A New Scorpionate Ligand: Tris(4,4-dimethyl-2-oxazolinyl)borate and Its Zirconium(IV) Complexes

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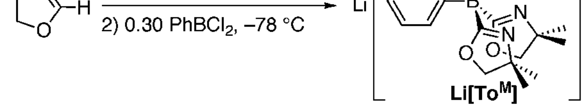
Summary: The first example of a new class of oxazoline-based scorpionate ligand, tris(4,4-dimethyl-2-oxazolinyl)phenyl borate, [To^M]$^-$, is prepared by reaction of 2-lithio-4,4-dimethyl-2-oxazolide and 0.3 equiv of dichlorophenylborane. The steric bulk of this ligand is greater than that of tris(3,5-Me$_2$-pyrazolyl)borate (Tp), as quantified by comparison of solid angles of crystallographically characterized zirconium(IV) complexes.*

Sterically encumbered tris(pyrazolyl)borate ligands, such as Tp* (HB(3,5-Me$_2$-pyrazolyl)$_3$), Tp$^{t\text{BuMe}}$ (HB(3-^{t}Bu-5-Me-pyrazolyl)$_3$), and Tp$^{\text{Mes}}$ (HB(3-mesitylpyrazolyl)$_3$), have recently captured attention as useful ancillary ligands in early transition metal chemistry.[1–4] Early transition metal complexes of these bulky ligands as well as those of parent tris(pyrazolyl)borate (Tp) show interesting stoichiometric chemistry[2–8] and display catalytic activity in reactions such as olefin polymerization.[2,4,8a,9,10] However, unsymmetrically substituted Tp derivatives (e.g., 3-mesitylpyrazolyl) are susceptible toward isomerization processes, giving mixtures of 3- and 5-substituted tris(pyrazolyl)borate complexes.[4] In highly reactive complexes such as [Zr(κ^3-Tp*)(CH$_2$C$_6$H$_5$)$_2$]$^+$, ligand decomposition through B−N cleavage hinders possible utility in catalysis.[2] In fact, isomerization via 1,2-sigmatropic shifts and B−N bond cleavage are common reaction pathways for pyrazolylborate ligands in a range of transition metal complexes.[1c,d,3,11]

To avoid this decomposition mechanism, we designed the tris(oxazolinyl)borate scorpionate ligand that contains B−C linkages, proposed to have greater resistance to cleavage and isomerization processes.[12] The synthesis of tris(4,4-dimethyl-2-oxazolinyl)phenyl borate, [To^M]$^-$, the first example of this new ligand class, and its coordination chemistry in new zirconium (IV) complexes are reported here. Lithium tris(4,4-dimethyl-2-oxazolin-2-yl)phenyl borate (Li[To^M]) is prepared by deprotonation of 4,4-dimethyl-2-oxazoline with *n*-BuLi (1.05 equiv) at −78 °C followed by addition of 0.30 equiv of dichlorophenylborane (eq 1).



Li[To^M]

89.9% yield

(1)

Quantitative deprotonation of the oxazoline is necessary, as mixtures of 2*H*-oxazoline, 2-lithio-oxazolide, and dichlorophenylborane produce Li[To^M] and several unidentified products. Independent experiments show that interaction of 4,4-dimethyl-2-oxazoline and PhBCl$_2$ in THF accounts for two of the side products. Also, a slight excess of 2-lithio-oxazolide (0.30 equiv of PhBCl$_2$) is necessary, as 0.33 equiv of PhBCl$_2$ and shorter reaction times (<26 h) afford inseparable mixtures of Li[To^M] and a species assigned as bis(4,4-dimethyl-2-oxazolin-2-yl)phenylborane on the basis of integration of its ^{1}H NMR spectrum and its ^{11}B NMR chemical shift (−7.26 ppm).

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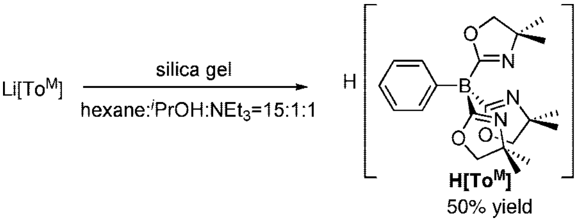
The ^{1}H NMR spectra of Li[To^M] dissolved in benzene-d_6, chloroform-d_1, or methylene chloride-d_2 contained broad resonances at 1.4 and 3.3 ppm as well as aryl resonances. In contrast, the 4,4-dimethyl and methylene groups (at 1.19 and 3.60 ppm) on equivalent oxazoline rings gave sharp singlet resonances in acetonitrile-d_3. The formation of the borate center is supported by the integrated ratio of oxazoline methyl to phenyl resonances (18:5 H) as well as the broad singlet observed at −16.9 ppm in the ^{11}B NMR spectrum.[13]

This salt elimination route to Li[To^M] is related to the synthesis of bis(oxazolinyl)diphenylborate ligands (borabox).[14] Borabox, which also is prepared via reaction of 2-lithium oxazolide and a chloroborane electrophile, forms in 4−12 h. In contrast to this short reaction time, preparation of the neutral ligand 1,1,1-tris(oxazolinyl)ethane (tris-ox) requires heating THF solutions of lithium bis(oxazoline) and 2-bromo-2-oxazoline at reflux for 5 days.[15] Interestingly, the reaction conditions needed for synthesis of Li[To^M] fall between these two ligands.

The acidic pro-ligand H[To^M] is prepared by flash chromatography of Li[To^M] on silica gel in C_6H_{14}/*i*-PrOH/NEt_3 (15:1:1), giving the product as an off-white solid (eq 2).[14]



(2)

The ^{1}H NMR spectrum of H[To^M] (benzene-d_6) contained sharp singlet resonances at 1.02 (Me) and 3.55 ppm (CH_2), in contrast to the broad resonances observed for Li[To^M] in this solvent. In acetonitrile-d_3, the oxazoline peaks are shifted downfield by 0.1 and 0.3 ppm (to 1.29 and 3.90 ppm) in comparison to Li[To^M]. Crystals of H[To^M] are obtained from the chromatography solvent mixture after slow evaporation. Although the crystals diffracted weakly, single-crystal X-ray diffraction confirms the constitution and connectivity of [To^M]$^-$, in particular the formation of a tetrahedral borate center containing four B−C bonds (Figure 1).

The symmetry of [To^M]$^-$ in the solid state is C_s, as two of the oxazolines' C═N are coplanar (N1═C7−C17═N3 dihedral = 0°), oriented toward each other as if to form a bidentate chelate, and related by a mirror plane. That mirror plane contains the phenyl group and the third oxazoline. However, the ^{1}H NMR spectrum of H[To^M] (benzene-d_6 or acetonitrile-d_3) indicates that all three oxazoline groups are equivalent in solution.

We have prepared [To^M]Zr(IV) complexes through salt metathesis with Li[To^M] and $ZrCl_4$ as well as via amine elimination with H[To^M] and $Zr(NMe_2)_4$. A salt elimination reaction occurs when a mixture of Li[To^M] and 1.05 equiv of $ZrCl_4$ suspended in methylene chloride is stirred for 4 days, giving a yellow solution of [Zr(κ^3-To^M)Cl_3] and suspended lithium chloride (eq 3).

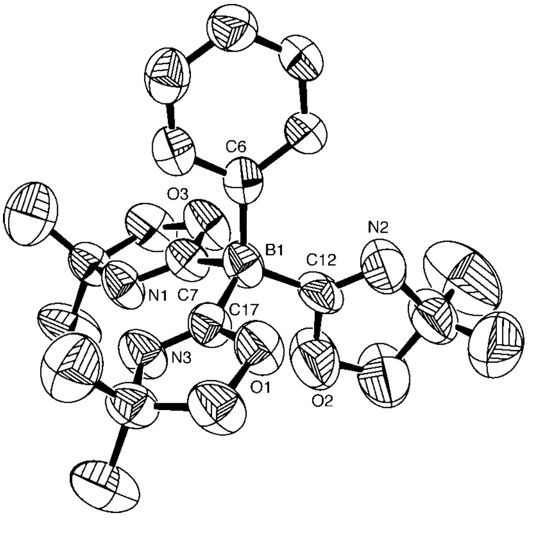
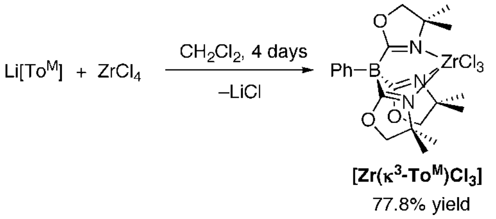


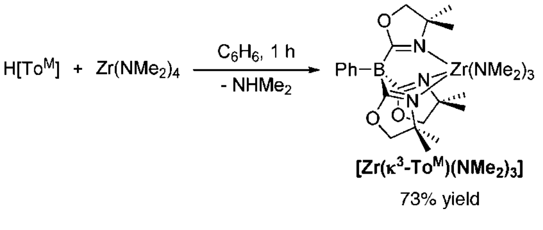
Figure 1. ORTEP diagram of H[To^M] at 50% probability. Hydrogen atoms are omitted for clarity.



(3)

The same compound is also obtained by heating a mixture of Li[To^M] and $ZrCl_4$ in toluene to reflux for 24 h. In fact, [Zr(κ^3-To^M)Cl_3] is recovered without decomposition after isolated material is redissolved and heated in toluene at reflux for 7 days. C_{3v}-Symmetric [Zr(κ^3-To^M)Cl_3] is characterized by equivalent oxazoline groups that are observed in the ^{1}H NMR spectrum (benzene-d_6) as singlet resonances at 3.28 (CH_2) and 1.36 ppm (Me). A comparison of the IR spectra of Li[To^M] versus [Zr(κ^3-To^M)Cl_3] showed the stretching frequency of the C═N double bond shifts from 1607 cm^{-1} to lower energy at 1545 cm^{-1}.

Amine elimination also proved to be a viable route for the preparation of [To^M]Zr compounds.[16] Thus, reaction of $Zr(NMe_2)_4$ and H[To^M] in benzene yields [Zr(κ^3-To^M)$(NMe_2)_3$] as a white solid (73%, eq 4). A micromolar scale reaction was monitored in situ by ^{1}H NMR spectroscopy, revealing that 1 equiv of $NHMe_2$ is rapidly formed (<10 min). The ^{1}H NMR spectrum (benzene-d_6) of the C_{3v}-symmetric product contained one set of oxazoline resonances (3.41 and 1.09 ppm) and a singlet corresponding to equivalent NMe_2 groups (3.15 ppm).



(4)

In contrast, salt metathesis of [Zr(κ^3-To^M)Cl_3] and 3 equiv of $LiNMe_2$ (benzene-d_6, room temperature, 24 h) provides a C_s-symmetric product. The ^{1}H NMR spectrum of the crude reaction mixture revealed a 1:1 ratio of [To^M]:NMe_2 groups,

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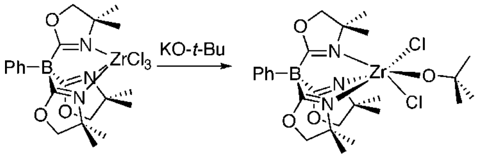
providing support for its assignment as [Zr(κ^3-To^M)(NMe$_2$)Cl$_2$]. Under more forcing conditions (6 equiv of LiNMe$_2$, 24 h, 60 °C), Zr(NMe$_2$)$_4$ and Li[To^M] are obtained. Although substitution of one chloride in [Zr(κ^3-To^M)Cl$_3$] by [NMe$_2$]$^-$ occurs, formation of [Zr(κ^3-To^M)(NMe$_2$)$_3$] via salt elimination has not been observed.

To further explore chloride substitutions, a toluene solution of [Zr(κ^3-To^M)Cl$_3$] and KO-*t*-Bu was stirred overnight at room temperature to provide [Zr(κ^3-To^M)(O-*t*-Bu)Cl$_2$].



(5)

[Zr(κ^3-To^M)(O-*t*-Bu)Cl$_2$]
80% yield

The ^{1}H NMR spectrum of [Zr(κ^3-To^M)(O-*t*-Bu)Cl$_2$] highlights its C_s-symmetry. As a result of the mirror plane that includes the *tert*-butoxide oxygen, zirconium center, and *trans*-oxazoline, the $-$CMe$_2-$ and $-$CH$_2-$ groups on that ring are equivalent and appear as singlet resonances (1.52 and 3.38, respectively, labeled as *trans* in the Newman projection in Figure 2).

Although the other two oxazoline rings are related by the mirror plane, the $-$CH$_2-$ within each ring are *endo* or *exo* with respect to the *tert*-butoxide and were observed as two coupled doublets (3.38 and 3.25 ppm, $^2J_{HH} = 8.72$ Hz). The methyl substituents in the CMe$_2$ groups of these oxazolines are also inequivalent (but not coupled), resulting in two singlet resonances (1.45 and 1.05 ppm are *exo* and *endo*, respectively, assigned with a NOESY experiment). Cross-peaks in a ^{1}H$-^{15}$N HMBC experiment verify that these two peaks are *cis* to the *tert*-butoxide, as they correlate to a ^{15}N resonance at 239 ppm (N *trans* is at 241 ppm).[11a,17]

A solid-state structure of the product confirmed the N,N,N-κ^3 coordination of [To^M]$^-$ to zirconium, as well as the overall connectivity of the molecule (Figure 3). The zirconium center's geometry is distorted octahedral with a relatively short Zr$-$O bond (1.891(3) Å) for a six-coordinate zirconium *tert*-butoxide. Interestingly, [Zr(κ^3-To^M)(O-*t*-Bu)Cl$_2$] is C_1-symmetric in the solid state due to inequivalent twist conformations of the three oxazoline rings such that the methyl groups on the 4-position are positioned equatorial (pointed toward zirconium) or axial. Thus, all Zr$\cdots$C (4-Me) distances are inequivalent, ranging from 3.76 to 4.23 Å, creating an unusual steric pocket around the zirconium center. The size of this pocket is best described by the solid angle for [To^M]$^-$,[18,19] determined from the crystallographic coordinates to be 5.40 steradians (164° corresponding to 43% of a sphere's surface). For comparison, the solid angle for Tp* is 3.62 steradians (130° corresponding to 30% of a sphere's surface, determined for Tp*Zr(CH$_2$C$_6$H$_5$)$_3$).[2]

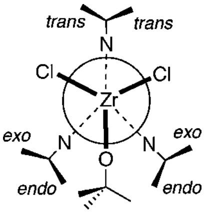


Figure 2. Newman projection illustrating the C_s-symmetry of [Zr(κ^3-To^M)(O-*t*-Bu)Cl$_2$]. The groups attached to N represent CH$_2$ and CMe$_2$ substituents on the oxazoline.

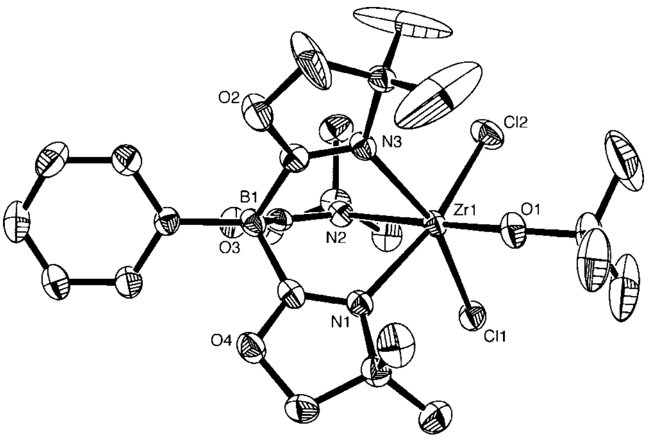


Figure 3. ORTEP diagram of [Zr(κ^3-To^M)(O-*t*-Bu)Cl$_2$] at 50% probability. Hydrogen atoms are omitted for clarity.

These values for solid angles show that the 4,4-dimethyloxazoline substituents in [To^M]$^-$ encompass the zirconium center to a greater extent than the 3,5-dimethylpyrazole groups in Tp*. Thus, tris(4,4-dimethyl-2-oxazolinyl)borate may offer enhanced steric protection for highly reactive metal centers, such as those of cationic zirconium alkyl and hydride complexes.[2] Additionally, optically active C_3-symmetric tris(oxazolinyl)borates are readily accessible due to the availability of enantiopure 2*H*-oxazolines.[20] These chiral tris(oxazolinyl)borates will complement the chemistry of the related optically active tris(pyrazolyl)borates pioneered by Tolman.[21] We are currently investigating our achiral complexes as catalysts, as well as preparing chiral analogues for stereoselective polymerizations.[15]

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Supporting Information Available: Experimental procedures, characterization, and X-ray crystallographic data are available free of charge at http://pubs.acs.org.

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