Synthesis and Oxidation Catalysis of [Tris(oxazolinyl)borato]cobalt(II) Scorpionates

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Synthesis and Oxidation Catalysis of [Tris(oxazolinyl)borato]cobalt(II) Scorpionates

Abstract
The reaction of CoCl₂·THF and thallium tris(4,4-dimethyl-2-oxazolinyl)phenylborate (TlToM) in tetrahydrofuran (THF) provides ToMCoCl (1) in 95% yield; however, appropriate solvents and starting materials are required to favor 1 over two other readily formed side-products, (ToM)₂Co (2) and {HToM}CoCl₂ (3). ESR, NMR, FTIR, and UV/Vis spectroscopies were used to distinguish these cobalt(II) products and probe their electronic and structural properties. Even after the structures indicated by these methods were confirmed by X-ray crystallography, the spectroscopic identification of trace contaminants in the material was challenging. The recognition of possible contaminants in the synthesis of ToMCoCl in combination with the paramagnetic nature of these complexes provided impetus for the utilization of X-ray powder diffraction to measure the purity of the ToMCoCl bulk sample. The X-ray powder diffraction results provide support for the bulk-phase purity of ToMCoCl in preparations that avoid 2 and 3. Thus, 1 is a precursor for new [tris(oxazolinyl)borato]cobalt chemistry, as exemplified by its reactions with KOᵗBu and NaOAc to give ToMCoOᵗBu (4) and ToMCoOAc (5), respectively. Compound 5 is a catalyst for the oxidation of cyclohexane with meta-chloroperoxybenzoic acid (mCPBA), and the rate constants and selectivity for cyclohexanol versus cyclohexanone and ε-caprolactone were assessed.

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This is the peer reviewed version of the following article: Reinig, Regina R., Debabrata Mukherjee, Zachary B. Weinstein, Weiwei Xie, Toshia Albright, Benjamin Baird, Tristan S. Gray et al. "Synthesis and Oxidation Catalysis of [Tris (oxazolinyl) borato] cobalt (II) Scorpionates." European Journal of Inorganic Chemistry 2016, no. 15-16 (2016): 2486-2494, which has been published in final form at DOI: 10.1002/ejic.201600237. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

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Regina R. Reinig, Debabrata Mukherjee, Zachary B. Weinstein, Weiwei Xie, Toshia Albright, Benjamin Baird, Tristan S. Gray, Arkady Ellern, Gordon J. Miller, Arthur H. Winter, Sergey L. Bud’ko, and Aaron D. Sadow*

**Abstract:** The reaction of CoCl$_2$-THF and thallium tris(4,4-di-methyl-2-oxazolinyl)phenylborate (TTiO$^+$) in tetrahydrofuran (THF) provides Ti$^+$CoCl (1) in 95 % yield; however, appropriate solvents and starting materials are required to favor 1 over two other readily formed side-products, (ToM)$_2$Co (2) and (HToM)CoCl$_2$ (3). ESR, NMR, FTIR, and UV/Vis spectrosopies were used to distinguish these cobalt(II) products and probe their electronic and structural properties. Even after the structures indicated by these methods were confirmed by X-ray crystallography, the spectroscopic identification of trace contaminants in the material was challenging. The recognition of possible contaminants in the synthesis of ToMCoCl in combination with the paramagnetic nature of these complexes provided impetus for the utilization of X-ray powder diffraction to measure the purity of the ToMCoCl bulk sample. The X-ray powder diffraction results provide support for the bulk-phase purity of ToMCoCl in preparations that avoid 2 and 3. Thus, 1 is a precursor for new [tris(oxazolinyl)borato]cobalt chemistry, as exemplified by its reactions with KOrBu and NaOAc to give ToMCoOOrBu (4) and ToMCoOAc (5), respectively. Compound 5 is a catalyst for the oxidation of cyclohexane with meta-chloroperoxybenzoic acid (mCPBA), and the rate constants and selectivity for cyclohexanol versus cyclohexanone and ε-caprolactone were assessed.

### Introduction

Tridentate fac-coordinating monoanionic scorpionate-type ligands support and stabilize first-row metal centers bonded to reactive moieties including hydride, alkyl groups containing β-hydrogen atoms, imido and oxido ligands, azides, and oxidizing moieties such as peroxides. In addition, 3d metal compounds coordinated by scorpionate ligands have served as models for metal sites in enzymes and provided motivation to study their spectroscopic and structural features in detail. Typically, sterically encumbered scorpionates are required to support reactive species such as peroxides and superoxides.

Variation of the steric and electronic properties of the ancillary scorpionate donors can greatly influence the stability of reactive moieties and the reactivity of the complexes. For example, the steric encumbrance of tris(3-tert-butyl-5-methylpyrazolyl)borate (TpBu,Me$^+$), known as the tetrahedral enforcer, stabilizes reactive groups such as alkyl peroxides. However, this stabilization may also limit catalytic oxidation chemistry of bulky scorpionates compared to the well-known reactivity of other first-metal complexes. The smaller parent tris(pyrazolyl)borate (Tp) or tris(3,5-dimethyl-pyrazolyl)borate (Tp*) ligands, which might provide more accessible metal centers, instead form octahedral {κ$^3$-Tp}$_2$M compounds. Even the bulkier tris(3-phenyl-5-methylpyrazolyl)borate (TpPh,Me$^+$) ligand forms octahedral TpPh,Me$_2$Co upon isomerization of a pyrazole ring. Thus, the steric properties of non-pyrazolyl-based scorpionate ligands, such as those involving nonplanar oxazoline donors, may sufficiently stabilize reactive moieties and also allow new metal-centered reactivity that involves switching between four- and five-coordinate species in a way not accessible with TpBu$^+$-based compounds.

Recently, we discovered that tris(4,4-di-methyl-2-oxazolinyl)phenylborate (ToM$^+$) supports reactive main-group complexes of mononuclear and tetrahedral zinc(II) and magnesium(II). For example, a catalytically active mononuclear zinc hydride was readily synthesized by the reaction of ToM$^+$ZnOrBu and PhSiH$_3$. The ToM$^+$ZnX system also supports and stabilizes alkyl peroxides, such that ToM$^+$ZnOOEt is thermally persistent even at temperatures above 100 °C. Moreover, ToM$^+$ZnEt is sufficiently reactive to undergo selective oxidation upon treatment with O$_2$ to give ToM$^+$ZnOOEt. ToM$^+$ gives a more open geometry and bowl-like steric profile, in contrast to the tetrahedral enforcer TpBu,Me$^+$ that typically stabilizes reactive moieties.

These examples provide motivation for studying the synthesis and reactivity of tetrahedral first-row transition-metal centers supported by ToM, in which redox-active metal centers could lead to new chemistry and catalysis. In particular, the electron-donating properties and bowl-like steric environment provided by the coordination pocket of ToM could stabilize reactive...
groups bonded to metal centers with accessible d electrons to facilitate catalytic chemistry. Moreover, a series of optically active tris(2,2'-oxazolyl)phenylborate ligands are also available for imposing chiral environments on tetrahedrally coordinated first-row transition-metal sites.

The present study describes the synthesis and characterization of TlToMCoCl (1) as a precursor to reactive complexes. We also provide syntheses and characterization data of CoCl₂·(HToM)CoCl₂ (2) and CoCl₃ (3), which are side-products discovered during exploratory syntheses toward 1. The open steric profile of the TlToM ligand results in additional synthetic challenges compared with syntheses of sterically encumbered tris(pyrazolyl)borate-based first-row metal compounds, in terms of controlling the formation of 1, 2, and 3. The chlorido ligand in 1 may be substituted through salt-metathesis reactions to give ToMCoCl (4) and ToMCoOAc (5) without ToM transmetalation or ligand redistribution demonstrating that 1 is a viable synthetic precursor for new cobalt(II) compounds. Complex (5) was studied as a catalyst for the oxidation of cyclohexane. Although the selective oxidation of cyclohexane remains a challenge, cobalt complexes have shown great promise in this area. [9d]

Results and Discussion

The reaction of TlToM and CoCl₂·THF (THF = tetrahydrofuran) affords TlToMCoCl (1) as a bright blue solid in excellent yield (Equation (1)). TlToMCoCl is paramagnetic, and its identity as a pseudotetrahedral d⁷ center is supported by a host of characteristic data including ¹H and ¹³B NMR spectroscopy, IR spectroscopy, UV/Vis spectroscopy, ESR spectroscopy, X-ray diffraction studies, elemental analysis, and magnetic measurements that included both magnetometry and the Evans method. Many of these tools were needed initially to interpret the spectroscopic data, as the identities of the paramagnetic products were challenging to establish, and later to demonstrate the purities of the isolated materials. As outlined below, the ratio of TlToM/CoCl₂, the use of CoCl₂·THF, and the choice of solvent are crucial to the high-yielding synthesis of 1 without contamination with the readily formed side-products ToM₂Co (2) and (HToM)CoCl₂ (3).

\[8 \text{ToMNNN} + \text{CoCl}_2\cdot\text{THF} \rightarrow \text{1, 95%} \]

The signals in the ¹H NMR spectrum of TlToMCoCl dissolved in [D₆]benzene were broad and dispersed over a large chemical-shift range, as expected for a paramagnetic compound. Despite these spectroscopic effects, the number of ¹H NMR signals and their integrated ratio provided characteristic data associated with a pseudo-⁴CN-symmetric oxazolylborate species. Broad resonances at δ = 8.38 (18 H) and 24.88 ppm (6 H) were assigned to the methyl and methylene groups, respectively, of equivalent oxazoline rings in the TlToM ligand. The equivalence of the rings suggested the tridentate coordination of the TlToM ligand to the cobalt center. A ¹⁵N NMR signal at δ = −29 ppm was shifted significantly from the isotropic value observed for the TlToM ligand in diamagnetic environments (e.g., the ¹⁵N NMR chemical shift of TlToM is δ = −16 ppm). This paramagnetically shifted ¹³B NMR resonance further indicated the successful conversion of diamagnetic TlToM to a new species, and we note that the ¹⁵N NMR spectrum is useful for counting the number of TlToM species in the reaction mixture.[16]

The infrared spectrum contained a band at ʋ = 1598 cm⁻¹ (KBr), which was assigned to the C=N stretching mode (ʋCN) of the oxazoline groups. Typically, higher-energy ʋCN bands (ʋ > 1615 cm⁻¹) are observed for dissociated oxazoline moieties in oxazolylborate ligands; therefore, this data further supports tridentate ligand coordination. In addition, the observation of only a single peak from the symmetric mode (the asymmetric ʋCN band had low intensity) in the solid-state and solution IR spectra (at ʋ = 1586 cm⁻¹) suggested a similar configuration in the two phases. The tetrahedral geometry of 1 was also supported by the electronic absorption spectrum (Figure 1), which contained a band from λ = 550 to 700 nm with λmax at 568 (ε = 362 M⁻¹ cm⁻¹) and 635 nm (ε = 641 M⁻¹ cm⁻¹). The larger peak was sandwiched by shoulders at λ ≈ 600 and 660 nm. The spectra of high-spin pseudotetrahedral cobalt(II) complexes show peaks in this range, and these signals are likely related to the many-featured ʋb band [⁴T₁(P) ← ⁴A₂(F)] observed for [CoCl₄]²⁻.[17] The TlToMCoCl spectrum is also similar to the spectra of related tris(pyrazolyl)borate (Tp) cobalt(II) complexes such as TpBu₄MeCoCl with maxima at λ = 526, 602, 636, and 660 nm[18] or Tp²B₄CoEt, which exhibited maxima at λ = 580, 610, and 690 nm.[19] For tetrahedral Co(II) complexes, two lower-energy transitions [⁴T₁(F) ← ⁴A₂(F)] and [⁴T₂(F) ← ⁴A₂(F)] are also expected. Indeed, a weak absorption was also observed at λ ≈ 1000 nm.

![UV-vis Absorption spectra](image)

Figure 1. UV/Vis spectra of TlToMCoCl (1), ToM₂Co (2), (HToM)CoCl₂ (3), and TlToMCoOBU (4).

The paramagnetic nature of 1 was further investigated by magnetic susceptibility measurements and ESR spectroscopy.
The Evans method revealed a solution magnetic moment of 4.5(2) \(\mu_B\). This data is consistent with a high-spin cobalt(II) complex (\(S = 3/2\), for which spin-only \(\mu_{\text{eff}} = 3.9 \mu_B\)) with the \(^4A_2\) ground state, as discussed above. This electronic configuration was maintained at low temperature according to magnetometry measurements, which showed \(\mu_{\text{eff}} = 4.3(1) \mu_B\) at 10.3 K. The ESR spectrum (X-band, 10 K) of a neat point sample revealed the low, rhombic site symmetry. The ESR spectrum was simulated for an \(S = 3/2\) spin system with anisotropic \(g\) values of \(g_x = 5.96(2)\), \(g_y = 3.50(2)\), and \(g_z = 2.10(2)\). Similar \(g\) values have been reported for other pseudotetrahedral cobalt(II) complexes featuring rhombic symmetry.\(^{[21,22]}\) Hyperfine coupling to \(^{59}\)Co (\(I = 7/2\)) was not detected under these conditions.\(^{[21]}\)

Blue crystals of 1, obtained from a saturated toluene solution cooled to –38 °C, were determined to be ToMCoCl through an X-ray diffraction study (Figure 2). The X-ray crystal structure revealed a pseudotetrahedral cobalt center coordinated by the tridentate tris(oxazolinyl)borate ligand. Compound 1 and ToM\(^{11}\)Zn\(^{2+}\)\(^{[23]}\) have similar structural features. For example, the Co–N and Zn–N bond lengths range from 2.0091(9) to 2.040(1) Å; the zinc complex has both the highest and the lowest bond lengths. The N–M–Cl angles range from 115.33(4) to 130.82(4)° for the two compounds, and the cobalt compound has the extreme angles. In addition, the B–M–Cl angles of 170.99(3) and 174.27(2)° for the cobalt and zinc complexes show a slight displacement of the Cl atom from the anticipated position in a pseudo-C\(_2\)\(_h\) structure, and this distortion is slightly larger for the cobalt complex. The structural similarity of diamagnetic zinc(III) and paramagnetic cobalt(II) compounds suggests that these distortions are sterically controlled rather than the result of electronic influences. The Co1–C11 bond length of 2.2025(4) Å in 1 is similar to that observed in other four-coordinate cobalt(II) scorpionate complexes [e.g., Tp\(^{11}\)MgCoCl, 2.2004(9) Å; Tp\(^{11}\)MnCoCl, 2.216(2) Å; and Tp\(^{11}\)MnCoCl, 2.2204(9) Å].\(^{[18,24]}\)

Although the reaction of TiTo\(^{11}\)M and CoCl\(_2\)-THF is reproducible, the choice of CoCl\(_2\)-THF is critical to a successful and high-yielding synthesis. In micromolar-scale reactions, equimolar amounts of TiTo\(^{11}\)M and CoCl\(_2\)-THF provide 1 quantitatively. Excess CoCl\(_2\)-THF (1.5 equiv.) is needed in larger-scale preparations to optimize the TiTo\(^{11}\)CoCl yield (calculated with respect to TiTo\(^{11}\)M), because the separation of TiTo\(^{11}\)CoCl from CoCl\(_2\)-THF is easier than that from (ToM)\(_2\)Co (2). In contrast, the reaction of anhydrous CoCl\(_2\) and TiTo\(^{11}\)M in THF provides a purple mixture of 1 and 2. During our initial synthetic studies, the appearance of two sets of signals in the \(^1H\) NMR spectra and the formation of purple material in these reactions made the isolation and characterization of pure TiTo\(^{11}\)CoCl challenging. The \(^1H\) NMR spectrum of the purple reaction mixture contained signals at \(\delta = 15.1\) and 12.5 ppm as well as the resonances later assigned to 1. The formation of two paramagnetic TiTo\(^{11}\)Co species was also suggested by the two \(^{11}B\) NMR signals at \(\delta = –29\) and 42 ppm; the former was assigned to TiTo\(^{11}\)CoCl, and the latter was assigned to (ToM)\(_2\)Co on the basis of a single-crystal X-ray diffraction study and its independent synthesis, which is described below. Repeated recrystallizations from saturated toluene solutions at –38 °C yielded purple X-ray-quality crystals, and a single-crystal diffraction study revealed that the substance was (ToM)\(_2\)Co (2; Figure 3).

The cobalt center in 2, as in 1, has a distorted tetrahedral geometry. Each of the tris(oxazolinyl)borate ligands in 2 is bidentate with one non-coordinated oxazoline ring, and the structure is similar to the solid-state structures of (ToM)\(_2\)Mg and (ToM)\(_2\)Zn.\(^{[13,25]}\) Although the (κ\(^2\)-Tp\(^{11}\))Co structure forms readily, the To\(^{11}\) ligand apparently does not support six-coordinate pseudo-sandwich-type first-row metal compounds, in contrast to (κ\(^2\)-Tp\(^{11}\))\(_2\)M compounds.\(^{[26]}\) Moreover, we have not observed disproportionation of TiTo\(^{11}\)CoCl into TiTo\(^{11}\)Co and CoCl\(_2\) therefore, TiTo\(^{11}\)CoCl may be a suitable precursor for the synthesis of new inorganic compounds through chloride substitution. The crystallographic data show that the metal centers are sterically protected by the oxazoline methyl groups, and this likely prevents the formation of the six-coordinate structure. Compound 2 has shorter Co–N interatomic distances than 1, and all of the
N–Co–N angles in 2 are larger than those in 1. The interatomic distances and angles of 2 fall between those of (ToM)2Mg and (ToM)2Zn and bear greater resemblance to those of the latter. For example, the Co–N bonds in 2 are shorter than those in (ToM)2Mg by ca. 0.05 Å but are equivalent within error to the Zn–N bonds encountered in (ToM)2Zn.

Unfortunately, purification by crystallization is not effective for preparative-scale separations of mixtures of (ToM)2Co and ToMCoCl. Moreover, the 1H NMR spectrum of the reaction mixture did not contain features that easily identified inequivalent oxazoline rings in the bidentate-coordinated structure. We prepared 2 independently to confirm that the unidentified signals in the 1H NMR spectrum of the mixture of cobalt species corresponded to 2. The reaction of CoCl2 and 2 equiv. of TlToM affords purple (ToM)2Co in excellent yield (Equation (2)). (ToM)2Co and ToMCoCl are similarly soluble in benzene, toluene, diethyl ether, THF, and dichloromethane, and this similarity likely causes the difficulties with the separation of mixtures of the two compounds.

The 1H and 11B NMR spectra of isolated 2 contained signals that matched those detected in the crude mixture with 1; therefore, (ToM)2Co is indeed the second product obtained when anhydrous CoCl2 is the starting material. However, these NMR spectroscopic data did not allow the direct quantitative estimation of the purity and offered few further structural insights. In contrast, the bands at $\tilde{\nu} = 1603$ and 1554 (KBr) or 1609 and 1555 cm$^{-1}$ (CH2Cl2) in the infrared spectrum of 2 were structurally consistent. These signals were assigned to the $v_{\text{CN}}$ modes of non-coordinated and coordinated oxazoline groups, respectively, with the bidentate bonding mode determined by X-ray crystallography.

Furthermore, the d–d transitions in the UV/Vis spectrum of 2 again appeared in the expected region for a high-spin tetrahedral Co$^{II}$ complex at $\lambda_{\text{max}} = 562$ ($\varepsilon = 539$ M$^{-1}$ cm$^{-1}$) and 576 nm ($\varepsilon = 552$ M$^{-1}$ cm$^{-1}$). These signals were similar to those observed for the four-coordinate C$_2$-symmetric Bp$_2$Co species [Bp = H$_2$B(C$_3$N$_2$H$_3$)$_2$].\(^{1(a)}\) The center of gravity of this band was blueshifted with respect to that for the related transition in 1 (see the absorption spectra in Figure 1). Note that a similar relationship was described between Bp$_2$Co and TpCoCl in terms of a blueshifted absorption for the $^4T_1(P) \leftrightarrow ^2A_2(F)$ transition (for the tetrahedral site).\(^{1(b)}\) A second, lower-energy band was observed at $\tilde{\nu} = 1040$ nm ($\varepsilon = 120$ M$^{-1}$ cm$^{-1}$), and this band was redshifted and more intense than the band for the transmetalation for CoCl$_2$ compared to 1, and these rates are likely influenced by the heterogeneous nature of the reaction mixture. This contrasts with the reactivity of bulky [tris(pyrazolyl)borato]cobalt compounds. For example, Tp$^{\text{Ph,Me}}$CoCl and Tp$^{\text{Ph,Me}}$Tl do not afford Tp$^{\text{Ph,Me}}$CoCl.\(^{1(11)}\)

In the course of our studies of the selective preparation of 1, polar solvents were tested to give a monophasic reaction (i.e., to improve the kinetics). In fact, the reaction of TlToM and CoCl2 under equivalent conditions. In the attempted synthesis of 1 from anhydrous CoCl2, the poor selectivity is hypothesized to come from the relative rates of transmetalation for CoCl2 versus 1, and these rates are likely influenced by the heterogeneous nature of the reaction mixture. This contrasts with the reactivity of bulky [tris(pyrazolyl)borato]cobalt compounds. For example, Tp$^{\text{Ph,Me}}$CoCl and Tp$^{\text{Ph,Me}}$Tl do not afford Tp$^{\text{Ph,Me}}$CoCl.

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The crystal structure of 3 shows a tetrahedral cobalt center featuring two chlorido ligands and a bidentate ToM–cobalt interaction. The third oxazoline ring is protonated, and HToM may be viewed as an overall charge-neutral ligand coordinated to CoCl₂. Thus, (HToM)CoCl₂ differs from 1 and 2 by its zwitterionic nature. Related iridium and rhodium compounds of protonated or methylated tris(oxazolinyl)borate complexes have been reported, as have zwitterionic cobalt(II) complexes stabilized by bulky tris(carbene)borate ligands.[16,27] Compared with 1, compound 3 features slightly longer Co–Cl bonds (by more than 0.034 Å) and shorter Co–N bonds (by more than 0.025 Å).

The reaction of 1 and [HOEt₂]Cl provides an independent synthesis of 3 [Equation (3)]. Alternatively, LiToM and CoCl₂ react in wet dichloromethane to provide crystals of 3 directly from the reaction mixture.

\[
\begin{align*}
\text{Ph-B} & \quad \text{Co-Cl} \\
\text{r.t., 0.5 h} & \quad \text{THF} \\
+ [\text{HOEt}_2]\text{Cl} & \quad 3 \\
\text{77%}
\end{align*}
\]

Compound 3 is highly soluble in dichloromethane and methanol but poorly soluble in benzene, toluene, tetrahydrofuran, and diethyl ether. The poor solubility of 3 and the high solubility of 1 in [D₆]benzene can result in erroneous interpretation of the purity of ToMCoCl on the basis of the NMR spectra of crude reactions mixtures. Thus, dry [D₂]dichloromethane is the best solvent for unambiguous NMR analysis of the purity of these compounds. The 'H NMR spectrum of 3 in dichloromethane showed paramagnetically shifted 'H NMR signals that were unassignable yet characteristic (Figure S5). The 11B NMR signal appeared at δ = -7.5 ppm, and this peak was much less shifted from the diamagnetic range than those of 1 and 2. The infrared spectrum was consistent with the crystallographically determined structure and provided structural insights. The bands at ν = 1588 and 1598 cm⁻¹ were assigned to νCN of cobalt-coordinated oxazoline and protonated oxazoline, respectively. Compound 3 was also a high-spin CoII species, on the basis of magnetometry experiments that indicated a μeff of 4.2(1) μB at 5 K.

As all three compounds were formed from the same starting materials and 'H NMR spectroscopy provided ambiguous results during the course of these synthetic studies, we instead utilized powder XRD measurements to characterize the bulk compositions of the samples. These experiments, along with solution and solid-state IR spectroscopy, provide a connection between the solid-state and molecular structures that usually relies on solution-phase NMR spectroscopy [which was structurally uninformative for these (oxazolinylborato)cobalt(II) compounds]. Powder XRD is an appealing alternative characterization technique, because it is not complicated by the electronic structure or unpaired electrons and probes the composition of the crystalline component of the bulk powder.

The experimental powder XRD patterns matched the corresponding XRD patterns calculated from the single-crystal data for samples of 1, 2, and 3 (Table S1). These results provided additional confidence that the single-crystal diffraction experiments corresponded to structures that describe the bulk samples. For example, the powder XRD experiments indicated that the preparation from CoCl₂-THF gives a reproducible and high-yielding route to 1 (Figure 5).

The viability of this method for the measurement of the purity was further tested with analytically pure 3/1 in a 50:50 ratio.

![Figure 5. X-ray powder diffraction pattern of ToMCoCl (1) at 293 K with Cu-Kα radiation. The observed pattern (A) is shown in black, and the calculated intensity pattern (B) is indicated by red solid lines.](image-url)

Figure 5. X-ray powder diffraction pattern of ToMCoCl (1) at 293 K with Cu-Kα radiation. The observed pattern (A) is shown in black, and the calculated intensity pattern (B) is indicated by red solid lines.
The XRD pattern of this mixture matched the expected powder pattern and verified that the presence of the two products could be identified by the diffraction method.

We also attempted to synthesize ToMCoX compounds using cobalt acetate as the starting material. However, the reaction of cobalt acetate and TlToM generated a mixture of 2 and another species, which was later identified as ToMCoOAc (see below). Thus, CoCl2·THF is the preferred starting material for the entry into the cobalt(II) chemistry of tris(oxazolinyl)borate ligands.

With isolable, fully characterized, and spectroscopically and analytically pure ToMCoCl in hand, we tested its reactivity in halide substitutions to prepare ToMCoO\textsubscript{t}Bu (4) and ToMCoOAc (5). The reaction of ToMCoCl and KO\textsubscript{t}Bu in tetrahydrofuran readily provides ToMCoO\textsubscript{t}Bu [Equation (4)].

\[
\text{To}^3\text{MCoCl} + \text{KO}^t\text{Bu} \rightarrow \text{To}^3\text{MCoO}^t\text{Bu}
\]

In the \(^1\)H NMR spectrum of 4, all of the signals were readily assigned by integration, including a new signal at \(\delta = 11.16\) ppm that integrated to 9 H relative to the ToM signals. This resonance was assigned to the O\textsubscript{t}Bu group. Moreover, a new \(^{11}\)B NMR signal was detected at \(\delta = 73\) ppm, which was further downfield than those of the other cobalt complexes. The paramagnetically shifted \(^{11}\)B NMR spectrum rules out the transmetalation of the ToM ligand to K.

Unlike blue ToMCoCl, compound 4 is purple. Accordingly, the UV/Vis absorption spectrum of 4 contained a broad peak with a blueshifted onset edge at \(\lambda \approx 500\) nm, as might be expected owing to the replacement of the weak-field chlorido ligand with a tert-butoxide ligand. The tridentate coordination of the tris(oxazolinyl)borate ligand to the cobalt center was suggested by a single strong IR band at \(\nu = 1590\) cm\(^{-1}\), which was assigned to the oxazoline \(\nu\text{CN} \) mode. Compound 4 is a high-spin cobalt(II) complex from room temperature to 36 K, as determined by magnetometry measurements [\(\mu_{\text{eff}} = 4.6(1)\mu_B\) at 36 K].

The recrystallization of 4 from toluene at –35 °C provided X-ray-quality crystals, and a single-crystal X-ray diffraction study confirmed the identity of 4 as ToMCoO\textsubscript{t}Bu (Figure 6). The Co–N bonds in 4 are longer than those in 1. In addition, the B1–Co1–O4 angle in 4 is smaller than the B1–Co1–Cl1 angle in 1. The Co1–O4–C22 angle is 134.2(2)°, and this angle wedges the \text{t}Bu group between the methyl groups of the N2 and N3 oxazolines.

The reaction of ToMCoCl and NaOAc in THF provides ToMCoOAc (5) as a light purple solid in high isolated yield \([97\%; \text{Equation (5)}]\). Compound 5 was characterized by \(^1\)H and \(^{11}\)B NMR spectroscopy. The \(^1\)H NMR spectrum contained new tris(oxazolyl)phenylborate signals, and the acetate signal appeared far downfield (\(\delta = 171.25\) ppm). The \(^{11}\)B NMR signal of 5 appeared at \(\delta = 95\) ppm, which is downfield relative to the signals for 1 and 4.

\[
\text{To}^3\text{MCoCl} + \text{NaOAc} \rightarrow \text{To}^3\text{MCoOAc}
\]

In the IR spectrum, a single band corresponding to the oxazoline \(\nu\text{CN} \) stretching mode was observed at \(\nu = 1591\) cm\(^{-1}\). Compound 5 is high spin \([\mu_{\text{eff}} = 4.8(2)\mu_B]\), as determined by the Evans method. X-ray-quality crystals were obtained by recrystallization from pentane at –35 °C (Figure 7). The Co–O bonds \([2.098(2)\text{ and } 2.089(2)\text{ Å}]\) are longer than the Co–O bond...
and determine the concentrations of cyclohexanol, cyclohexanone, and ε-caprolactone. In this oxidation catalysis, selectivity for a single oxidation to cyclohexanol, rather than over-oxidation to cyclohexanone or ε-caprolactone, is desired. Despite the important role of cobalt in oxidation chemistry, TpCoX-based compounds are reported as not effective for cyclohexane oxidation, so a study of ToMCoOAc as an oxidation catalyst provides a comparison with the pyrazolylborate analogues.

Complex 5 catalyzes the oxidation of cyclohexane to cyclohexanol with meta-chloroperoxybenzoic acid (mCPBA) as the terminal oxidant and affords 536 equiv. of cyclohexanol per 1 equiv. of catalyst after 7 h. At the early stages of the reaction (3 h), the product ratio for cyclohexanol/cyclohexanone/ε-caprolactone is 20:1.5:1 with 337 equiv. of cyclohexanol formed per 1 equiv. of 5. This selectivity decreases as the reaction proceeds, and ε-caprolactone is formed from the reaction of mCPBA and cyclohexanone. Cumene hydroperoxide and tert-butyl hydroperoxide were tested as oxidants for this catalytic transformation, but only mCPBA afforded the desired conversion. A control experiment, in which cyclohexane and mCPBA were mixed at room temperature, did not provide detectable quantities of cyclohexanol, cyclohexanone, or ε-caprolactone. Furthermore, anhydrous CoCl₂ or anhydrous Co(OAc)₂ [as Co₂(OAc)₃·OH] are poorly soluble under these reaction conditions, and this limits comparisons with 5. However, the partially soluble suspended materials give lower activities and poorer selectivities than 5 under comparable conditions.

To better identify the parameters associated with the oxidation process, the reaction mixture was monitored by GC to determine the concentrations of cyclohexanol, cyclohexanone, and ε-caprolactone. In a reaction with 0.16 mM 5, the concentration of cyclohexanol reaches a steady state after ca. 300 min. The plot of [cyclohexanol] versus time in Figure 8 can be fitted with a nonlinear least-squares regression (R = 0.98) to Equation (6).

\[ [\text{C}_6\text{H}_{12}\text{O}]_t = \frac{k_1}{k_2 - k_1} \{e^{-k_1 t} - e^{-k_2 t}\} \]

From this analysis, the observed rate constant for the oxidation of cyclohexane to cyclohexanol (k₁) is 1.69(8) × 10⁻⁴ s⁻¹, and that for the oxidation of cyclohexanol is 3.91(1) × 10⁻³ s⁻¹ (average of four experiments, see the Supporting Information for individual curves). Thus, the selectivity for cyclohexanol production comes largely from the high initial [C₆H₁₂]. On the basis of these results, we are currently studying reaction conditions (temperature, solvent polarity, and reagent concentrations) and catalyst structures that favor higher k₁ values and smaller k₂ values.

Conclusions

The synthesis of 1 from TlToM and CoCl₂·THF provides an entry point into [tris(oxazolinyl)borato]cobalt chemistry. Like zinc and magnesium compounds, four-coordinate pseudotetrahedral cobalt complexes are supported by the tris(oxazolinyl)borate ligand, despite its reduced steric profile with respect to that of the highly bulky tert-butyl-substituted tris(pyrazolyl)borate scorpionates. The starting materials and reaction conditions are critical for obtaining 1, rather than 2 or 3. However, these other two compounds can be prepared by using 2 equiv. of TlToM or polar protic solvents, respectively. Once the paramagnetic compounds were fully characterized by X-ray diffraction as well as IR, NMR, and UV/Vis spectroscopy, the characteristic spectroscopic signatures in the ¹¹B NMR spectra, ¹H NMR spectra, and powder XRD patterns are useful for establishing the synthetic reproducibility and product identities as well as the purities of the materials.

ToMCoCl is reactive with KOtBu and NaOAc in salt-metathesis reactions. In this context, we are currently working to synthesize, characterize, and study the reactivity of alkylcobalt(III) compounds supported by tris(oxazolinyl)borate ligands. ToMCoOAc is a catalyst for the selective oxidation of cyclohexane, in contrast to [tris(pyrazolyl)borato]cobalt compounds. We are currently preparing optically active analogues to study enantioselective C–H bond functionalization.

Experimental Section

General Experimental Methods: All reactions were performed by standard Schlenk techniques under dry argon. Tetrahydrofuran, diethyl ether, and toluene were dried and deoxygenated with an IT PureSolv system. [D₆]Benzene was heated under reflux over Na/K alloy and vacuum-transferred. CoCl₂ (Strem) was used to prepare CoCl₂·THF by Soxhlet extraction of CoCl₂ with THF. TlToM was synthesized according to reported procedures.

Caution: Thallium salts are highly toxic, and thallium-containing compounds and waste should be handled appropriately.
KOrBu was purified by sublimation. mCPBA was purified by washing with K$_2$HPO$_4$/KH$_2$PO$_4$ buffer solution (pH 7.5).\textsuperscript{32} The 1H and 11B NMR spectra were recorded with a Bruker Avance III 600 spectrometer. The 13C NMR spectra were referenced to an external sample of BF$_3$-Et$_2$O. The infrared spectra were measured with a Bruker Vertex 80 FTIR spectrometer. The electron paramagnetic resonance (EPR) spectra were obtained with an X-band Elexsy 580 FT-EP spectrometer in continuous-wave mode, and the spectra were simulated with XSophe. The direct current (DC) magnetization was measured with a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) magnetometer. The UV/Vis spectra were recorded with an Agilent 8453 UV/Vis spectrophotometer with the analyte (2 mm) in dichloromethane. Elemental analyses were performed with a Perkin-Elmer 2400 Series II CHN/S analyzer. The catalytic cyclohexane oxidation experiments and the kinetic studies were performed with a Chemspeed Technologies SWING-XL automated platform. GC–MS was performed with conditions similar to those previously reported by Hickichi et al.\textsuperscript{30,32} A reaction flask was charged with cyclohexane (1.6 mL, 15 mmol, 2.45 M) and ToMCoOAc (1 μmol, 0.024 mmol, 96.7 %). X-ray-quality crystals were obtained from pentane at –40 °C. 1H NMR (D$_2$O, benzene, 600 MHz): δ = 171.25 (3 H, O2CMe), 33.36 (2 H, C$_6$H$_5$), 17.86 (2 H, C$_6$H$_5$), 15.06 (s, 1 H, p-C$_6$H$_5$), 12.40 (s, 6 H, CNCMe$_2$CMe), 10.22 (s, 18 H, CNCMe$_2$O) ppm. 11B NMR (D$_2$O, benzene, 128 MHz): δ = 23.3 ppm. IR (KBr): ν = 2966 (m), 2930 (m), 2889 (m), 1590 (m), 1465 (m), 1343 (m), 1264 (m), 1278 (m), 1251 (m), 1193 (m), 1158 (m), 1022 (m), 966 (m), 928 (m) cm$^{-1}$. UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (ε) = 524 (245), 575 (327), 624 (179), 657 (148 m$^{-1}$ cm$^{-1}$) nm. C$_{25}$H$_{38}$BCoN$_3$O$_4$ (514.3) calcd. C 58.38, H 6.11, N 7.62; found C 58.37, H 6.14, N 7.57. M.p. 218–221 °C (dec.).

ToMCoCl$_2$ (2): Complex 1 (0.199 g, 0.417 mmol) was dissolved in THF (10 mL) and the solution was added to KOzBu (0.053 g, 0.472 mmol) to instantly afford a purple solution. The reaction mixture was stirred overnight, and then KCl was removed by filtration. The volatiles were evaporated in vacuo to afford a bright purple solid. The purple solid was washed with pentane (3 × 5 mL) and dried under vacuum to yield ToMCoCl$_2$ (0.192 g, 0.367 mmol, 86.8 %). X-ray-quality crystals were obtained from pentane at –40 °C. 1H NMR (D$_2$O, benzene, 600 MHz): δ = 171.25 (3 H, O2CMe), 33.36 (2 H, C$_6$H$_5$), 17.86 (2 H, C$_6$H$_5$), 15.06 (s, 1 H, p-C$_6$H$_5$), 12.40 (s, 6 H, CNCMe$_2$CMe), 10.22 (s, 18 H, CNCMe$_2$O) ppm. 11B NMR (D$_2$O, benzene, 128 MHz): δ = 23.3 ppm. IR (KBr): ν = 2966 (m), 2930 (m), 2889 (m), 1590 (m), 1465 (m), 1343 (m), 1264 (m), 1278 (m), 1251 (m), 1193 (m), 1158 (m), 1022 (m), 966 (m), 928 (m) cm$^{-1}$. UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (ε) = 524 (245), 575 (327), 624 (179), 657 (148 m$^{-1}$ cm$^{-1}$) nm. C$_{23}$H$_{34}$BCoN$_5$O$_6$ (513.1) calcd. C 58.38, H 6.11, N 7.62; found C 58.37, H 6.14, N 7.57. M.p. 218–221 °C (dec.).
Acknowledgments

This research was supported by the U.S. Department of Energy through the Ames Laboratory (Contract No. DE-AC02-07CH11358). Synthesis and catalysis work were supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. The powder XRD and SQUID measurements were supported by the Division of Materials Science. The Chemspeed SwingXL Automated Robotic Catalysis Platform was supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

Keywords: Scorpionates · Oxazolines · Cobalt · Structure elucidation · Oxidation