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Removing the Sting from the Tail: Reversible Protonation of Scorpionate Ligands in Cobalt(II) Tris(carbene)borate Complexes

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Low-temperature deprotonation of the phenylborane dications, $PhB(RIm)_3OTf_2$ (R = ^{t}Bu, Mes), followed by in situ reaction with $CoCl_2(thf)_{1.5}$, results in the formation of the four-coordinate complexes, κ^3-$PhB(RIm)_3CoCl$, in which the metal is supported by tripodal N-heterocyclic carbene-based ligands. The chloride complexes are exceptionally sensitive to acid and can be reversibly protonated to form the zwitterions κ^2-$\{PhB(RIm)_2(RIm{\cdot}H)\}CoCl_2$. This unexpected reactivity is attributed to the highly basic nature of the tris(carbene)borate ligands. Reaction of the chloride complexes with methylating reagents results in products that depend on the N-heterocyclic carbene substituent. For R = ^{t}Bu, the four-coordinate high-spin complex, κ^3-$PhB(^tBuIm)_3CoMe$, is formed, while for R = Mes, reduction to a multitude of complexes occurs.

Introduction

Since the introduction of bulky "second-generation" tris(pyrazolyl)borates in the 1980s, these ligands have found widespread application in bioinorganic, organometallic, and materials chemistry.[1] Tris(pyrazolyl)borates are also known as "scorpionates" since their binding to metals is reminiscent to that of a scorpion grabbing its prey. Two pyrazolyl groups are typically coordinated to the metal ion, and the conformation of the resulting six-membered ring allows the third pyrazolyl group to bend over and "sting" the metal ion.

This ligand motif has served as a template for the design of other facially coordinating, anionic ligands. Other tripodal borate ligands based on donor groups such as thioethers,[2] 2-thioimidazoles,[3] and phosphines[4] have subsequently been introduced. The scorpionate ligand class provides great flexibility in tuning the ligand properties and therefore controlling the reactivity of the resultant metal complexes. In addition to modifying ligand properties by different donor atoms, the electronic and steric properties can be fine-tuned by modifying the substituents on the donor groups. Control over both the coordination number[1] and spin state[5] of the metal center is thus possible.

Since scorpionate ligands are typically required to be spectator ligands in metal-centered transformations, it is important to understand their degradation pathways. It is known that tris(pyrazolyl)borate ligands are susceptible to protonation, and it is speculated that cleavage of the B−N bond in some systems is due to reaction with in situ generated acids.[6] Protonation need not lead to destruction of the Tp ligand. For example, the acid-assisted reductive elimination

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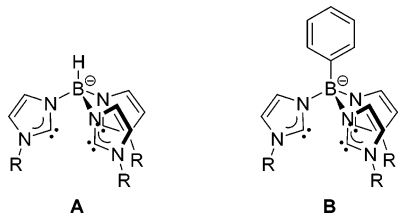

Figure 1. Hydrotris(carbene)borates (A) and phenyltris(carbene)borates (B).

of alkanes from Pt(IV) tris(pyrazolyl)borate complexes is accompanied by protonation of one pyrazolyl arm.[7]

Scorpionate ligands based on N-heterocyclic carbenes (NHCs) were first introduced by Fehlhammer and co-workers.[8] Sterically undemanding tris(carbene)borate ligands (Figure 1A, R = Me, Et) allow for preparation of stable six-coordinate iron(III) and cobalt(III) complexes. We have subsequently expanded this ligand class to include bulkier tris(carbene)borates (Figure 1A, R = ^{t}Bu) that are able to stabilize coordinatively unsaturated metal centers.[9]

In this paper, we have modified the tris(carbene)borate ligand class to incorporate a phenyl group on the boron atom (Figure 1B, R = ^{t}Bu, Mes). These bulky ligands stabilize coordinatively unsaturated cobalt(II) centers, but unexpectedly, the cobalt complexes are extremely acid-sensitive with the "tail" of the scorpionate ligand undergoing reversible protonation.

Results

Ligand Synthesis. Heating a 1:2:3 mixture of $PhBCl_2$, Me_3SiOTf, and 1-*tert*-butylimidazole in toluene results in the formation of the borane dication $PhB(^tBuIm)_3(OTf)_2$ as a white solid in high yield (Scheme 1, route A). The product has been fully characterized. Similar to $HB(^tBuIm)_3Br_2$,[9] a characteristic feature of this compound is a resonance in the ^{1}H NMR spectrum that is shifted far downfield at δ 8.56 ppm (DMSO-d_6). Interestingly, the chemical shift of this proton is solvent-dependent, appearing at δ 8.10 ppm in CD_3CN and δ 8.38 ppm in $CDCl_3$. The synthetic methodology is readily extended to the synthesis of the boron dication $PhB(MesIm)_3(OTf)_2$ from 1-mesitylimidazole. Both bis(triflate) salts are white air- and moisture-stable solids.

An alternate route to the borane dications involves exchanging the chloride groups on $PhBCl_2$ for iodides. Thus, heating a mixture 1:2:3 mixture of $PhBCl_2$, NaI, and 1-mesitylimidazole in MeCN, followed by metathesis with $NaPF_6$, yields the boron dication $PhB(MesIm)_3(PF_6)_2$ (Scheme 1, route B). This product has also been fully characterized. Unlike its triflate congener, this compound tenaciously retains many polar solvents, including CH_2Cl_2, which can only be removed by extended heating under vacuum.

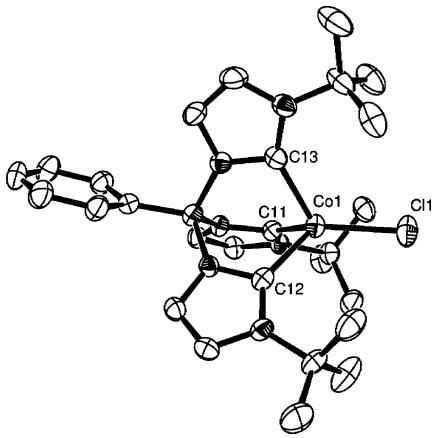

Figure 2. ORTEP diagram of **1**. Thermal ellipsoids shown at 50% probability, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co−C13 2.016(2), Co−C12 2.044(2), Co−C11, 2.045(2), Co−Cl 2.2581(7), C13−Co−C12 94.35(9), C13−Co−C11 93.68(10), C12−Co−C11 91.66(9), C13−Co−Cl 120.84(7), C12−Co−Cl 124.93(7), C11−Co−Cl 123.07(7).

Low-temperature reaction of $PhB(^tBuIm)_3(OTf)_2$ with 3 equiv of LDA in THF results in rapid dissolution of the borane dication and formation of a colorless solution. The ^{1}H NMR spectrum of the crude material is consistent with the formation of "$PhB(^tBuIm)_3Li$". All peaks in the spectrum are shifted upfield relative to the starting material, and only two resonances, at δ 6.95 and 6.69 ppm, are observed for the protons of the imidazol-2-ylidene ring. Similarly, resonances consistent with "$PhB(MesIm)_3Li$" are observed in the ^{1}H NMR spectrum after low-temperature deprotonation of $PhB(MesIm)_3(OTf)_2$. We have not observed any signals from the carbene carbons in the $^{13}C\{^1H\}$ NMR spectrum of either ligand.

Synthesis of Cobalt(II) Chloride Complexes. Addition of cobalt(II) salts to the in situ prepared tris(carbene)borate ligands results in new cobalt complexes. Thus, addition of $CoCl_2(thf)_{1.5}$ to "$PhB(^tBuIm)_3Li$" leads to the isolation of deep blue $PhB(^tBuIm)_3CoCl$ (**1**) in good yield. The molecular structure of this complex was determined by single-crystal X-ray diffraction (Figure 2). As expected, the bulky tris(carbene)borate ligand stabilizes a four-coordinate cobalt(II) chloride complex. The metrical parameters are similar to other four-coordinate cobalt(II) complexes of tripodal NHC ligands.[10,11] Furthermore, the metrical parameters are not significantly different from those of the topologically similar tris(pyrazolyl)borate ligand.[12]

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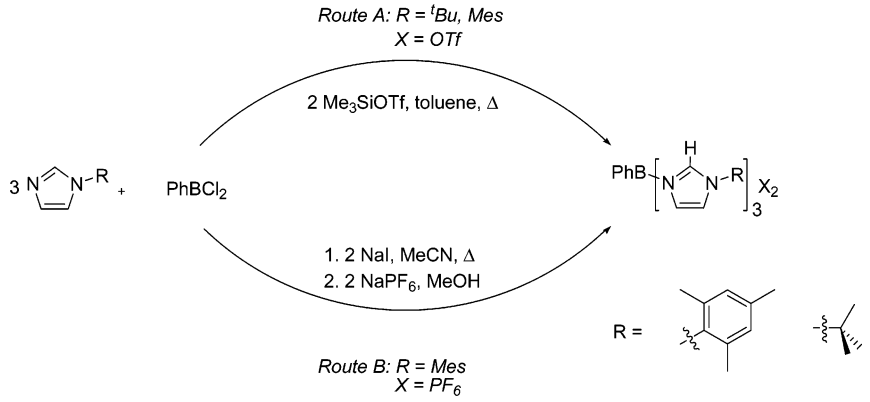
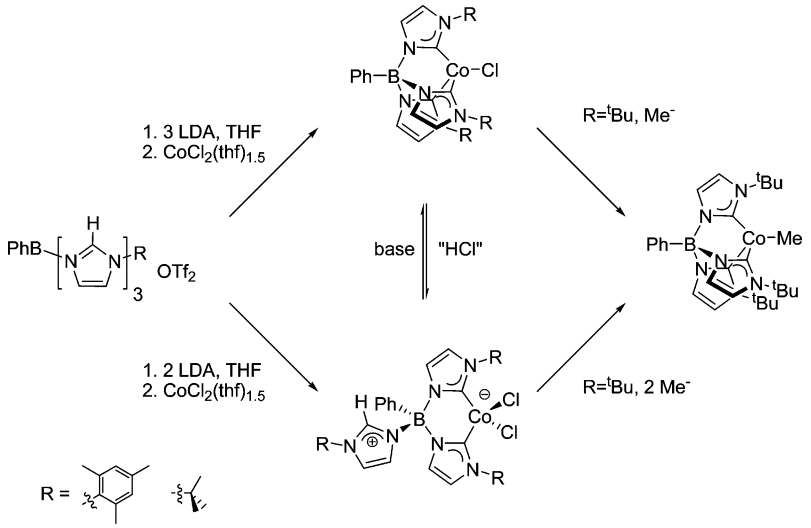
(12) A comparison of bond lengths and angles for all complexes in this paper with the average parameters from the structures of 29 cobalt(II) tris(pyrazolyl)borate complexes is given in the Supporting Information.

Scheme 1



Scheme 2



This complex has also been spectroscopically characterized. Six paramagnetically shifted peaks are observed in the ^{1}H NMR spectrum, consistent with 3-fold symmetry about the cobalt atom. The peaks can be assigned on the basis of integration. The two resonances that are most shifted downfield, at δ 96.4 and 35.0 ppm, are those assigned to the imidazol-2-ylidene protons. The resonance from the *tert*-butyl groups is observed at δ 11.3 ppm, while signals due to the phenyl protons are observed at δ 5.6, 5.2, and 2.0 ppm. The solution magnetic moment, determined by the Evans method (4.2(3) BM) is consistent with $S = 3/2$ cobalt.

Exposing **1** to sources of HCl results in protonation of one of the NHC donors and formation of the zwitterion κ^2-{PhB(^{t}BuIm)$_2$(^{t}BuIm·H)}CoCl$_2$ (**2**) (Scheme 2). The product has also been crystallographically characterized (Figure 3). The X-ray structure reveals that one of the NHC donors has been protonated, with the chloride taken up by the cobalt atom. The imidazolium hydrogen atom was identified directly from the Fourier maps. All the bond lengths to cobalt increase slightly from **1** to **2** and the C−Co−C angle is 5° larger in **2**. Significantly, no intermolecular interactions involving H(13) were identified in the crystal structure.

The solution magnetic moment of **2** (μ_{eff} = 3.9(3) BM) is consistent with high-spin cobalt(II). The ^{1}H NMR spectrum is quite distinct from that of **1** and is consistent with higher symmetry than is observed in the crystal structure. All three arms of the tris(carbene)borate ligand are equivalent in the room temperature ^{1}H NMR spectrum. Thus, a single resonance is observed for the three *tert*-butyl groups at δ 14.3 ppm and two resonances for the imidazol-2-ylidene protons (δ 51.5 and 30.5 ppm). The higher symmetry presumably arises from rapid shuttling of the hydrogen atom between the three carbene ligand arms. In an attempt to probe this fluxional behavior, we studied the temperature dependence of the ^{1}H NMR spectrum. However, no evidence for decoalescence was observed at temperatures down to −30 °C.

Adventitious acid sources also lead to the formation of **2**, and this complex is slowly formed over time from **1**, both in solution and in the solid state. The extent of conversion can be reduced by silylation or by washing glassware with dilute aqueous ammonia solutions prior to drying. Formation of the zwitterion is reversible and a variety of bulky alkali metal bases (e.g., LDA, LiN(SiMe$_3$)$_2$, or lithium 2,2′,6,6′-tetramethylpiperidine (LiTMP)) can deprotonate the free ligand arm of **2** to regenerate **1**. Smaller and more nucleophilic bases, such as MeLi, also dehydrohalogenate **2** but react further with **1** (see below).

Similar behavior is observed for the cobalt complex of the tris(*N*-mesitylcarbene)borate ligand (Scheme 2). Addition of CoCl$_2$(thf)$_{1.5}$ to "PhB(MesIm)$_3$Li" results in a complex that has similar spectral features to **1**. Eight paramagnetically

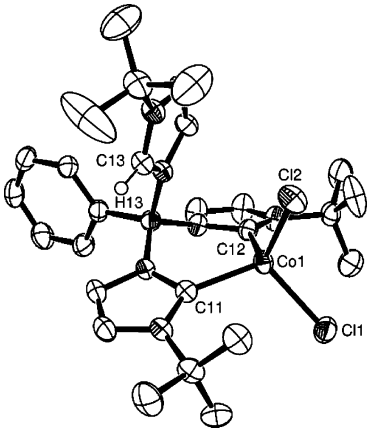


Figure 3. ORTEP diagram of **2**. Thermal ellipsoids shown at 50% probability, all hydrogen atoms except for H13 omitted for clarity. Selected bond lengths (Å) and angles (°): Co−C12 2.062(2), Co−C11, 2.069(2), Co−Cl2 2.2838(8), Co−Cl1 2.2916(9), C12−Co−C11 98.87(7), C12−Co−Cl2 114.47(5), C11−Co−Cl2 111.33(5), C12−Co−Cl1 110.45(5), C11−Co−Cl1 111.69(5), Cl2−Co−Cl1 109.69(2).

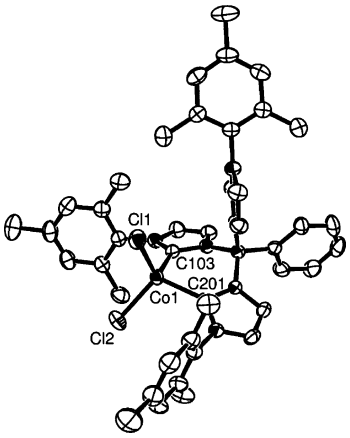


Figure 4. ORTEP diagram of **3**. Thermal ellipsoids shown at 50% probability, all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co1−C201 2.037(3), Co1−C103, 2.055(3), Co1−Cl1 2.2664(9), Co1−Cl2 2.2653(8), C201−Co1−C103 94.4(1), C201−Co1−Cl1 114.44(8), C201−Co1−Cl2 108.58(8), C103−Co1−Cl2 111.55(7), C103−Co1−Cl1 113.16(8), Cll-Co−Cl2 113.26(3).

shifted resonances are observed in the ^{1}H NMR spectrum, with the peaks assigned to the imidazol-2-ylidene protons at δ 93.3 and 36.9 ppm. The spectral data are consistent with a complex having the formulation PhB(MesIm)$_3$CoCl. However, this complex is even more sensitive to trace acid than **1**, and we have only been able to isolate the zwitterion κ^2-{PhB(MesIm)$_2$(MesIm·H)}CoCl$_2$ **3**. The X-ray crystal structure of the complex (Figure 4) shows similar features to that of **2**, although the bond lengths to cobalt are shorter, possibly due to the different steric pressure exerted by the mesityl group.

Reactions with Methylating Reagents. Low-temperature reaction of **1** with methyllithium or MeMgBr results in formation of indigo blue **4** in good yield. This complex can also be prepared by addition of 2 equiv of methylating reagent to **2** (Scheme 2).

The product has been characterized by X-ray crystallography (Figure 5). Compared to the chloride precursor **1**, the Co−C$_{carbene}$ bonds are somewhat longer. The Co−CH$_3$ bond length, at 2.042(2) Å, is shorter than the Co−CH$_3$ bond

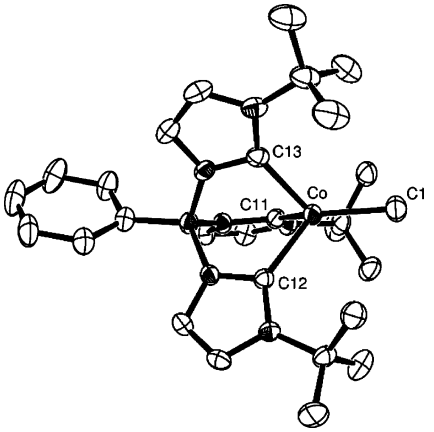


Figure 5. ORTEP diagram of **4**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co−C11 2.061(2), Co−C12 2.067(2), Co−C13 2.035(2), Co−C15 2.042(2), C15−Co−C13 123.59(9), C15−Co−C11 123.87(9), C15−Co−C12 124.73(8), C13−Co−C11 92.86(7), C13−Co−C12 91.50-(7), C11−Co−C12 90.71(7).

length of 2.12(1) Å in the related Tp′CoMe complex (Tp′ = tris(3-*tert*-butyl-5-methyl-pyrazolyl)hydroborate)[13] but compares well with other structurally characterized four-coordinate cobalt(II) alkyl complexes.[14] There is no evidence for agostic interactions as the closest Co···H−C distance is over 2.80 Å.

The ^{1}H NMR spectrum of **4** is similar to that of **1**, with seven paramagnetically shifted resonances observed. The solution magnetic moment of 4.1(3) BM is consistent with high-spin Co(II). This complex is thermally stable, showing no signs of decomposition when heated for days at 75 °C in benzene. The complex does not have the same extreme acid sensitivity as its chloride precursor and appears to be indefinitely stable in a nitrogen atmosphere. Interestingly, addition of one equivalent of 2,6-lutidinium chloride to **4** results in a 1:1 mixture of **2** and **4**, with no evidence for **1** in the ^{1}H NMR spectrum.

Reaction of **3** with methylating reagents results in the formation of unidentified, NMR silent product(s). In an attempt to trap potential intermediate species, the methylation reaction was conducted in the presence of CO at −78 °C. Two bands are observed in the IR spectrum at 1974 and 1886 cm^{-1}, consistent with terminal CO ligands, while the ^{1}H NMR spectrum suggests that a mixture of diamagnetic products is formed.

Discussion

Ligand and Metal Complex Synthesis. Our route to tris(carbene)phenylborate ligands utilizes a strategy similar to that used for the synthesis of bulky tris(carbene)hydroborate ligands, namely, by preparation of a substituted tris(imidazolium)borane dication, followed by 3-fold deprotonation.

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Our initial experiments focused on developing a protocol for the synthesis of the *tert*-butyl-substituted ligand, $PhB(^tBuIm)_3^-$, from which we could generalize to the incorporation of other substituted imidazoles.

Since heating solutions of $PhBCl_2$ and 1-*tert*-butylimidazole did not result in the formation of the desired borane dication $PhB(^tBuIm)_3Cl_2$, we sought methods for introducing better leaving groups on boron. It has been shown that boron triflate groups can be substituted by Lewis bases to yield boron monocations.[15] These groups can be introduced by reaction of B−Cl bonds with TMSOTf.[16] Thus, the addition of TMSOTf to $PhBCl_2$ in the presence of *tert*-butylimidazole leads to the formation of $PhB(^tBuIm)_3(OTf)_2$ in high yield. A similar approach, in which the B−Cl groups are exchanged for B−I bonds by addition of NaI in MeCN,[17] leads to $PhB(MesIm)_3I_2$ when conducted in the presence of 1-mesitylimidazole. Anion metathesis with $NaPF_6$ results in the formation of $PhB(MesIm)_3PF_6$.

Deprotonation of the dications to yield the tris(carbene)borate ligands is readily achieved by addition of bulky lithium bases such as LDA, LiTMP, and $LiN(SiMe_3)_2$. Bases of other alkali metals, such as KO^tBu or $KN(SiMe_3)_2$, as well as magnesium-containing bases lead to brightly colored solutions whose ^1H NMR spectra suggest mixtures of products. Successful deprotonation of the borane dications is critically dependent on complete removal of the solvents used in their synthesis, in particular CH_2Cl_2 and MeOH. While the triflate salts could be readily freed from solvents, $PhB(MesIm)_3PF_6$ tenaciously retains solvent, making this precursor less useful for ligand synthesis.

We have been unable to isolate "$PhB(RIm)_3Li$" free of the lithium salt byproducts. The crude material obtained after removal of the volatile byproducts is highly soluble in noncoordinating solvents such as toluene and benzene, possibly due to formation of aggregates with the lithium salt byproducts. However, the ^1H NMR spectra of the crude material is consistent with the formulation "$PhB(RIm)_3Li$", and we have conducted ligand transfer reactions with in situ prepared ligand to form low coordinate cobalt(II) chloride complexes.

Alkylation of the cobalt center is sensitive to the imidazol-2-ylidene substituent. In the case of **1**, reaction with methylating reagents results in the formation of **4**, while no methyl complex is formed from **3**. To determine if $PhB(MesIm)_3CoMe$ was indeed formed and then subsequently decomposed, we conducted the reaction in the presence of CO. Although multiple complexes appear to be formed, it is significant that no bands suggestive of acyl ligands are observed in the IR spectrum. It is most likely that alkylation of the metal does not occur and that the methylating reagent serves to reduce the metal center. Furthermore, the Co−C(carbene) bonds appear to be unreactive toward CO insertion.

Protonation of the Tris(carbene)borate Ligand in Cobalt(II) Chloride Complexes. In contrast to cobalt(II) complexes of other scorpionate ligands, such as tris(pyrazolyl)borates, tris(phosphino)borates, and tris(thioether)borates,[1,2,4] the tris(carbene)borate cobalt chloride **1** and $PhB(MesIm)_3CoCl$ complexes are extremely acid-sensitive. While NHC ligands are known to couple with alkyl ligands through reductive elimination from square planar complexes,[18] protonation has been less commonly observed[19] despite the extremely high basicity[20] and proton affinity[21] of these ligands. In contrast to the chloride complexes, **4** is not nearly as acid-sensitive and is protonated at the methyl ligand.

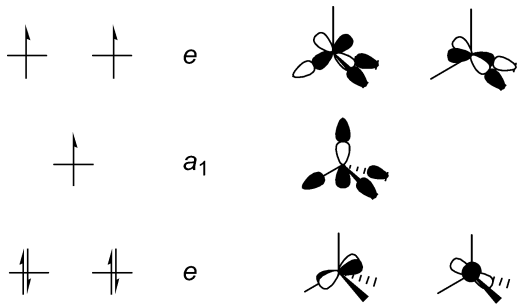

Figure 6. Qualitative frontier orbital diagram for four-coordinate, C_{3v} complex.

A qualitative MO diagram provides insight into differing reactivities of the $PhB(RIm)_3CoX$ complexes (Figure 6). Assuming C_{3v} symmetry and considering only σ interactions, the MO diagram is expected to be similar to those determined for related tripodal cobalt(II) complexes.[5,14b,22] Two sets of metal-based orbitals have significant metal−ligand σ^* character, namely, the e orbitals, which are antibonding with respect to the tripodal ligand, and the a_1 orbital, which is antibonding with respect to the X ligand. As shown in Figure 6, the e orbitals are highest in energy, and protonation is expected to occur at the tripodal ligand. If the X ligand is sufficiently basic to raise the energy of the a_1 orbital above that of the e levels, protonation is expected to occur at the X ligand.

Molecular orbital calculations (B3LYP/6-31G*) of **1** and **4** confirm these qualitative insights. The highest, singly occupied molecular orbital of **1** has significant Co−C(carbene) antibonding character (Figure 7a) whereas the SOMO of **4** is antibonding with respect to the $Co-CH_3$ linkage (Figure 7b). Therefore, the more basic methyl ligand raises the energy of the Co-X σ^* orbital, and protonation occurs at this site. It is also likely that the larger steric profile of the methyl ligand compared to chloride attenuates the sensitivity of the complex toward protonation.

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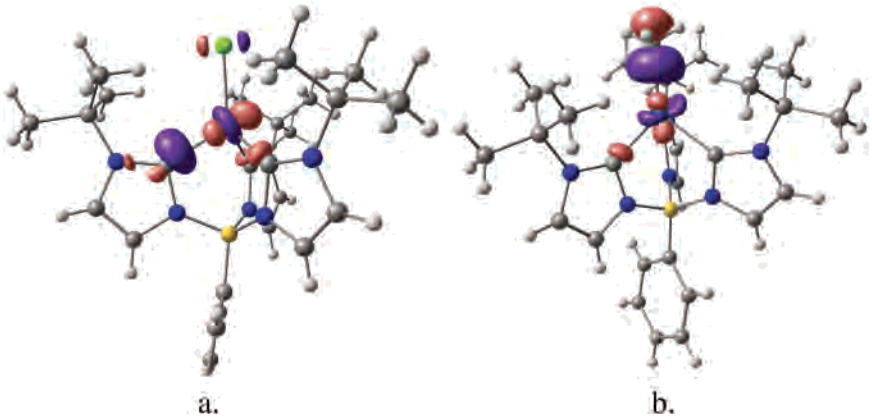

Figure 7. Kohn−Sham orbitals depicting the SOMO of (a) **1** and (b) **4**.

Conclusions

We have developed a new synthetic pathway to the synthesis of bulky tris(carbene)phenylborate ligands and their cobalt(II) complexes. The cobalt chloride complexes of these ligands are highly sensitive to protonation, reversibly forming κ^2-{PhB(RIm)$_2$(RIm·H)}CoCl$_2$ by reaction with trace acid sources. In the case of R = ^{t}Bu, reaction with methylating reagents leads to **4**, which is significantly more stable to adventitous acid. It is anticipated that other complexes of sufficiently basic ligands will have similar stability, and thus PhB(^{t}BuIm)$_3^-$ provides a suitable platform for the further development of cobalt(II) chemistry.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an MBraun Labmaster glovebox maintained at or below 1 ppm of O_2 and H_2O. Glassware was dried at 150 °C overnight. Celite was dried overnight at 200 °C under vacuum. ^{1}H NMR data were recorded on either a Varian Unity 400 (400 MHz) or Varian Gemini 200 (200 MHz) spectrometer at 22 °C. All peaks in the ^{1}H NMR spectra are referenced to residual $CHCl_3$ at δ 7.26 ppm, C_6D_5H at δ 7.16 ppm, CD_2HCN at δ 1.94 ppm, or $(CD_2H)CD_3SO$ at δ 2.49 ppm, respectively. All peaks in the ^{13}C NMR spectra are referenced to residual C_6D_6 at δ 128.1 ppm or $(CD_3)_2SO$ at δ 39.51 ppm. Electrospray mass spectral data were collected using a Waters-Micromass ZQ2000 mass spectrometer using CH_3CN as solvent. Solution magnetic susceptibilities were determined by the Evans method.[23] Toluene, dichloromethane, acetonitrile, diethyl ether, and tetrahydrofuran were purified by the Glass Contour solvent purification system. Deuterated benzene and hexamethyldisiloxane were first dried over CaH_2 and then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. 1-Mesitylimidazole was prepared according to a literature procedure[24] and purified by vacuum sublimation. $CoCl_2(thf)_{1.5}$ was prepared by heating anhydrous $CoCl_2$ overnight in THF and removing the solvent in vacuo.[25] Solid lithium diisopropylamide was prepared by addition of ^{n}BuLi to a solution of diisopropylamine in pentane at −78 °C, filtered, dried under vacuum, and stored at −35 °C. NaI·2H_2O was vacuum-dried at 100 °C overnight. All other chemicals were obtained commercially and used as received. Elemental analyses were determined by Desert Analytics, Tucson, AZ. Single-crystal X-ray data were obtained at the New Mexico State X-ray facility at the University of New Mexico in Albuquerque, NM.

Calculations. Density functional calculations were performed for **1** and **4** using Gaussian03.[26] Unrestricted calculations were performed at the B3LYP/6-31G* level. Single-point calculations were carried out using the X-ray coordinates for **1** and **4**. The calculations were performed for a quartet electronic ground state.

Preparation of 1-*tert*-Butylimidazole. 1-*tert*-Butylimidazole was prepared by adaptation of a literature procedure.[27] A 500 mL flask was charged with glyoxal (19.2 g of glyoxal trimer dihydrate, 0.27 mol, 1.0 equiv), *tert*-butylamine (20.0 g, 0.27 mol, 1.0 equiv), methanol (200 mL) and distilled water (50 mL). Upon heating to 70 °C, formaldehyde (22.2 g of 37% aqueous solution, 0.27 mol, 1.0 equiv) was added neat, followed by the dropwise addition of aqueous ammonia (20 mL, 28 wt %, 0.27 mol, 1.0 equiv). After 6 h, the reaction was cooled, and volatiles were removed in vacuo. Dichloromethane (150 mL) was added to the resulting brown oil and was washed in a separatory funnel with three 200-mL portions of distilled water. The solvent was removed in vacuo, and colorless 1-*tert*-butylimidazole was distilled at reduced pressure (bp ∼50 °C at 1 mbar) from the brown oil (21 g, 62%). ^{1}H NMR ($CDCl_3$, 400

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MHz, δ): 7.63 (s, 1H, ^{t}Bu*Im*), 7.06 (s, 1H, ^{t}Bu*Im*), 7.03 (s, 1H, ^{t}Bu*Im*), 1.56 (s, 9H, *^{t}Bu*Im). The product was subjected to three freeze−pump−thaw cycles and stored in the glovebox before use.

Preparation of [PhB(^{t}BuIm)$_3$](OTf)$_2$. 1-*tert*-Butylimidazole (10.0 g, 0.081 mol) was added to a stirred solution of $PhBCl_2$ (4.2 g, 0.026 mol) in toluene (70 mL). After 5 min, TMSOTf (12.0 g, 0.054 mol) was added, and the slurry was heated to 100 °C for 1 day. After cooling to room temperature, the toluene was decanted, and CH_2Cl_2 (ca. 100 mL) was refluxed with the thick tan glassy solid until it was completely dissolved. The CH_2Cl_2 solution was concentrated to ca. 70 mL and cooled to −25 °C to afford a colorless solid which was collected by filtration, washed with diethyl ether (30 mL), and dried in vacuo (17.7 g, 90%).

^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.56 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 8.07 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 7.45 (m, 3H, *Ph*B(^{t}BuIm)$_3$), 7.40 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 7.13 (m, 2H, *Ph*B(^{t}BuIm)$_3$), 1.58 (s, 27H, PhB(*^{t}Bu*Im)$_3$). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.38 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 7.43 (m, 3H, *Ph*B(^{t}BuIm)$_3$), 7.40 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 7.25 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 7.23 (m, 2H, *Ph*B(^{t}BuIm)$_3$), 1.69 (s, 27H, PhB(*^{t}Bu*Im)$_3$). ^{1}H NMR (400 MHz, CD_3CN, δ): 8.10 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 7.67 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 7.53 (m, 3H, *Ph*B(^{t}BuIm)$_3$), 7.24 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 7.19 (m, 2H, *Ph*B(^{t}BuIm)$_3$), 1.63 (s, 27H, PhB(*^{t}Bu*Im)$_3$). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, δ): 136.3, 132.6, 129.0, 128.4, 124.4, 121.1, 59.1, 29.0 ppm. ESI$^+$-MS: 609 ($C_{28}H_{41}N_6O_3BSF_3^+$). Anal. Cald for $C_{29}H_{41}N_6BF_6O_6S$ (944.75): C, 45.92; H, 5.45; N, 11.08. Found: C, 45.82; H, 5.22; N, 10.95.

Preparation of [PhB(MesIm)$_3$](OTf)$_2$. Method A: Silver triflate (1.4 g, 5.4 mmol) was added to a stirred solution of $PhBCl_2$ (0.43 g, 2.7 mmol) in toluene (10 mL) and diethyl ether (5 mL). The resulting slurry was filtered through Celite after 20 min, and 1-mesitylimidazole (1.5 g, 8.1 mmol) was added to the supernatant solution. The reaction mixture was heated to 50 °C for 1 day, and the light tan solid was collected by filtration, washed with diethyl ether (20 mL), and dried in vacuo (1.8 g, 71%).

Method B: 1-Mesitylimidazole (2.5 g, 13.4 mmol) was added to a stirred solution of $PhBCl_2$ (0.69 g, 4.3 mmol) in toluene (30 mL). After 5 min, TMSOTf (2.0 g, 9.1 mmol) was added, and the mixture was heated to 70 °C for 1 day. The resulting suspension was cooled, and the tan precipitate was collected by filtration and dissolved in a minimum amount of warm CH_2Cl_2 (ca. 50 mL). Cooling this solution to −25 °C afforded a white solid that was collected by filtration, washed with Et_2O, and dried in vacuo (3.6 g, 88%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.65 (s, 3H, PhB(Mes*Im*)$_3$), 7.76 (s, 3H, PhB(Mes*Im*)$_3$), 7.47 (m, 3H, *Ph*B(MesIm)$_3$), 7.37 (s, 3H, PhB(Mes*Im*)$_3$), 7.24 (m, 2H, *Ph*B(MesIm)$_3$), 7.00 (s, 6H, PhB(*Mes*Im)$_3$), 2.33 (s, 9H, PhB(*Mes*Im)$_3$), 2.08 (s, 18H, PhB(*Mes*Im)$_3$). ^{1}H NMR (400 MHz,DMSO-d_6, δ): 9.18 (s, 3H, PhB(Mes*Im*)$_3$), 8.07 (s, 3H, PhB(Mes*Im*)$_3$), 7.81 (s, 3H, PhB(Mes*Im*)$_3$), 7.44 (m, 3H, *Ph*B(MesIm)$_3$), 7.21 (m, 2H, *Ph*B(MesIm)$_3$), 7.13 (s, 6H, PhB(*Mes*Im)$_3$), 2.30 (s, 9H, PhB(*Mes*Im)$_3$), 2.03 (s, 18H, PhB(*Mes*Im)^3). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO, δ): 140.1, 139.9, 134.2, 132.2, 131.4, 129.1, 128.6, 125.2, 124.9, 20.5, 17.1 ppm. Anal. Cald for $C_{44}H_{47}N_6BF_6O_6S$ (944.75): C, 55.95: H, 5.01: N, 8.09. Found: C, 55.14: H, 5.24: N, 8.76.

Preparation of [PhB(MesIm)$_3$](PF$_6$)$_2$. Sodium iodide (2.8 g, 19 mmol) was added to a stirred solution of $PhBCl_2$ (1.3 g, 8.4 mmol) in acetonitrile (25 mL). 1-Mesitylimidazole (5.0 g, 27 mmol) was added, and the slurry was heated to 70 °C for 18 h. The resulting suspension was evaporated to dryness and dissolved in 100 mL of methanol. The addition of a solution of $NaPF_6$ (3.5 g, 21 mmol) in 20 mL of methanol induced precipitation of a white solid that was collected by filtration after 10 min, washed with diethyl ether (20 mL), and dried in vacuo (4.7 g, 60%).

^{1}H NMR (200 MHz, DMSO-d_6, δ): 9.20 (s, 3H, PhB(Mes*Im*)$_3$), 8.09 (s, 3H, PhB(Mes*Im*)$_3$), 7.83 (s, 3H, PhB(Mes*Im*)$_3$), 7.46 (m, 3H, *Ph*B(MesIm)$_3$), 7.23 (m, 2H, *Ph*B(MesIm)$_3$), 7.15 (s, 6H, PhB(*Mes*Im)$_3$), 2.32 (s, 9H, PhB(*Mes*Im)$_3$), 2.05 (s, 18H, PhB(*Mes*Im)$_3$). ^{1}H NMR (400 MHz, CD_3CN, δ): 8.40 (s, 3H, PhB(Mes*Im*)$_3$), 7.62 (s, 3H, PhB(Mes*Im*)$_3$), 7.54 (s, 3H, PhB(Mes*Im*)$_3$), 7.48 (m, 3H, *Ph*B(MesIm)$_3$), 7.22 (m, 2H, *Ph*B(MesIm)$_3$), 7.11 (s, 6H, PhB(*Mes*Im)$_3$), 2.34 (s, 9H, PhB(*Mes*Im)$_3$), 2.06 (s, 18H, PhB(*Mes*Im)$_3$). Anal. Cald for $C_{42}H_{47}N_6BF_{12}P_2$ (936.65): C, 53.86; H, 5.06; N, 8.98. Found: C, 53.40; H, 4.67; N, 8.75.

Preparation of "PhB(^{t}BuIm)$_3$Li". A solution of LDA (48 mg, 0.45 mmol) in THF (2 mL), precooled to −78 °C, was added to a slurry of PhB(^{t}BuIm)$_3$(OTf)$_2$ (100 mg, 0.13 mmol) in THF (5 mL) at −78 °C. The mixture was stirred 2 h at −78 °C, slowly warmed to room temperature, and stirred an additional 2 h. The volatiles were removed in vacuo to afford a light orange amorphous solid.

^{1}H NMR (400 MHz, C_6D_6, δ): 7.58 (d, J = 7.3 Hz, 2H, *Ph*B(^{t}BuIm)$_3$), 7.30 (m, 3H, *Ph*B(^{t}BuIm)$_3$), 6.95 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 6.69 (s, 3H, PhB(^{t}Bu*Im*)$_3$), 1.41 ppm (s, 27H, PhB(*^{t}Bu*Im)$_3$). ^{13}C-{^{1}H} NMR (100 MHz, δ): 135.3, 127.7, 125.4, 122.3, 115.2, 55.7, 31.9 ppm.

Preparation of "PhB(MesIm)$_3$Li". A solution of LDA (27 mg, 0.29 mmol) in THF (2 mL), precooled to −78 °C, was added to a slurry of PhB(MesIm)$_3$(OTf)$_2$ (64 mg, 0.068 mmol) in THF (3 mL) at −78 °C. The mixture was stirred 2 h at −78 °C and then slowly brought to room temperature. The volatiles were removed in vacuo to afford a yellow amorphous solid.

^{1}H NMR (400 MHz, C_6D_6, δ): 7.43 (m, 3H, *Ph*B(MesIm)$_3$), 7.31 (m, 2H, *Ph*B(MesIm)$_3$), 7.11 (s, 3H, PhB(Mes*Im*)$_3$), 6.72 (s, 6H, PhB(*Mes*Im)$_3$), 6.48 (s, 3H, PhB(Mes*Im*)$_3$), 2.06 (s, 9H, PhB(*Mes*Im)$_3$), 2.03 ppm (s, 18H, PhB(*Mes*Im)$_3$). ^{13}C{^{1}H} NMR (100 MHz, δ): 135.9, 129.2, 128.7, 127.0, 124.9, 18.1, 17.1 ppm.

Preparation of PhB(^{t}BuIm)$_3$CoCl (1). Chilled LDA (1.82 g, 17 mmol) in THF (5 mL) was added to a −78 °C slurry of PhB(^{t}BuIm)$_3$OTf$_2$ (4.22 g, 5.6 mmol) in THF (40 mL). The solution was stirred at −78 °C for 45 min and then brought to room temperature. Immediately $CoCl_2(thf)_{1.5}$ was added as a solid (1.39 g, 5.8 mmol), and the solution was stirred for 16 h at room temperature. The solvent was removed in vacuo while heating at 70 °C to yield a dark blue powder. The residue was extracted into dichloromethane (3 × 30 mL), and a gray solid was removed by filtration over Celite. The supernatant was dried in vacuo to afford a deep blue crystalline solid (2.49 g, 81%). Crystals suitable for X-ray analysis were grown by diffusion of saturated diethyl ether solution into hexamethyldisiloxane at −35 °C. ^{1}H NMR (400 MHz, C_6D_6, δ): 96.4 (3H, Im-H), 35.0 (3H, Im-H), 11.3 (27H, ^{t}Bu), 5.57 (1H, *p*-H), 5.18 (2H, *o*/*m*-H), 1.99 (2H, *o*/*m*-H). ^{1}H NMR (400 MHz, CD_3CN, δ): 97.7 (3H, Im-H), 34.1 (3H, Im-H), 11.4 (27H, ^{t}Bu), 5.60 (1H, *p*-H), 5.17 (2H, *o*/*m*-H), 1.94 (2H, *o*/*m*-H). μ_{eff} (C_6D_6) = 4.2(3) BM. UV−Vis (THF): λ (nm), ϵ (cm^{-1} M^{-1}): 230 (4200), 586 (550), 616 (810), 674 (1250). ESI$^+$-MS 552 ($C_{27}H_{38}N_6BCoCl^+$).

Preparation of κ^2-{PhB(^{t}BuIm)$_2$(^{t}BuIm·H)}CoCl$_2$ (2). A precooled solution of LDA (220 mg, 2.1 mmol) in THF (5 mL) was added to a slurry of PhB(^{t}BuIm)$_3$OTf$_2$ (750 mg, 0.99 mmol, 1.0 equiv) in 15 mL of THF at −78 °C. After stirring the resulting solution for 15 min, solid $CoCl_2(thf)_{1.5}$ (240 mg, 1.1 mmol) was added to the mixture, affording a deep blue solution. After stirring 4 h, the solvent was removed in vacuo and removed from the glovebox. The solid was dissolved in dichloromethane (30 mL) and washed in a separatory funnel with three 30-mL portions of

Table 1. Crystal Data, Data Collection, and Refinement Parameters

complex	**1**	**2**·CH_3CN	**3**	**4**
empirical formula	$C_{27}H_{38}BClCoN_6$	$C_{29}H_{42}BCl_2CoN_7$	$C_{42}H_{45}BCl_2CoN_6$	$C_{28}H_{41}BCoN_6$
fw	551.52	629.34	773.25	531.41
temp/K	203(2)	203(2)	203(2)	203(2)
wavelength/Å	0.71073	0.71069	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/n$	orthorhombic, $Pna2_1$	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
a/Å	9.6994(4)	13.863(5)	11.673(1)	10.2600(3)
b/Å	17.9166(8)	14.070(5)	14.118(1)	17.4153(5)
c/Å	16.4777(7)	16.840(5)	15.932(2)	16.1319(4)
α/deg	90	90	67.488(5)	90
β/deg	92.423(3)	90	80.318(5)	92.687(2)
γ/deg	90	90	70.862(5)	90
volume/Å^3, Z	2860.9(2), 4	3284.7(19), 4	2288.7(4), 3	2879.29(14), 4
calculated density	1.281 g/cm^3	1.273 g/cm^3	1.231 g/cm^3	1.226 g/cm^3
abs coeff/mm^{-1}	0.720	0.715	0.531	0.623
F(000)	1164	1324	885	1132
Cryst size/mm	0.12 × 0.07 × 0.02	0.24 × 0.20 × 0.08	0.50 × 0.45 × 0.12	0.30 × 0.20 × 0.07
θ range for data collection/°	1.68 to 24.56	1.89 to 29.13	1.63 to 22.00	1.72 to 27.78
limiting indices	$-11 \le h \le 11$, $-20 \le k \le 18$, $-19 \le l \le 19$	$-18 \le h \le 18$, $-19 \le k \le 19$, $-23 \le l \le 21$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-13 \le h \le 13$, $-22 \le k \le 21$, $-21 \le l \le 21$
reflns collected/unique	28583/4783 [R(int) = 0.0466]	53202/8554 [R(int) = 0.0249]	36883/5607 [R(int) = 0.0235]	33667/6796 [R(int) = 0.0446]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/parameters	4783/326	8554/374	5607/521	6796/489
GOF on F^2	1.023	1.167	1.099	1.017
final R indices [$I > 2\sigma(I)$]	R1 = 0.0351,[a] wR2 = 0.0748[b]	R1 = 0.0295, wR2 = 0.0728	R1 = 0.0481, wR2 = 0.1410	R1 = 0.0349, wR2 = 0.0761
R indices (all data)	R1 = 0.0555, wR2 = 0.0834	R1 = 0.0358, wR2 = 0.0826	R1 = 0.0533, wR2 = 0.1500	R1 = 0.0570, wR2 = 0.0854

[a] $R1 = \sum||F_o| - |F_c|/\sum|F_o|$(based on reflections with $I > 2\sigma(I)$). [b] $Rw2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (all data); a, b = const.

dilute aqueous HCl (~0.01 M) and finally with distilled water. The organic fraction was dried with $MgSO_4$ and filtered. The solvent was removed to afford a dark blue solid (413 mg, 71%). Crystals suitable for X-ray analysis were grown by slowly diffusing the solvent out of a saturated acetonitrile solution into hexamethyldisiloxane at −35 °C. ^{1}H NMR (400 MHz, CD_3CN, δ): 51.5 (3H, Im-H), 30.5 (3H, Im-H), 14.3 (27H, ^{t}Bu), 7.83 (4H, *o*/*m*-H), 7.70 (1H, *p*-H). μ_{eff} (CD_3CN) = 3.9(3) BM. UV−Vis (THF): λ (nm), ϵ (cm^{-1} M^{-1}): 634 (430), 586 (220), 215 (6400). ESI$^+$-MS 588 ($C_{27}H_{39}N_6BCoCl_2^+$) Anal. Calcd for $C_{27}H_{39}N_6BCl_2Co$ (588.30): C, 55.12; H, 6.68; N, 14.29. Found: C, 55.19; H, 6.82; N, 15.48.

Preparation of κ^2-PhB(MesIm)$_2$(MesImH)CoCl$_2$ (3). A solution of PhB(MesIm)$_3$OTf$_2$ (500 mg, 529 μmol) in THF (5 mL) was cooled to −78 °C. To this was added a precooled solution of LDA (173 mg, 1.61 mmol), and the reaction was slowly warmed to room temperature. After 45 min, solid $CoCl_2(thf)_{1.5}$ (132 mg, 555 μmol) was added to give a dark blue solution. The reaction was stirred overnight at RT, and the solvent was removed while heating at 80 °C. The residue was extracted into CH_2Cl_2, filtered through Celite, and dried to yield a blue solid (404 mg). The ^{1}H NMR spectrum of the crude material showed signals consistent with κ^3-PhB(MesIm)$_3$CoCl, but substantial quantities of **3** (ca. 25%) were also present. Crystals of **3** were grown by diffusion of diethyl ether into a toluene solution of the mixture. Attempts to isolate κ^3-PhB(MesIm)$_3$CoCl free of **3** have been unsuccessful. ^{1}H NMR (400 MHz, CD_3CN, δ): 41.4, 34.2, 10.4, 8.8, 8.6, 6.8, 6.4, 5.5, 5.4, 5.3, 2.4, 2.2, 1.9, 1.1, −1.0, −2.1. ESI$^+$-MS 779 ($C_{42}H_{45}N_6BCoCl{\cdot}CH_3CN^+$). Spectral data for κ^3-PhB(MesIm)$_3$CoCl: ^{1}H NMR (400 MHz, C_6D_6, δ): 93.3 (3H, Im-H), 36.9 (3H, Im-H), 14.9 (18H, Mes *o*-Me), 7.4 (6H, Mes *m*-H), 5.1 (1H, *p*-H), 4.5 (2H, *o*/*m*-H), 1.9 (9H, Mes *p*-Me), 0.2 (2H, *o*/*m*-H). ESI$^+$-MS 778 ($C_{42}H_{44}N_6BCoCl{\cdot}CH_3CN^+$).

Interconversion of 1 and 2. Preparation of κ^2-{PhB(^{t}BuIm)$_2$(^{t}BuIm·H)}CoCl$_2$: 2,6-Lutidinium hydrochloride (7 mg, 0.05 mmol) was added as a solid to a stirred solution of **1** (25 mg, 0.05 mmol) in THF (3 mL). After 2 h and the removal of solvent, the products were determined by ^{1}H NMR spectroscopy to be identical to 2,6-lutidine and **2**. Preparation of PhB(^{t}BuIm)$_3$CoCl: To a stirred solution of 2 (40 mg, 0.07 mmol, 1.0 eq) in THF (2 mL), solid LDA (11 mg, 0.1 mmol, 1.5 equiv) was added. After 2 h and the removal of solvent, the products were determined by ^{1}H NMR spectroscopy to be identical to diisopropylamine and **1**.

Preparation of PhB(^{t}BuIm)$_3$CoMe (4). A methyllithium solution in diethyl ether (1.6 M, 1.1 mL) was added to a solution of **1** (850 mg, 1.5 mmol) in diethyl ether (20 mL) at −78 °C. After 1 h at −78 °C, the solution was allowed to slowly warm to room temperature and was stirred for another 18 h. A brownish solid was removed by filtration through Celite, and the supernatant was dried in vacuo to afford an indigo blue crystalline solid (500 mg, 61%). Crystals suitable for X-ray analysis were grown by cooling a saturated diethyl ether solution to −35 °C. ^{1}H NMR (400 MHz, C_6D_6, δ): 81.5 (3H, Im-H), 51.3 (3H, Im-H), 10.6 (3H, Co−CH_3), 8.52 (3H, *o*/*m*-H, *p*-H), 8.27 (2H, *o*/*m*-H), −0.38 (27H, ^{t}Bu). μ_{eff} (C_6D_6) = 4.1(3) BM. UV−vis (pentane) λ (nm), ϵ (cm^{-1} M^{-1}): 209 (32564), 262 (8244), 348 (2763), 580 (983), 673 (876), 703 (2347). ESI$^+$-MS 531 ($C_{28}H_{41}N_6BCo$).

Reaction of 3 with MeMgBr. A flask was charged with 3 (87 mg, 0.11 mmol) and THF (10 mL) and sealed with a rubber septum. Carbon monoxide was bubbled through the solution, which was then cooled to −78 °C. A solution of MeMgBr in Et_2O (0.10 mL, 3.0 M, 0.30 mmol) was added, and the reaction mixture was slowly brought to room temperature. After 1 h, the volatiles were removed under vacuum to afford an aqua-green solid. IR (THF): 1974(s),

1886(s) cm^{-1}. The ^1H NMR spectrum indicated the formation of multiple diamagnetic products.

X-ray Crystallography. X-ray quality crystals for each complex were grown as indicated in the experimental procedures. Crystals were coated with Paratone N oil and mounted on a standard Bruker X8 Apex2 CCD-based X-ray diffractometer equipped with an Oxford Cryostream 700 low-temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operating at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 203(2) K. The data were integrated using the Bruker SAINT software package with a narrow frame algorithm.[28] The SADABS program was used for the absorption correction.[29]

All structures have been solved by direct methods and refined by full matrix least-squares techniques with the SHELX97 software package.[30] In a typical procedure, first all non-hydrogen atoms have been found and assigned from the Fourier maps and their thermal parameters refined anisotropically. Next, the hydrogen atoms have been added to the refinement, usually as riding models, and their thermal parameters refined isotropically. In some special cases such as **2** where the location of the protonated site(s) was of ultimate importance, the corresponding hydrogen atoms have been located directly from the Fourier maps, added to the refinement, and their thermal parameters refined isotropically. After all refinements converged, close examinations and testing using the PLATON program have been routinely carried out in order to confirm the accuracy of the solutions and the lack of higher symmetry.[31] The main crystallographic data for the complexes are listed in Table 1. The full crystallographic details are included in tables as Supporting Information. Crystallographic data have been deposited at the Cambridge Structural Database, the CCDC deposition numbers are 284745 (**1**), 288112 (**2**), 614453 (**3**) and 612568 (**4**).

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Supporting Information Available: Complete crystallographic details and comparative metrical data for cobalt tris(pyrazolyl)-borate complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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