Structural Consequences of the Use of Hard and Soft Tripodal Ligands during Metathesis Reactions: Synthesis of the [Bis(hydrotris(methimazolyl)borato]bismuth(III) [Bis(hydrotris(pyrazolyl)borato]sodiate

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Tripodal ligands such as the hydrotris(pyrazolyl)borate anion (Tp) have found great favor in studies of structure and reactivity[1] relevant to catalysis[2] and inorganic biochemistry.[3] Considering the accepted synthetic utility of Tp-based ligand systems, it is surprising that the range of analogous soft tripodal ligands is so limited.[4] By replacing pyrazole with methimazole (2-mercapto-1-methylimidazole) in the synthetic method of Trofimenko[5] (Scheme 1) we were recently successful[6] in the direct synthesis of the simple tridentate, sulfur-based ligand, hydrotris(meth-imazolyl)borate (Tm).

Scheme 1
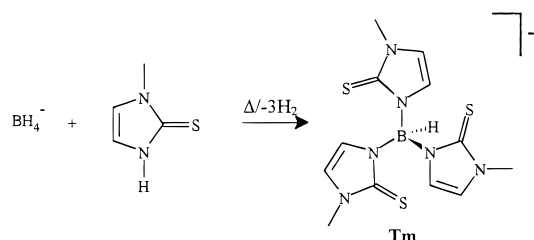
Tm is directly analogous to the more sterically demanding variant of Tp, namely, $[HB(3\text{-Mepz})_3]^-$.[7] This similarity was demonstrated in our earlier report,[6] where the product derived from the reaction of Tm with zinc(II) bromide was found to have a structure similar to that of $[HB(3\text{-Mepz})_3]ZnBr$. However, the synthesis of soft tripodal ligands was driven by a desire to modulate the structure and reactivity of metal complexes which had previously utilized Tp as the dominant ligand. An example of the modulation possible was given by the inability of TmCu(I) to coordinate carbon monoxide[6] in contrast to its Tp analogue which readily forms TpCuCO.[8,9] In an attempt to allow Tm to further display the effects of changing donor atoms from nitrogen to sulfur, it was decided to try to completely negate the steric influences important in the formation of complexes with small cations (e.g., zinc) and investigate the chemistry of a bigger, softer metal such as Bi. In addition, the larger charge (+3) carried by Bi creates the potential for the metal to bind more than 1 equiv of ligand and in different modes (e.g., mono-, di-, or tridentate).

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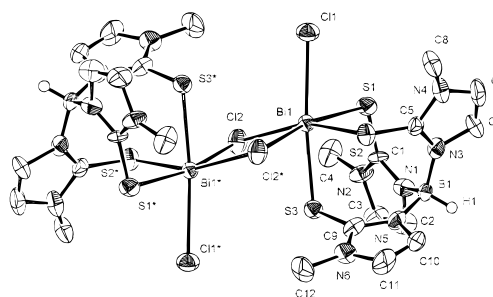(9) Bruce, M. I.; Ostazewski, A. P. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433.

Figure 1. ORTEP diagram of $[(Tm)BiCl(\mu\text{-}Cl)]_2$ showing the atom numbering scheme, with thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (deg): Bi(1)−S(1) = 2.635(4), Bi(1)−S(2) = 2.687(5), Bi(1)−S(3) = 2.714(5), Bi(1)−Cl(1) = 2.807(5), Bi(1)−Cl(2) = 2.887(5), Bi(1)−Cl(2*) = 3.009(5), S(1)−C(1) = 1.72(2), S(2)−C(5) = 1.72(2), S(3)−C(9) = 1.74(2), B(1)−N(1) = 1.54(3); B(1)−N(3) = 1.55(2), B(1)−N(5) = 1.55(2); S(1)−Bi(1)−S(2) =92.2(1), S(1)−Bi-(1)−S(3) = 89.8(1), S(2)−Bi(1)−S(3) = 87.8(1), Cl(1)−Bi(1)−S(1) = 75.5(1), Cl(1)−Bi(1)−S(2) = 99.1(1), Cl(1)−Bi(1)−S(3) = 163.9(1), Cl-(1)−Bi(1)−Cl(2*) = 99.7(1), Cl(1)−Bi(1)−Cl(2) = 110.4(1), Cl(2)−Bi(1)−Cl(2*) = 97.7(1), Cl(2)−Bi(1)−S(1) = 95.3(1), Cl(2)−Bi(1)−S(2) = 160.9(1), Cl(2)−Bi(1)−S(3) = 74.7(1), Cl(2*)−Bi(1)−S(1) = 164.5(1), Cl(2*)−Bi(1)−S(2) = 72.9(1), Cl(2*)−Bi(1)−S(3) = 85.5(1), N(1)−B(1)−N(3) = 113(1), N(1)−B(1)−N(5) = 111(1), N(3)−B(1)−N(5) = 110(1).

During the treatment of $BiCl_3$ with 3 equiv of NaTm, crystals were obtained which were structurally analyzed by X-ray methods as $[TmBiCl(\mu\text{-}Cl)]_2$[10] (Figure 1). However, spectroscopic and elemental analyses of the bulk solid were found to be more consistent with those of $[Tm_2BiCl]$. An avenue explored in an attempt to remove the ambiguity existing in this material was to further react this poorly defined product with 2 equiv of NaTp (Scheme 2). From the reaction we obtained a product which

Scheme 2
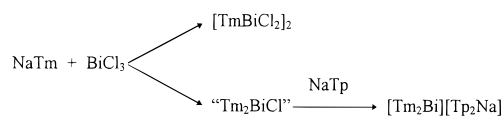
generated consistent structural[11] (Figure 2), spectroscopic, and analytical data[12] for the highly unusual salt, $[Tm_2Bi][Tp_2Na]\cdot 4CH_2Cl_2\cdot Cl(CH_2)_2Cl$. The product generated in this reaction is unprecedented. Initially our attention was focused on the motif generated around the bismuth center. This is only the second complex of this relatively new and highly novel soft analogue of Tp to be structurally characterized and the first $[M(Tm)_2]^+$ moiety. Here the organization of the two tripodal $6e^-$ ligands is reminiscent of a sandwich-type configuration. The bismuth is bonded by six thione donors with only minimal departure from regular octahedral geometry; the Bi−S bond lengths (2.806(2), 2.802(2) and 2.802(2), Å) are identical within the systematic errors, whereas the maximum deviation from 90° in the S−Bi−S

(10) $C_{24}H_{32}B_2Bi_2Cl_4N_{12}S_6\cdot2CH_2Cl_2$: orange plate, 0.22 × 0.10 × 0.05 mm, a = 10.120(4) Å, b = 13.306(6) Å, c = 9.354(6) Å, α = 101.80(4), β = 91.56(5), γ = 74.24(3) °, V = 1186(1) Å³, Z = 1. Triclinic, P1̄ (No. 2). Rigaku AFC7S diffractometer, graphite monchromated Mo Kα radiation. Data range 2.5 ≤ θ ≤ 55°. Temperature, 293 K. 5748 measured reflections, 5436 unique (R_{int} = 0.108) observed 2572 ($I ≥ 2\sigma(I)$), 253 parameters. R = 0.057, R_w = 0.059, GOF = 1.36.
(11) $C_{42}H_{52}B_4BiN_{24}NaS_6\cdot4CH_2Cl_2\cdot C_2H_4Cl_2$: red plate, 0.55 × 0.45 × 0.10 mm. a = 12.968(4) Å, b = 13.279(5) Å, c = 12.825(4) Å, α = 109.21(3), β = 95.38(3), γ = 114.22(2)°, V = 1833(1) Å³, Z = 1. Triclinic, P1̄ (No 2). Rigaku AFC7S diffractometer, graphite monochromated Mo Kα radiation. Data range 2.5 ≤ 2θ ≤ 50°. Temperature 123 K. 7014 measured reflections, 6413 unique (R_{int} = 0.032), observed 5047 ($I ≥ 2.00\sigma(I)$) 431 parameters. R = 0.053, R_w = 0.063, GOF = 1.39.
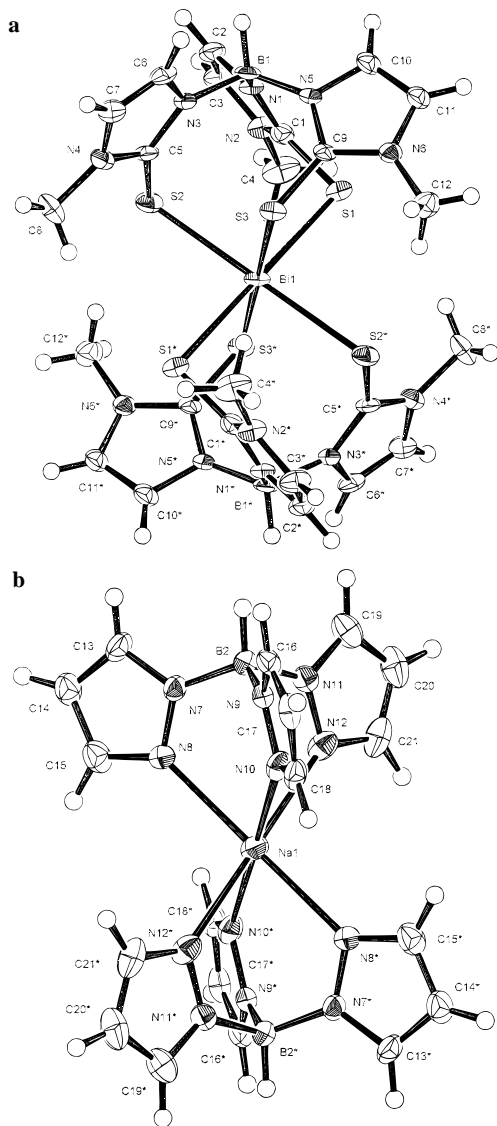
Figure 2. ORTEP diagrams of (a) the [Bi(Tm)$_2$]$^+$ cation and (b) the [Na(Tp)$_2$]$^-$ anion. The thermal ellipsoids are drawn at the 50% level. Selected bond lengths (Å): Bi(1)−S(1) = 2.806(2), Bi(1)−S(2) = 2.802-(2), Bi(1)−S(3) = 2.802(2). S(1)−C(1) = 1.722(9), S(2)−C(5) = 1.719-(8), S(3)−C(9) = 1.704(8), Na(1)−N(8) = 2.525(7), Na(1)−N(10) = 2.431(8), Na(1)−N(12) = 2.553(8). Selected bond angles (deg): S(1)−Bi(1)-S(2) = 89.81(7), S(1)−Bi(1)-S(3) = 91.31(6), S(2)−Bi(1)-S(3) = 90.72(6), S(1)−Bi(1)-S(2*) = 90.19(7), S(1)−Bi(1)-S(3*) = 88.69(6), S(2)−Bi(1)-S(3*) = 89.28(6), N(8)−Na(1)-N(10) = 82.7(2), N(8)−Na-(1)-N(12) = 75.6(2), N(10)−Na(1)-N(12) = 74.9(3), N(8)−Na(1)-N(10*) = 97.3(2), N(8)−Na(1)-N(12*) = 104.4(2), N(10)−Na(1)-N(12*) = 105.1(3), N(1)−B(1)-N(3) = 112.0(7), N(1)−B(1)-N(5) = 111.1(7), N(3)−B(1)-N(5) = 111.6(7), N(7)−B(2)-N(9) = 112.5(7), N(7)−B(2)-N(11) = 110.1(7), N(9)−B(2)-N(11) = 109.2(7).

angles is only 1.3°. There is thus no structural evidence for a stereochemically active lone pair in this species. The ligand adopts a propeller-like configuration with approximate local C_3 symmetry, closely paralleling that observed in TmZnBr.[6] The bond angles around boron also vary only slightly from regular tetrahedral angles. It would appear that little strain is required in the flexible ligand framework to accommodate the large Bi^{3+} ion. The C−S bond lengths at ca. 1.7 Å are intermediate between single and double bond values which, together with the bond lengths within the methimazolyl rings (C−C = 1.35(1); C−N = 1.34(1)−1.39(1) Å) and the observed planarity of the nitrogen atoms, imply extensive delocalization of the π-electron density in the ligand. Possibly of greater interest, however, is the structure

of the anion. Although many Tp structures have been reported[13] this is the first example of a discreet anionic [M^I(Tp)$_2$]$^-$ complex ion. Once again a sandwich-type structure is observed, but the metal coordination sphere is rather more distorted. The Na−N distances are in the range 2.431(8)−2.553(8) Å, the ligand bite angles, N−Na−N, are rather less than 90° (82.7(2), 75.6(2), 74.9-(3) °), whereas the inter ligand angles are correspondingly larger than 90°. In this case the pyrazole rings do not twist to accommodate the metal cation.

The formation of this fascinating salt is dictated by the unique relationship between the ligands (Tm, Tp) and the metal ions in the mixture during the metathesis reaction. Ligand-matching dictates that once the reaction is complete, the soft Tm ligands remain in the coordination sphere of the soft metal, and the Tp ligands complex with the alkali metal. Thus, the formation of the [Tm$_2$Bi]$^+$ cation is prearranged on chloride abstraction from the Tm$_2$BiCl starting material (Scheme 2). In contrast, the formation of the [Tp$_2$Na]$^-$ anion is driven by two synergistic effects arising from the behavior of Tp in coordination chemistry. First, Tp is a poor counterion preferring to act as a ligand. At this time no salts having a discrete Tp anion have been reported, and it would seem to be unwilling to act as a simple counterion. In contrast, Tp is a proficient ligand. However, in all of the reported structures of alkali metal cations with Tp the metal requires a coordination number of at least 4. Typically in the neutral species, Tp bridges the metals to form polymeric materials, thus satisfying this constraint. Any additional vacant metal coordination sites are occupied by neutral donor species,[13] normally solvent. This is true of NaTp·2H$_2$O which has been crystallized recently in our laboratory.[14] Thus, as a consequence of the formation of the bismuth cation (Tm$_2$Bi$^+$) and the subsequent need to maintain electrical neutrality within the salt, the sodium center is coerced into accepting a second Tp to both complete its coordination sphere and form a suitable counteranion for the emerging [Tm$_2$Bi][Tp$_2$Na] salt.

The Tm, Cp, and Tp anions could be considered to be a series of 6e$^-$ facial ligands of increasing hardness. This can be elegantly demonstrated by comparing the structures of Cp complexes with those reported here. In reactions with sodium, Cp can be induced to form the [Cp$_2$Na] anion[15] which is iso-structural with the [Tp$_2$-Na] anion, i.e., both species are sandwich complexes. In contrast, with the softer bismuth, substituted Cp ligands form species of general formula [CpBiCl$_2$]$_2$[16,17] and [Cp$_2$Bi]$^+$.[18] These are highly comparable with the two TmBi complexes reported above.

(12) Three equivalents of NaTm were mixed with BiCl$_3$ in dichloromethane. The sample was filtered to remove the sodium chloride. The volume of the sample was reduced, whereupon an orange solid was produced. This was recrystallized from dichloromethane. The orange salt was treated with 2 equiv of NaTp (based on [TmBiClμ-Cl]$_2$). The deep purple solution was filtered to remove sodium chloride and reduced in volume. The sample was left at −10 °C overnight, whereupon a deep purple solid was obtained. This material was crystallized from dichloromethane. Yield 68% based on [Tm$_2$BiCl]. Anal. Calcd for C$_{42}$H$_{52}$N$_{24}$S$_6$B$_4$Na$_1$Bi$_1$·2CH$_2$Cl$_2$·C$_2$H$_4$Cl$_2$: C, 34.53; H, 3.69; N, 21.96; S, 12.57; Cl, 9.27. Found: C, 33.92; H, 3.72; N, 21.32; S, 12.39; Cl, 8.98. ^{1}H NMR (400 MHz, CDCl$_3$ at 20 °C) δ 3.75, s (broad), 3H, CH$_3$; δ 5.35, s, CH_2Cl$_2$; δ 6.35, s, 1H, CH(pz); δ 6.85, s (broad), 2H, CH(mt); δ 7.62, s, 2H, CH(pz). ^{13}C−{^{1}H} NMR 35.3 ppm, CH$_3$, 105.4 ppm; *C*H, 118.7 ppm; *C*H, 121.6 ppm; *C*H, 124.2 ppm; *C*H, 134.1 ppm; *C*H, 145.7 ppm, *C*=S. IR (solution cm^{-1}): 2426 (ν_{BH}).

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