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Communication

Sterically Bulky Tris(triazolyl)borate Ligands as Water-Soluble Analogues of Tris(pyrazolyl)borate

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The recently synthesized 3-*tert*-butyl-5-methyl-1,2,4-triazole reacted with KBH$_4$ to give the new potassium tris(3-*tert*-butyl-5-methyl-1,2,4-triazolyl)borate K(Ttz^{tBu,Me}) ligand. Ttz^{tBu,Me} formed a four-coordinate (Ttz^{tBu,Me})CoCl complex and five-coordinate (Ttz^{tBu,Me})CoNO$_3$ and (Ttz^{tBu,Me})ZnOAc complexes. When these complexes were compared to their Tp^{tBu,Me} analogues, it was found that Ttz^{tBu,Me} resulted in negligible steric differences. K(Ttz^{tBu,Me}) is more water-soluble than K(Tp^{tBu,Me}), so bulky tris(triazolyl)borate ligands should lead to functional models for enzyme active sites in an aqueous environment and the creation of water-soluble analogues of Tp catalysts.

The chemistry of scorpionate-supported transition-metal complexes has been the subject of intense research with in excess of 2000 papers published on poly(pyrazolyl)borate complexes spanning over 70 elements of the periodic table.[1] The Cambridge Structural Database (CSD) includes data for over 2900 crystal structures of tris(pyrazolyl)borate (Tp) metal complexes,[2] with many bulky derivatives. In stark contrast, only 25 tris(triazolyl)borate (Ttz) metal complexes are reported in the CSD,[3,4] consisting predominantly of unsubstituted triazoles and just three tris(3,5-dimethyltriazolyl)borate complexes.[4] Thus far, no examples of sterically demanding triazolylborate ligands have been reported. This is particularly significant given that bulky Tp ligands have been found to be well suited for the isolation of low-coordinate metal complexes of importance to the disparate areas of nonaqueous lanthanide chemistry and biomimetic transition-metal chemistry. Those with *tert*-butyl groups attached to the pyrazolyl 3 positions have been referred to as tetrahedral enforcers.[5] The tris(3-*tert*-butyl-5-methylpyra-

zolyl)borate ligand readily stabilizes five-coordinate and even putatively four-coordinate divalent lanthanide complexes.[6] Of the many tripod–zinc complexes employed to model zinc enzymes, those with appropriately substituted Tp ligands have received considerable attention.[7]

With these features in mind, our groups independently became interested in examining the analogous chemistry using the tris(3-*tert*-butyl-5-methyl-1,2,4-triazolyl)borate (Ttz^{tBu,Me}) ligand. The change from Tp to Ttz ligands should result in negligible steric, but potentially significant, electronic differences. Subtle changes in the supporting ligand environment commonly leads to a substantive difference in the chemistry of corresponding lanthanide complexes. With relatively few versatile ligands established for divalent lanthanides, even the modest change from Tp^{tBu,Me} to Ttz^{tBu,Me} is likely to prove fruitful. While the impact on transition-metal chemistry may, at first, be anticipated to be modest, it

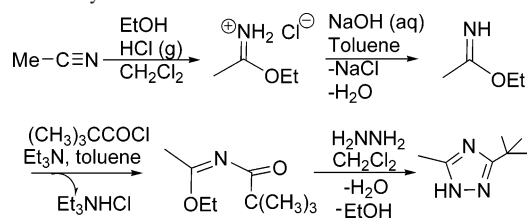* To whom correspondence should be addressed. E-mail: etpapish@salisbury.edu (E.T.P.), ferrence@ilstu.edu (G.M.F.).
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Scheme 1. Synthesis of HTz^{tBu,Me}

Figure 1. Molecular diagram of Htz^{tBu,Me}. Ellipsoids are shown at 30% probability.

has long been known that the third N in triazole rings confers water solubility to Ttz metal complexes that is absent in the Tp congeners.[8] This makes Ttz complexes good candidates for productive biomimetic investigations, particularly when using a bulky variant such as Ttz^{tBu,Me}. However, salts of this ligand as well as the precursor 3-*tert*-butyl-5-methyl-1,2,4-triazole (HTz^{tBu,Me}) are hitherto unreported.
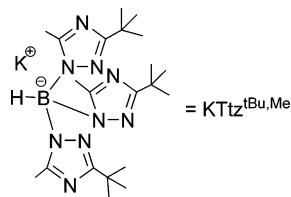
For the synthesis of HTz^{tBu,Me}, we sought a general route to 3-R-5-R′-1,2,4-triazoles that could be easily modified to include any R groups. By modification of literature procedures,[9] the route in Scheme 1 proved successful and can be modified to start from other nitriles or other acid chlorides. The overall yield for all four steps was 15%, allowing multigram quantities of triazole to be synthesized. The structure of Htz^{tBu,Me} has been confirmed by ^{1}H and ^{13}C NMR and IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (Figure 1). The water solubility of 1,2,4-triazoles is believed to be due to hydrogen bond donation to the third N.[8] Because Htz^{tBu,Me} is water-soluble, we suspected that this N was still accessible. From the crystal structure, it is clear that the steric bulk has not hindered the formation of hydrogen bonds;[10] each N2 is 2.883(2) Å from N3 on a neighboring triazole ring. The packing diagram illustrates that a linear network of NH···N hydrogen bonds extends along the *c* direction of the unit cell.

Following a literature procedure for the synthesis of Tp complexes,[1b] KBH$_4$ was combined with a 5.8-fold molar excess of Htz^{tBu,Me} and the mixture was melted at 200 °C. After evolution of H$_2$ ceased, potassium tris(3-*tert*-butyl-5-methyl-1,2,4-triazolyl)borate [K(Tz^{tBu,Me})] was isolated in 96% yield by subliming off the excess triazole. This ligand is water-soluble and has been characterized by ^{1}H and ^{13}C NMR and IR spectroscopy; further evidence of the structure comes from characterization of its products.

K(Ttz^{tBu,Me}) reacts with Zn(OAc)$_2$·2H$_2$O in CH$_2$Cl$_2$ or MeOH to give (Ttz^{tBu,Me})ZnOAc in 91% yield, which has been characterized by NMR (^{1}H and ^{13}C in the Supporting Information), IR, single-crystal X-ray diffraction (Figure 2), and high-resolution mass spectrometry. The Zn atom is between four- and five-coordinate: N1, N4, N7, and O2 are
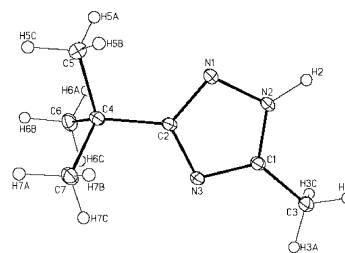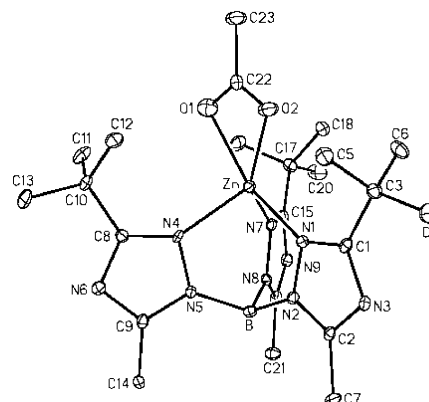
Figure 2. Molecular diagram of (Ttz^{tBu,Me})ZnOAc·H$_2$O. Ellipsoids are shown at 30% probability, and H atoms and noncoordinating solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn–N1 2.103(4), Zn–N4 2.084(4), Zn–N7 2.089(4), Zn–O2 1.978-(4), Zn–O1 2.362(5); O2–Zn–O1 59.32(16), N7–Zn–N1 91.75(15), N4–Zn–N1 92.77(15), N4–Zn–N7 94.46(16), N4–Zn–O1 99.80(16), N7–Zn–O1 99.53(15), O2–Zn–N1 103.04(16), O2–Zn–N4 129.92(18), O2–Zn–N7 131.39(17), N1–Zn–O1 162.33(15).

strongly bound [Zn–O2 = 1.978(4) Å], but the Zn–O1 distance of 2.362(5) Å indicates a weak interaction. Overall, the structure is closer to trigonal-bipyramidal with O1 and N1 axial ($\tau = 0.515$)[11] than square-pyramidal. The crystal structure contained one H$_2$O molecule per (Ttz^{tBu,Me})ZnOAc, and the packing diagram shows that each H$_2$O has two O–H···N hydrogen bonds[10] to two triazole rings with O–N6 and O–N9 distances of 2.925(10) and 2.935(10) Å, respectively.

Similarly, K(Ttz^{tBu,Me}) reacts with Co(NO$_3$)$_2$·6H$_2$O to give a purple (Ttz^{tBu,Me})CoNO$_3$ complex in 96% yield, which has been characterized by single-crystal X-ray diffraction (Figure 3). The Co atom is five-coordinate and closer to trigonal-bipyramidal than square-pyramidal ($\tau = 0.632$).[11] As with the zinc structure, the axial O is further from the metal than the other donors. One explanation may be that the axial N1 and O2 atoms both interact with the d$_{z^2}$ orbital, but because the triazole N is a stronger donor, the Co–O2 bond distance [2.239(2) Å] becomes elongated compared to the Co–O1 distance [1.9988(19) Å]. K(Ttz^{tBu,Me}) also reacted with CoCl$_2$ to produce the blue complex (Ttz^{tBu,Me})CoCl in 84% yield, which has a tetrahedral Co atom by single-crystal X-ray diffraction (Figure 4). (Ttz^{tBu,Me})CoNO$_3$ and (Ttz^{tBu,Me})CoCl were also characterized by IR, high-resolution mass spectrometry, ^{1}H NMR spectra consistent with paramagnetic complexes, and magnetic susceptibility measurements consistent with μ_{eff} = 3.3 μ_B and 4.3 μ_B, respectively. UV–vis

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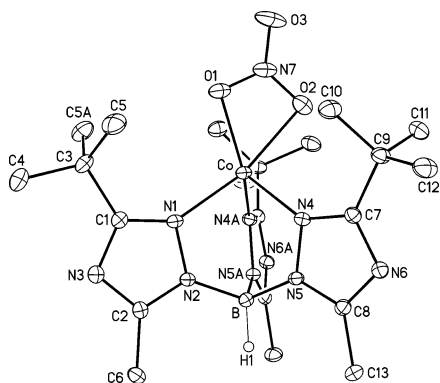
Figure 3. Molecular diagram of (Ttz^{tBu,Me})CoNO$_3$. Ellipsoids are shown at 30% probability, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co−N1 2.057(2), Co−N4 2.0562(14), Co−O1 1.9988(19), Co−O2 2.239(2); O1−Co−O2 60.49(8), N4−Co−N1 91.65(5), N4−Co−O2 97.21(5), N4−Co−N4 97.84(8), O1−Co−N1 105.99-(8), O1−Co−N4 128.55(4), N1−Co−O2 166.48(8).
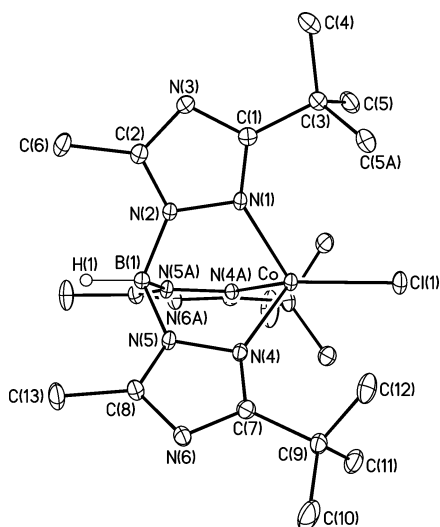

Figure 4. Molecular diagram of (Ttz^{tBu,Me})CoCl·2CHCl$_3$. Ellipsoids are shown at 30% probability, and H atoms and noncoordinating solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co−N1 2.022(4), Co−N4 2.036(3), Co−Cl1 2.2035(14); N1−Co−N4 94.34(11), N4−Co−N4 94.79(16), N4−Co−Cl1 122.00(8), N1−Co−Cl1 122.06(12).

spectra in CH$_2$Cl$_2$ gave λ_{max} (ϵ) values of 597 nm (83 M^{-1} cm^{-1}) for (Ttz^{tBu,Me})CoNO$_3$ and 625 nm (494 M^{-1} cm^{-1}) for (Ttz^{tBu,Me})CoCl, consistent with five- and four-coordinate geometries, respectively.[12]

The environment around the metal in both (Ttz^{tBu,Me})-ZnOAc and (Ttz^{tBu,Me})CoNO$_3$ bears resemblance to metalloenzyme active sites that contain a mixture of N and O donors from histidine and aspartate residues.[13] Additionally, this shows that Ttz^{tBu,Me} is not a strict tetrahedral enforcer: as with Tp^{tBu,Me} complexes,[1b] the metal is five coordinate when bound to Ttz^{tBu,Me} and bidentate small molecules.

Upon comparing the crystal structures reported herein to the analogous structures from the literature, we find that the bond lengths and angles are remarkably similar. Most bond lengths in Htz^{tBu,Me} are within 0.03 Å of the comparable lengths in 3-*tert*-butyl-5-methylpyrazole,[14] only the C1═N3 distance of 1.331(2)Å is significantly shorter than the corresponding C═C distance of 1.397 Å. Similarly, there are no significant differences between (Ttz^{tBu,Me})CoCl, (Tp^{tBu,Me})-CoCl,[15] and (Tp^{tBu})CoCl[16] or between (Ttz^{tBu,Me})CoNO$_3$ and (Tp^{tBu})CoNO$_3$.[17] Only the geometry of the weakly κ^2-acetate ligand in (Ttz^{tBu,Me})ZnOAc is significantly different when compared to analogous Tp complexes that have κ^1-acetate. (Tp^{tBu,Me})ZnOAc[18] has O atoms at 1.870(4) and 3.242(4) Å and (Tp^{tBu})ZnOAc[19] has O atoms at 1.858(6) and 2.950(6) Å from Zn. Given that there are far more similarities than differences, one could conclude from looking at these structures that the minor change in geometry between Tp^{tBu} and Tp^{tBu,Me} is greater than the change from Tp^{tBu,Me} to Ttz^{tBu,Me}.

Water-soluble triazoles are promising for a range of environmentally friendly "green" chemistry applications.[20] Even the synthesis of our metal complexes can be carried out in water! Because K(Ttz^{tBu,Me}) is soluble in water (99 mg/mL) but (Ttz^{tBu,Me})ZnOAc is sparingly soluble, when K(Ttz^{tBu,Me}) is combined with Zn(OAc)$_2$·2H$_2$O in water, the (Ttz^{tBu,Me})ZnOAc product precipitates out and can be cleanly isolated in 34% yield by filtration. Spectroscopically pure samples are thus obtained that can potentially be used for catalysis or environmental applications.

In conclusion, the ligand Ttz^{tBu,Me} is water-soluble and can be made and used in an environmentally friendly manner. It has a steric bulk similar to that of Tp^{tBu,Me}, and the third N in the triazole ring does not appear to have a significant effect on the geometry of the complexes. However, its water solubility makes it especially promising for aqueous catalysis of hydrolytic reactions. The complexes of this ligand can provide a structural and functional model for metalloenzymes in water.

Supporting Information Available: Experimental details for all new compounds, selected spectra, packing diagrams, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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