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Easily Prepared Chiral Scorpionates: Tris(2-oxazolinyl)boratoiridium(I) Compounds and Their Interactions with MeOTf

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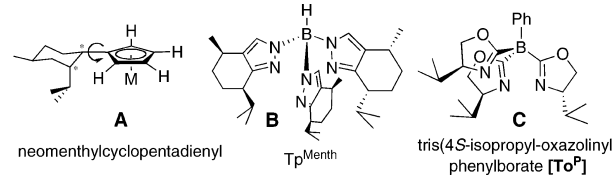
Optically active C_3-symmetric monoanionic ligands are uncommon in organometallic chemistry. Here we describe the synthesis of readily prepared tris(4*S*-isopropyl-2-oxazolinyl)phenylborate [To^P] and fluxional, zwitterionic four- and five-coordinate iridium(I) compounds [Ir(To^P)-(η^4-C_8H_{12})] (**4**) and [Ir(To^P)(CO)$_2$] (**5**). The highly fluxional nature of **4** and **5** makes structural assignment difficult, and the interaction between the iridium(I) center and the [To^P] ligand is established by solid-state and solution ^{15}N NMR methods that permit the direct comparison between solution and solid-state structures. Although iridium cyclooctadiene **4** is a mixture of four- and five-coordinate species, the dicarbonyl **5** is only the five-coordinate isomer. The addition of electrophiles MeOTf and MeI provides the oxazoline N-methylated product rather than the iridium methyl oxidative addition product. N-Methylation was unequivocally proven by through-bond coupling observed in ^{1}H−^{15}N HMBC experiments.

Optically active tris(pyrazolyl)borate (Tp) and cyclopentadienyl (Cp) ligands have found fewer applications in asymmetric catalysis relative to ubiquitous chiral phosphines.[1−3] This contrasts the prominence of Cp and Tp in a wide range of metal-mediated processes[4] but may be related to the difficulty in precisely and systematically tuning chiral Cp- and Tp-type ligands. For example, in piano-stool complexes containing a pendant chiral group, the stereocenters are removed from the metal center and free rotation gives a range of possible conformations (Chart 1, **A**).[1] C_3-symmetric Tp ligands such as HB(2*R*,5*R*-menthylpz)$_3$ (**B**) offer an improvement by fixing stereogenic centers proximal to the metal;[2] however, acid- or metal-mediated 1,2-borotropic shifts result in ligand isomerization and decomposition,[5] and systematic modification of these ligands is synthetically challenging.[6] To facilitate the use of dissymmetric L_2X-type ligands in organometallic chemistry,[7] we have prepared a new class of scorpionate ligand in which three oxazoline groups are linked through a borate center (**C**).[8]

Chart 1. Optically Active L_2X-Type Ligands



Recently, achiral *fac*-coordinating L_2X-type borate ligands, including tris(phosphino)borates (BP$_3$),[9] tris(thioether)borates,[10] and tris(carbene)borates,[11] have been shown to stabilize reactive transition-metal centers. The oxazoline moiety is well-established as a ligand for transition-metal centers, and oxazoline-based compounds often provide good selectivities in asymmetric

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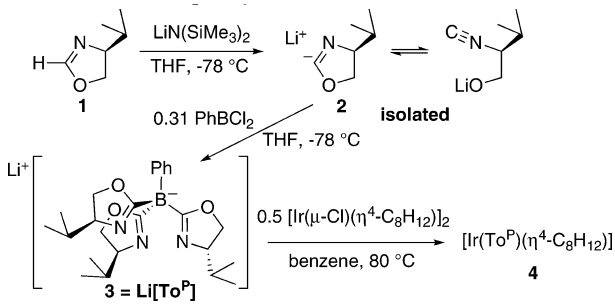
Scheme 1



catalysis.[12,13] Recently, Pfaltz and co-workers have prepared LX-type bis(oxazolinyl)borate ligands (borabox), and the zwitterionic catalysts containing these ligands have improved enantioselectivities versus cationic bisoxazoline catalysts in copper(II)-catalyzed cyclopropanation.[14] Furthermore, neutral (L_3) tris(oxazolinyl)ethane (tris-ox) ligands also show good enantioselectivity in a range of catalytic transformations, including stereoselective 1-hexene polymerization, allylic substitution, and Mannich reactions of β-ketoesters.[15] Therefore, we prepared an optically active tris(oxazolinyl)borate as a chiral surrogate for Cp and Tp and as a monoanionic relative of tris-ox. Herein we describe its synthesis and our initial investigations of the ligand's reactivity in iridium(I) complexes.

Tris(4*S*-isopropyl-2-oxazolinyl)phenylborate ([To^P]$^-$) is prepared by deprotonation of 4*S*-isopropyloxazoline (**1**) to give 2-lithio-4*S*-isopropyl-2-oxazolide (**2**), followed by reaction with 0.31 equiv of $PhBCl_2$ in a second step (Scheme 1). Although deprotonation of 2*H*-oxazolines with *n*-BuLi followed by reaction with electrophilic reagents such as Ph_3B and Ph_2BCl is established,[14,16] we obtain intractable mixtures when **1** is treated sequentially with *n*-BuLi followed by $PhBCl_2$. This failure is especially surprising because the achiral analogue tris(4,4-dimethyl-2-oxazolinyl)phenylborate and Pfaltz's chiral bis(2-oxazolinyl)diphenylborate (borabox) are synthesized by this sequence.[8,14] The difference is due to the fact that *n*-BuLi and **1** give **2** in only 80% yield,[17] and the interaction of unreacted **1** and $PhBCl_2$ interferes with the formation of Li[To^P]. Although **1** reacts quantitatively with $LiN(SiMe_3)_2$ to give **2**,[17] the $HN(SiMe_3)_2$ byproduct and $PhBCl_2$ also react rapidly and inhibit B−C bond formation. Fortunately, analytically pure **2** is isolated in near-quantitative yield by the reaction of $LiN(SiMe_3)_2$ and **1** followed by removal of the volatile materials and an Et_2O wash.

Although only the cyclic form of **2** is observed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy down to 200 K, both isocyanide ν_{CN} (2173 cm^{-1}) and oxazolinyl ν_{CN} (1629 cm^{-1}) are observed in the IR spectrum, indicating that the two isomers are rapidly exchanging on the NMR time scale.[17,18] Despite potential complications due to lithium alkoxide/isocyanide interconversion, the reaction of 3.3 equiv of isolated **2** and $PhBCl_2$ affords the desired Li[To^P] (**3**) in excellent yield (92%). Only one set of oxazoline resonances was observed in the ^{1}H NMR spectrum of **3**, with a 3:1 oxazoline-to-phenyl ratio.

The enantiopurity of [To^P]$^-$ is proven by the ^{1}H NMR spectrum of a single diastereomer as the *S*,*S*,*S* enantiomer. The identity of **3** is further supported by ^{11}B NMR spectroscopy (δ −16.8, consistent with a four-coordinate borate center)[19] as well as solid-state ^{13}C and ^{15}N NMR spectra (see the Supporting Information for details). In the IR spectrum, oxazoline C═N stretches are observed at 1589 cm^{-1}; isocyanide peaks are not detected. Importantly, **3** is not hydrolyzed in wet methanol.

Iridium(I) centers in coordination geometries distorted from square planar are expected to be highly reactive.[20] Therefore, we prepared [Ir(To^P)(COD)] (**4**; COD = 1,5-C_8H_{12}) by reaction of **3** and 0.5 equiv of [Ir(μ-Cl)(COD)]$_2$ (Scheme 1). The ^{1}H NMR spectrum of **4** in benzene-d_6 indicates that COD is η^4-coordinated while [To^P] appears C_3-symmetric. Thus, **4** is fluxional. As observed with several d^8 TpIr^I and TpRh^I compounds,[20−23] the process(es) responsible is (are) rapid on the ^{1}H NMR time scale. In fact, the ^{1}H NMR chemical shifts of **4** are identical at −80 °C and room temperature. When a benzene solution of **4** is placed under an atmosphere of CO, the cyclooctadiene is rapidly substituted to give [Ir(To^P)(CO)$_2$] (**5**), which also contains a single set of oxazoline resonances in its ^{1}H NMR spectrum and appears C_3-symmetric.

The ^{15}N NMR solution spectra of **4** and **5**, obtained at natural abundance using ^{1}H−^{15}N HMBC experiments,[21,24] each contain one cross peak due to rapidly exchanging oxazoline groups (Table 1). In the solid state, the static ^{1}H NMR spectrum of **4** indicates that the structures are fully rigid. The ^{15}N CPMAS NMR spectrum of **4** contains four broad resonances in an approximately 1:2:2:1 ratio determined by a peak-fitting algorithm; the resolution is insufficient to distinguish the magnetically inequivalent oxazolines coordinated *trans* to COD. The resonance at −147 ppm (1

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Table 1. ^{15}N NMR Data Obtained by ^{1}H−^{15}N HMBC Experiments

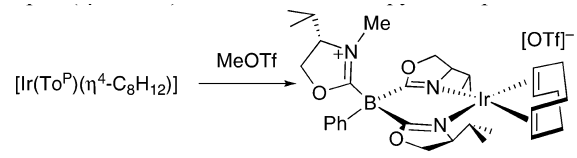
	^{15}N NMR	
compound	solution	solid state
2H-Ox^{i}Pr (**1**)	−150	n.a.
Li[Ox^{i}Pr] (**2**)	−207	n.a.
Li[To^{P}] (**3**)	−166	−161 (1 N), −171 (2 N)
[Ir(To^{P})(COD)] (**4**)	−182	−147 (1 N), −202 (2 N), −210 (2 N), −217 (1 N)
[Ir(To^{P})(CO)$_2$] (**5**)	−184	−195 (1 N), −201 (2 N)
4 + MeOTf (**6**)	−221 (NMe); −198, −192 (*trans* to olefin)	n.a.
5 + MeOTf (**7**)	−219.4 (NMe); −199.5, −199.8 (*trans* to CO)	n.a.
1 + MeOTf	−224	n.a.

N) is assigned as a noncoordinated oxazoline based on its similarity to the solution ^{15}N NMR chemical shift of **1** (−150 ppm). The other ^{15}N NMR resonances correspond to Ir-coordinated oxazoline groups, assigned by comparison with nonfluxional iridium(I) compounds (see below, Table 1, and the Supporting Information). These data indicate that both [Ir(κ^2-To^{P})(COD)] and [Ir(κ^3-To^{P})(COD)] isomers are present in the solid state, and the two isomers are rapidly equilibrating in solution.

In contrast, the ^{15}N CPMAS NMR spectrum of **5** contains a broad non-Gaussian-shaped resonance at −201 ppm with a shoulder at −195 ppm in an approximate 2:1 ratio (determined by peak fitting; see the Supporting Information). No resonances are detected in the range of noncoordinated oxazolinyl groups (∼−150 ppm). Furthermore, a 2:1 ratio of oxazoline resonances is observed in the solid-state ^{13}C NMR spectrum. These data suggest that only one ligand configuration is present in **5**. IR spectroscopy supports this assignment because the carbonyl region contains only two bands (KBr, ν_{CO} = 2064 and 1987 cm^{-1}; CH_2Cl_2, 2065 and 1991 cm^{-1}). Thus, the data from solid-state NMR and IR spectroscopies indicate that [Ir(To^{P})(CO)$_2$] is five-coordinate, containing a (κ^3-To^{P})−Ir interaction, although its reactivity indicates that the third oxazoline group is labile. In contrast, [Rh(tris-ox)(COD)]$^+$ is only κ^2 in the solid state (X-ray diffraction).[15a]

These ^{15}N NMR spectroscopic measurements are a powerful tool for understanding metal−ligand interactions (κ^2 vs κ^3) for d^8 iridium (oxazolinyl)borate compounds. Tp compounds containing d^8 metal centers are frequently fluxional, and their characterization as κ^2 or κ^3 isomers is often difficult to determine.[20−23] Previous ^{1}H−^{15}N HMBC experiments on TpML$_2$-type compounds were limited to the parent pyrazole because of weak J_{NH} coupling.[21] Although several empirical correlations of spectroscopic data and ligand coordination number in Tp compounds have assisted in the characterization of five-coordinate compounds, these methods are indirect (^{11}B NMR chemical shift or ν_{BH} in IR spectra),[22,23] limited (ν_{CO} restricted to dicarbonyls),[21] and sometimes problematic for comparing solution and solid-state structures obtained by X-ray crystallography. Clear advantages of ^{15}N NMR spectroscopy include direct observation of the coordinated versus dissociated oxazolines, an identical spectroscopic handle for solution and solid-state measurements, and potential application in the characterization of catalytically important oxazoline-coordinated compounds.[13−15,24] This becomes particularly valuable for amorphous materials such as **4**.

The addition of MeOTf to a benzene-d_6 solution of **4** affords the adduct [Ir(κ^2-To^{P}−Me)(η^4-C$_8$H$_{12}$)][OTf] (**6**; eq 1) quantitatively in 3 h rather than a methylated iridium(III) compound. Likewise, the addition of MeOTf to **5** gives the adduct [Ir(κ^2-To^{P}−Me)(CO)$_2$][OTf] (**7**). These transformations are unexpected because oxidative addition to iridium would have provided 18-electron complexes. For comparison, additions of H$^+$ to TpIrL$_2$ [L$_2$ = (CO)$_2$ or (η^2-C$_2$H$_4$)PPh$_3$] usually give the iridium(III) hydrides, although Tp*Ir(η^4-C$_8$H$_{12}$) and HOTf result in pyrazole protonation.[25]



6 = [Ir(κ^2-To^{P}–Me)(η^4-C$_8$H$_{12}$)][OTf]

Three sets of resonances corresponding to inequivalent oxazoline groups are observed in the ^{1}H NMR spectra of **6** and **7**. The ^{1}H−^{15}N HMBC spectra contain three ^{15}N NMR chemical shifts that correlate to ^{1}H NMR resonances of the three inequivalent oxazoline rings (see Table 1). Tellingly, the ^{15}N NMR resonance at −221 ppm also contains a strong cross peak with a singlet at 3.33 ppm (3 H) corresponding to a N−CH$_3$ through-bond interaction. We have no evidence for an iridium methyl species at any stage of the transformations. Interestingly, the reaction of **4** and MeI provides the oxazoline-methylated species, while the reaction of MeI and carbonyl compound **5** affords a complex mixture of products.

Given the ubiquity of oxazolines as ligands in catalytic processes involving electrophiles such as allylic substitution, this oxazoline alkylation may represent an important route for catalyst deactivation.[13] Therefore, we are currently exploring the reactions of [Ir(To^{P})L$_2$] complexes with catalytically relevant electrophiles while preparing a range of C_3-symmetric tris(2-oxazolinyl)borate complexes for stereoselective catalysis.

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Supporting Information Available: Experimental procedures and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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