]$[24f] because the pyrazolyl substituents crowd the coordination sphere. From Figure 3 it is apparent that the complexes **1** and **2** suffer considerable skewing of the alkyne relative to these more symmetrical examples. Two minor perturbations to Templeton and Etienne's scheme might be considered for the complexes **1** and **2**. First, the potent methimazolyl π donors[7a] will raise the energy of the d_{xz}/d_{yz} pair of orbitals, thereby enhancing retrodonation to the alkyne but at the expense of alkyne π donation. The second aspect concerns the intrinsic chirality of the $HB(mt)_3$ ligand, which provides an unsymmetric pocket for alkyne coordination (Figure S1, Supporting Information). Thus the distortions observed, manifest not only in skewing of the alkyne (most dramatically for **1**) but also in the disparate Ta−C bond lengths for the alkyne, are consistent with the minimization of interligand steric repulsion, with very little apparent cost in electronic terms.

Experimental Section

General Considerations. All manipulations were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line, and inert atmosphere drybox techniques, with dried and degassed solvents, which were distilled from either calcium hydride (CH_2Cl_2) or sodium-potassium alloy and benzophenone (ethers and paraffins). NMR spectra were obtained at 25 °C on a Varian Gemini 300BB spectrometer (^{1}H at 300 MHz, ^{13}C at 75.4 MHz). The elemental microanalysis was carried out by the microanalytical service of the Australian National University. The compounds $Na[HB(mt)_3]$,[11a] $[TaCl_3(\eta\text{-}PhC{\equiv}CPh)(dme)]$,[22] and $[TaCl_3(\eta\text{-}EtC{\equiv}CEt)(dme)]$[22] were prepared according to the indicated published procedures.

Synthesis of $[TaCl_2(\eta\text{-}PhC{\equiv}CPh)\{HB(mt)_3\}]$ (1). A suspension of $Na[HB(mt)_3]$ (0.56 g, 1.5 mmol)[11a] and $[Ta(\eta^2\text{-}PhC{\equiv}CPh)Cl_3(dme)]$ (0.85 g, 1.5 mmol)[22] in thf (25 mL) was stirred at −78 °C (dry ice/propanone bath) for 12 h and then allowed to warm to room temperature. The orange supernatant was separated from NaCl by cannula filtration, diluted with hexane (ca 10 mL), concentrated in vacuo to ca. 10 mL, and cooled (−20 °C) to provide a bright orange solid, which was recrystallized from CH_2Cl_2 (−20 °C) to provide a tris(CH_2Cl_2) solvate on the basis of X-ray crystallography, which however partially desolvates on prolonged standing. Elemental microanalytical data for a sample dried in vacuo correspond approximately to a 1:1 solvate. Yield: 0.77 g (67%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 2.88, 3.67, 3.96 (s × 3, 3H × 3, NCH_3), 3.62 (s, v br, 1H, BH), 6.66, 6.74, 6.83, 6.89, 6.93, 6.99 (d × 6, 1H × 6, NCH═CHN, $^3J_{HH}$ = 1.9 Hz), 7.26, 7.40, 7.71 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ 34.2, 34.8, 35.5 (NCH_3), 120.1, 120.4, 121.5, 122.6, 124.5 (NCH═CHN), 128.3, 129.8 [$C^{2,3,5,6}(C_6H_5)$], 128.6 [$C^4(C_6H_5)$], 144.36 [$C^1(C_6H_5)$] (weak quaternary CS resonances not unambiguously identified), 240.6 (C≡C). Anal. Found: C, 37.66; H, 3.47; N, 9.91. Calcd for $C_{26}H_{26}BCl_2N_6S_3Ta.CH_2Cl_2$: C, 37.43; H, 3.26; N, 9.70. Crystal data for **1**·$(CH_2Cl_2)_3$: $C_{26}H_{26}BCl_2N_6S_3Ta{\cdot}(CH_2Cl_2)_3$, M_w = 1018.42, monoclinic, $P2_1/c$, a = 9.4900(19) Å, b = 17.456(4) Å, c = 23.418(5) Å, β = 90.02(3)°, V = 3879.4(13) Å^3, Z = 4, D_{calcd} = 1.744 Mg m^{-3}, μ(Mo Kα) = 3.543 mm^{-1}, T = 200(2) K, 6828 independent reflections. F^2 refinement, R = 0.055, wR = 0.130 for 5327 reflections, [$I > 2\sigma(I)$, $2\theta_{max}$ = 50°], 438 parameters, CCDC 247960.

Synthesis of $[TaCl_2(\eta\text{-}EtC{\equiv}CEt)\{HB(mt)_3\}]$ (2). As described for **1**, $[Ta(\eta^2\text{-}EtC{\equiv}CEt)Cl_3(dme)]$ (0.88 g, 1.92 mmol) provided bright orange **2**. Yield: 0.89 g (67%). ^{1}H NMR (C_6D_6, 25 °C): δ 1.34 (m, 6H, CCH_3), 2.83, 3.03, 3.33 (s × 3, 3H × 3, NCH_3), 3.37−3.53 (m, 4H, CH_2), 3.95 (s, v br, 1H, BH), 6.310, 6.317, 6.324, 6.332, 6.435, 6.442 (s × 6, 1H × 6, NCH═CHN, $^3J_{HH}$ not resolved). $^{13}C\{^1H\}$ NMR: δ 12.4 (CCH_3), 33.0 (CH_2), 34.7, 35.0, 35.5 (NCH_3), 120.2 (2C), 121.3 (1C), 122.3 (1C), 124.5 (2C) (NCH═CHN), 157.7 (CS), 246.2 (C≡C). Anal. Found: C, 28.41; H, 3.38; N, 9.46. Calcd for $C_{18}H_{26}BCl_2N_6S_3Ta{\cdot}(CH_2Cl_2)_2$: C, 28.09; H, 3.54; N, 9.83. Crystal data for **2**·$(CH_2Cl_2)_2$: $C_{18}H_{26}BCl_2N_6S_3Ta{\cdot}(CH_2Cl_2)_2$, M_w = 855.14, monoclinic, $P2_1/c$, a = 9.909(2) Å, b = 17.594(4) Å, c = 18.391(4) Å, β = 98.08(3)°, V = 3174.5(1) Å^3, Z = 4, D_x = 1.789 Mg m^{-3}, μ(Mo Kα) = 4.188 mm^{-1}, T = 200(2) K, 7263 independent reflections. F^2 refinement, R = 0.036, wR = 0.081 for 5450 reflections, [$I > 2\sigma(I)$, $2\theta_{max}$ = 55°], 339 parameters, CCDC 288686.

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Supporting Information Available: Full details of the crystal structure determinations of **1**·$(CH_2Cl_2)_3$ (CCDC 247960) and **2**·$(CH_2Cl_2)_2$ (CCDC 288686) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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