

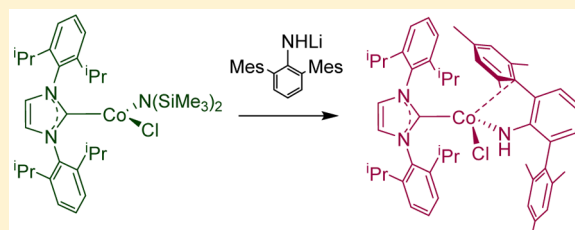
Protonolysis and Amide Exchange Reactions of a Three-Coordinate Cobalt Amide Complex Supported by an N-Heterocyclic Carbene Ligand

Christopher B. Hansen,* Richard F. Jordan, and Gregory L. Hillhouse†

Department of Chemistry, The University of Chicago, 929 East 57th Street, Chicago, Illinois 60637, United States

Supporting Information

ABSTRACT: A three-coordinate cobalt species, $\text{IPrCoCl}\{\text{N}(\text{SiMe}_3)_2\}$ (**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene), was synthesized by the reaction of $\{\text{IPrCoCl}_2\}_2$ with $\text{NaN}(\text{SiMe}_3)_2$. Compound **1** is a useful starting material for low-coordinate (IPr)Co species. **1** reacts with 2,6-di-*tert*-butyl-4-methylphenol (BHT-H) via aminolysis of the Co–N bond to generate a three-coordinate phenoxide complex, $\text{IPrCoCl}(\text{O}-2,6\text{-}^t\text{Bu}_2\text{-4-MeC}_6\text{H}_2)$ (**2**). The reaction of **1** with 2,6-diisopropylaniline (NH_2DIPP) generates $\text{IPrCoCl}(\text{NHDIPP})$ (**4**), which undergoes disproportionation to form a mixture of **4**, $\{\text{IPrCoCl}_2\}_2$, and $\text{IPrCo}(\text{NHDIPP})_2$ (**3**). The same product mixture is formed by the reaction of **1** with $\text{Li}[\text{NH}(\text{DIPP})]$, which unexpectedly proceeds by amide exchange. Compound **3** was synthesized independently by the reaction of $\{\text{IPrCoCl}_2\}_2$ with 4 equiv of $\text{Li}[\text{NH}(\text{DIPP})]$. The reaction of **1** with the bulkier lithium 2,6-dimesitylanilide (LiNHDMMP) also proceeds by amide exchange to generate $\text{IPrCoCl}(\text{NHDMMP})$ (**5**), which is stable toward disproportionation. Compounds **1** and **2** exhibit trigonal-planar geometries at cobalt in the solid state. The solid-state structure of **3** also contains a trigonal-planar cobalt center and exhibits close Co–H contacts involving the methine hydrogen atoms of the $\text{NH}(\text{DIPP})$ groups in the axial positions. The solid-state structure of **5** features an interaction between cobalt and a flanking aryl group of the anilide ligand, resulting in pyramidalization of the cobalt center.



INTRODUCTION

Cobalt N-heterocyclic carbene (NHC) compounds have found increasing utility as catalysts for cross coupling,¹ alkyne trimerization,² alkene hydroarylation,³ and other reactions.⁴ Additionally, NHC-supported cobalt species have been shown to activate aryl C–H bonds for further functionalization.⁵ While in most of these cases the active cobalt species is generated in situ and its structure is unknown, it is likely that low-coordinate cobalt complexes are involved in critical steps of these reactions. The preparation and characterization of such species is important to better understand the mechanisms and optimize the performance of these catalysts.

Several routes to low-coordinate NHC complexes of first-row late transition metals have been reported. Salt metathesis reaction of metal halides with alkali-metal alkyl, aryl, and amido reagents is the most common route of accessing these iron, cobalt, and nickel species. As a representative example, $\{\text{IPrCoCl}_2\}_2$ [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] reacts with 4 equiv of $\text{Mg}(\text{CH}_2\text{SiMe}_3)\text{Br}$ to afford $\text{IPrCo}(\text{CH}_2\text{SiMe}_3)_2$ (eq 1).¹⁸ Alternatively, displacement of weaker ligands or coordination of unsaturated fragments allows for access to two- and three-coordinate iron, cobalt, and nickel species. This approach may be illustrated by the displacement of PPh_3 from $\text{CoCl}(\text{PPh}_3)_3$ by 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) to yield $(\text{IMes})_2\text{CoCl}$ (eq 2).⁶ Protonolysis of highly basic ligands offers another route of accessing low-coordinate species. The double amine elimination

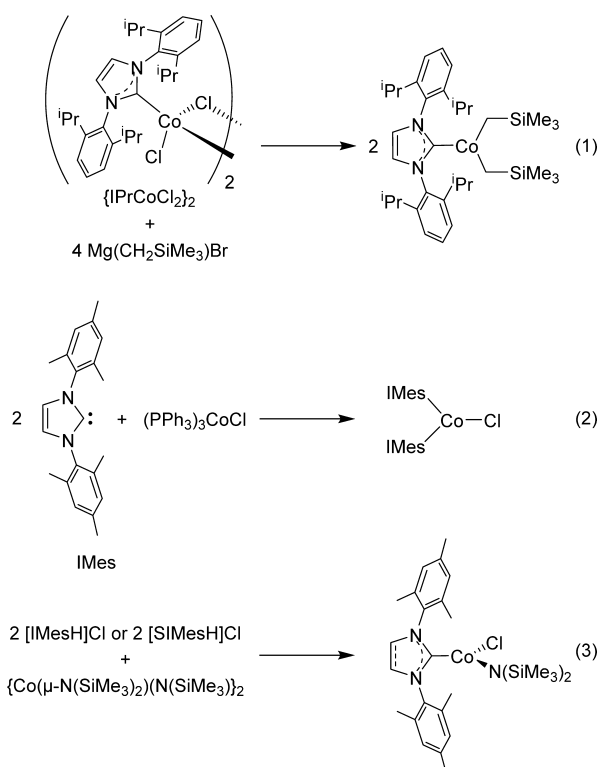
reaction of $\{\text{Co}(\mu\text{-N}(\text{SiMe}_3)_2)\text{N}(\text{SiMe}_3)_2\}_2$ with $[\text{NHC-H}]\text{Br}$ imidazolium salts yields $(\text{NHC})_2\text{CoBr}_2$ compounds.⁷ However, it was recently discovered that by using bulky $[\text{NHC-H}]\text{Cl}$ salts such as $[\text{IMesH}]\text{Cl}$ or $[\text{SIMesH}]\text{Cl}$ [$\text{SIMes} = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-4,5-dihydroimidazolin-2-ylidene}$], the three-coordinate mono-NHC species $(\text{NHC})\text{CoCl}\{\text{N}(\text{SiMe}_3)_2\}$ could be isolated (eq 3).⁸ This route has the advantage that compounds of NHC ligands that are not stable as free carbenes may be efficiently synthesized. However, there are limitations to this route. To obtain the mixed chloride amide $(\text{NHC})\text{CoCl}\{\text{N}(\text{SiMe}_3)_2\}$ species, the steric environment of the NHC must be carefully selected to avoid oversubstitution or the formation of ionic salts.⁸ The cobalt starting material for this preparation, $\{\text{Co}(\mu\text{-N}(\text{SiMe}_3)_2)\text{N}(\text{SiMe}_3)_2\}_2$, is somewhat complicated to prepare and does not store well.^{9–12} Here we describe the synthesis of the mixed (NHC)Co amide chloride species $\text{IPrCoCl}\{\text{N}(\text{SiMe}_3)_2\}$ (**1**) and its utility as a synthetic entry point to other low-coordinate cobalt species.

RESULTS AND DISCUSSION

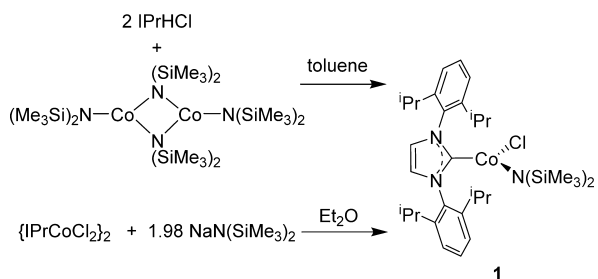
Synthesis and Structure of 1. The amine elimination reaction of $\{\text{Co}(\mu\text{-N}(\text{SiMe}_3)_2)\text{N}(\text{SiMe}_3)_2\}_2$ with 2 equiv of $[\text{IPrH}]\text{Cl}$ affords **1** (Scheme 1) as a bright-green air-sensitive

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Scheme 1



solid in 60% isolated yield. In our hands, however, this route proved to be problematic. The $\{Co(\mu-N(SiMe_3)_2)N(SiMe_3)_2\}_2$ starting material is time-consuming to prepare, requiring distillation and subsequent recrystallization,^{9–12} and the HN-(SiMe₃)₂ coproduct from the reaction with [IPrH]Cl is difficult to remove. The method is viable, but to avoid these issues, we devised an alternative route to **1**, as shown in Scheme 1. The reaction of 1.98 equiv of NaN(SiMe₃)₂ with {IPrCoCl₂}₂^{15g} in Et₂O also affords **1** in 93% isolated yield. The use of slightly less than 2 equiv of NaN(SiMe₃)₂ is important to avoid challenges associated with removal of this starting material from the final product. This route gave a better yield and cleaner product and was more amenable to producing **1** on a large scale compared to the amine elimination route. Furthermore, {IPrCoCl₂}₂ is easier to prepare than $\{Co(\mu-N(SiMe_3)_2)N(SiMe_3)_2\}_2$.^{9–12} Compound **1** is highly air-sensitive, changing from green to blue upon exposure to the atmosphere.

Crystals of **1** suitable for X-ray diffraction were obtained by crystallization from a 1:1 toluene/hexanes solution at –35 °C to afford **1** as bright-green needles. The solid-state structure of **1** is shown in Figure 1. The geometry around cobalt is trigonal-planar, with the sum of the angles being 359.99(7)°. Steric interactions between the NHC and –N(SiMe₃)₂ ligands result in the C7–Co1–N1 angle being opened to 133.78(7)°, with a

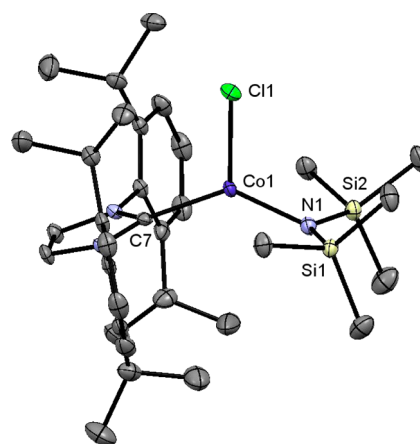


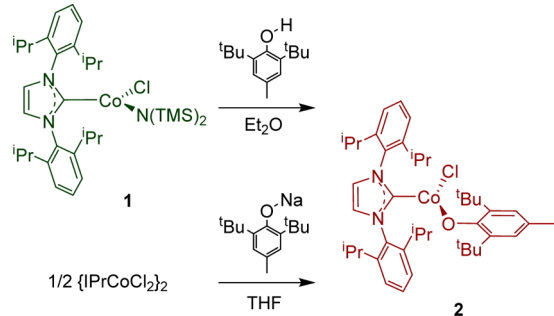
Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted. Selected metrical parameters (Å and deg): Co1–N1 1.9046(16), Co1–C7 2.055(2), Co1–Cl1 2.2324(6); N1–Co1–C7 133.78(7), N1–Co1–Cl1 112.94(5), C7–Co1–Cl1 113.27(5).

concomitant contraction of the C7–Co1–Cl1 and N1–Co–Cl1 bond angles. The plane of the NHC ring is almost perpendicular to the cobalt trigonal plane [angle between planes = 86.60(6)°]. Layfield has noted that the torsion angle between the NHC plane and the cobalt trigonal plane in related (NHC)Co{N(SiMe₃)₂}₂ compounds can be correlated with the overall bulk of the combined ligands, with bulkier ligands favoring smaller torsion angles.¹³ The presence of a nearly perpendicular torsion angle in **1** is consistent with this observation because a chloride provides less steric crowding than a second –N(SiMe₃)₂ ligand. The amide group is nearly planar at nitrogen, with the slight deviation from planarity again being attributable to steric crowding with the NHC ligand. The Si1–N1–Si2 plane is nearly perpendicular to the cobalt trigonal plane [angle between planes = 88.44(4)°].

Compound **1** exhibits a solution magnetic moment of 5.0(1) μ_B as measured by the Evans method. This value is larger than the predicted spin-only moment for high-spin cobalt(II) in a trigonal-planar environment ($S = 3/2$; 3.87 μ_B) but is comparable to values for similar compounds. For example, IMesCoCl{N(SiMe₃)₂}₂,⁸ SIMesCoCl{N(SiMe₃)₂}₂,⁸ IPrCo{N(SiMe₃)₂}₂,¹³ and (nacnac)CoN(SiMe₃)₂¹⁴ exhibit solution magnetic moments of 4.8, 4.9, 4.7, and 4.9 μ_B , respectively. Other trigonal-planar three-coordinate cobalt(II) complexes also exhibit μ_{eff} values in this range.^{12,13} The higher-than-spin-only magnetic moments in these compounds have been attributed to large zero-field splitting and g-tensor anisotropy.^{12,14} In accordance with the paramagnetic nature of **1**, the ¹H NMR spectrum is broad and contains resonances in the range of δ +93 to –45, but this spectrum is assignable based on peak integrations.

Reaction of 1 with 2,6-Di-tert-butyl-4-methylphenol (BHT-H) To Yield IPrCoCl(BHT) (2). The reaction of **1** with BHT-H in Et₂O produces **2**, which was isolated by crystallization from Et₂O/hexanes in 71% yield as an air-sensitive red powder (Scheme 2). Compound **2** can also be prepared in 65% yield as a red microcrystalline solid by the reaction of 2 equiv of Na[BHT] with {IPrCoCl₂}₂ in tetrahydrofuran (THF) followed by crystallization from toluene. However, the product from this route was consistently contaminated with small amounts of impurities, one of which was identified by X-ray diffraction as the green salt [IPrH][Co(BHT)₃] (see the Supporting Information, SI).

Scheme 2



Slow diffusion of hexanes into a dilute Et_2O solution of **2** at $-35\text{ }^\circ\text{C}$ afforded X-ray-quality block-shaped red crystals. The solid-state structure of **2** (Figure 2) is similar to that of **1**. The geometry at cobalt is trigonal-planar with a sum of angles at cobalt equal to $357.28(9)^\circ$. The plane of the NHC ligand is nearly perpendicular to the $\text{Cl}-\text{Co1}-\text{O1}$ plane; however, the cobalt center is displaced 0.23 \AA out of the NHC plane toward the chloride as a result of steric crowding between ^tBu groups of the phenoxide ligand and isopropyl groups of the NHC ligand, as illustrated in Figure 2b,c.

Compound **2** exhibits a solution magnetic moment of $5.1(1)\mu_{\text{B}}$ (Evans method). This value is similar that of **1** [$5.1(1)\mu_{\text{B}}$]. All nine of the expected ^1H NMR resonances for **2** are observed in the range of $\delta +110$ to -66 and can be assigned based on peak integrations and a comparison to the spectrum of **1**.

Generation of $\text{IPrCoCl}(\text{NHDIPP})$ (4**) and Disproportionation to $\text{IPrCo}(\text{NHDIPP})_2$ (**3**) and $\{\text{IPrCoCl}_2\}_2$.** The reaction of **1** with 1 equiv of 2,6-diisopropylaniline (NH_2DIPP) in toluene at room temperature over several days generates a mixture of $\{\text{IPrCoCl}_2\}_2$, **3**, and a species assigned as **4**, along with unreacted starting materials (Scheme 3). Heating the reaction to $70\text{ }^\circ\text{C}$ in toluene- d^8 for 36 h results in essentially quantitative conversion of **1** to $\{\text{IPrCoCl}_2\}_2$, **3**, and **4**, along with $\text{HN}(\text{SiMe}_3)_2$. Compound **3** was prepared independently as described below. Interestingly, the reaction of **1** with 1 equiv of $\text{Li}[\text{NH}(\text{DIPP})]$ also generates the same mixture of $\{\text{IPrCoCl}_2\}_2$, **3**, and **4** although much more rapidly, implying that lithium amide reacts with **1** via net amide exchange rather than the expected salt metathesis with the $\text{Co}-\text{Cl}$ group (Scheme 3). Finally, the reaction of $\{\text{IPrCoCl}_2\}_2$ with 2 equiv of $\text{Li}[\text{NH}(\text{DIPP})]$ also generates a mixture of $\{\text{IPrCoCl}_2\}_2$, **3**, and **4** (Scheme 3), as observed with the aminolysis and amide-exchange reactions of **1**. These results suggest that **4** is formed initially in these reactions and undergoes disproportionation to an equilibrium mixture of **4**, **3**, and $\{\text{IPrCoCl}_2\}_2$. The reaction of $\{\text{IPrCoCl}_2\}_2$ with isolated **3** also generates a mixture of $\{\text{IPrCoCl}_2\}_2$, **3**, and **4**, confirming that these three species are in equilibrium in solution. The equilibrium in benzene favors $\{\text{IPrCoCl}_2\}_2$ and **3**. The addition of an additional 1 equiv of $\text{Li}[\text{NH}(\text{DIPP})]$ to the equilibrium mixture of $\{\text{IPrCoCl}_2\}_2$, **3**, and **4** results in complete conversion to **3**.

Generation of the same mixture of $\{\text{IPrCoCl}_2\}_2$, **3**, and **4** via several different routes (Scheme 3) and the ability to convert this

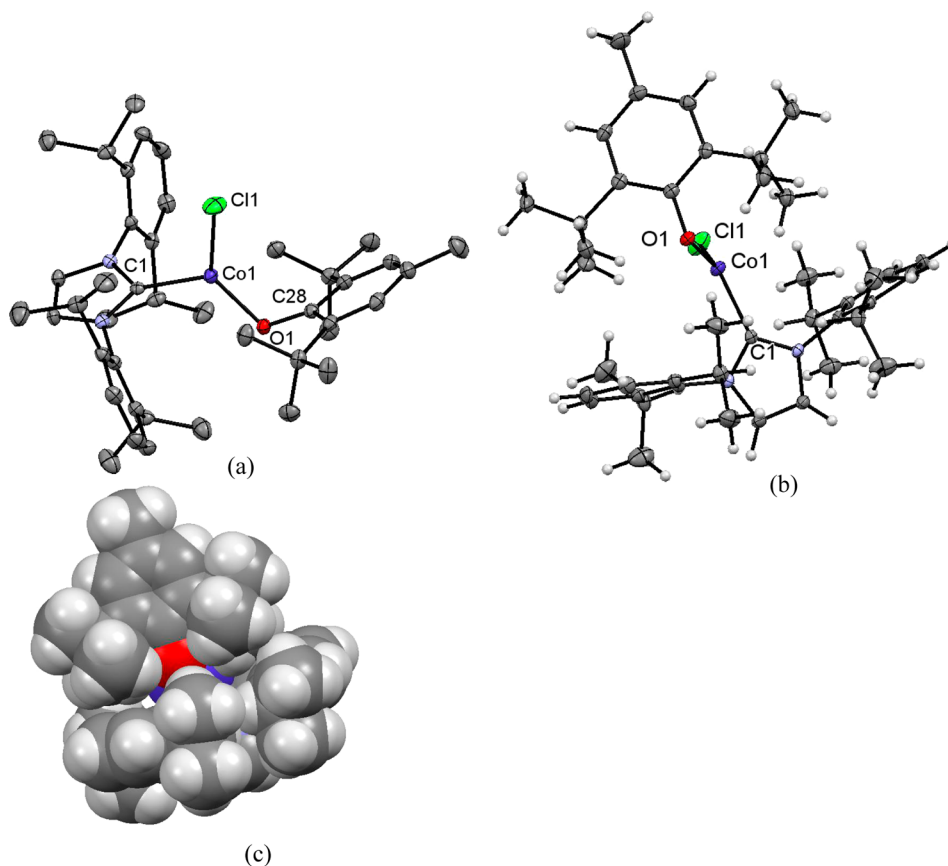
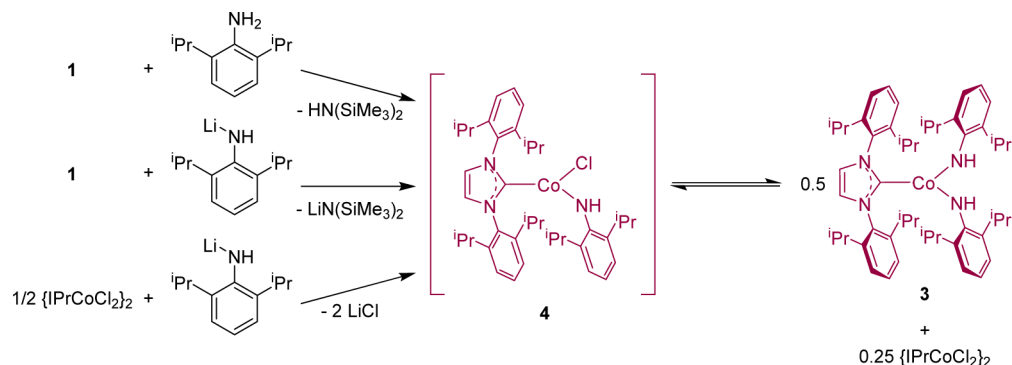


Figure 2. (a) Molecular structure of **2**. Hydrogen atoms are omitted. Selected metrical parameters (\AA and deg): $\text{Co1}-\text{C1}$ $2.033(2)$, $\text{Co1}-\text{O1}$ $1.8756(14)$, $\text{Co1}-\text{Cl1}$ $2.2061(6)$; $\text{O1}-\text{Co1}-\text{C1}$ $124.71(7)$, $\text{O1}-\text{Co1}-\text{Cl1}$ $120.53(4)$, $\text{C1}-\text{Co1}-\text{Cl1}$ $112.04(5)$. (b) Alternate view of **2** with hydrogen atoms included. (c) Space-filling view of **2** in the same perspective as part b, illustrating the steric interactions between the ^iPr and ^tBu groups.

Scheme 3



mixture entirely to **3** by adding $\text{Li}[\text{NH}(\text{DIPP})]$ support the assignment of **4** as the mixed anilide chloride complex. An analogous compound with a less sterically encumbering NHC ligand, $\{\text{SiMe}_3\text{Co}(\mu\text{-Cl})(\text{NHDIPP})\}_2$, was recently reported and shown to adopt a dimeric structure with bridging chlorides in the solid state.¹⁵

The observed conversion of **1** to **4** and **3** via reaction with $\text{Li}[\text{NH}(\text{DIPP})]$ and NH_2DIPP has parallels in iron chemistry. The iron analogue of **1**, $\text{IPrFeCl}\{\text{N}(\text{SiMe}_3)_2\}$, also reacts with either $\text{Li}[\text{NHDIPP}]$ or NH_2DIPP to afford $\text{IPrFe}(\text{NHDIPP})_2$.⁸ Similarly, $(\text{Cp}')\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}$ ($\text{Cp}' = 1,2,4\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$) reacts with $\text{Li}[\text{NH}(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)]$ to yield an equilibrium mixture of $(\text{Cp}')\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}$ and $(\text{Cp}')\text{Fe}\{\text{NH}(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)\}$. $(\text{Cp}')\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}$ also reacts with *p*-toluidine to yield $[(\text{Cp}')\text{Fe}\{\text{NH}(4\text{-Me-C}_6\text{H}_4)\}]_2$.¹⁶ The $\text{p}K_a$ of $\text{HN}(\text{SiMe}_3)_2$ is 26 in dimethyl sulfoxide (DMSO)¹⁷ and 25.8 in THF.¹⁸ A $\text{p}K_a$ value for NH_2DIPP could not be located, but it may reasonably be approximated to be at least as large as that for NH_2Ph , which is 30.6 in DMSO.¹⁹ The displacement of $[\text{N}(\text{SiMe}_3)_2]^-$ by $[\text{NH}(\text{DIPP})]^-$ in the cobalt and iron systems can be ascribed to the greater basicity and nucleophilicity of $[\text{NH}(\text{DIPP})]^-$. While simple acid–base considerations predict that NH_2DIPP is not sufficiently acidic for protonolysis of $\text{Co-N}(\text{SiMe}_3)_2$ or $\text{Fe-N}(\text{SiMe}_3)_2$ bonds, these compounds do not behave as simple salts because of the covalency in the $\text{M-N}(\text{SiMe}_3)_2$ bonds.

Synthesis and Characterization of 3. Compound **3** can be prepared independently by the reaction of $\{\text{IPrCoCl}_2\}_2$ with 4 equiv of $\text{Li}[\text{NH}(\text{DIPP})]$ in THF. Removal of the solvent under vacuum and extraction into dichloromethane affords **3** as an air-sensitive dark-violet solid in 94% isolated yield (Scheme 4). Alternatively, the reaction of **1** with 2 equiv of $\text{Li}[\text{NH}(\text{DIPP})]$ generates **3** as the only product (Scheme 4).

Single crystals of **3** were obtained from a concentrated pentane solution at $-35\text{ }^\circ\text{C}$ as dark-violet needles. The solid-state structure of **3** is shown in Figure 3. Like compounds **1** and **2**, **3** exhibits a trigonal-planar three-coordinate cobalt core. In

Scheme 4

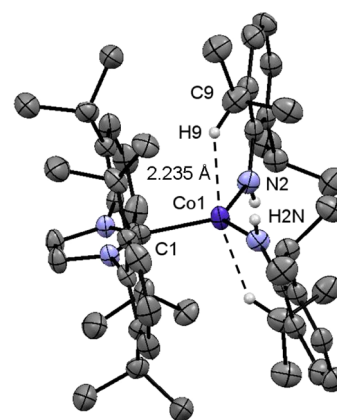
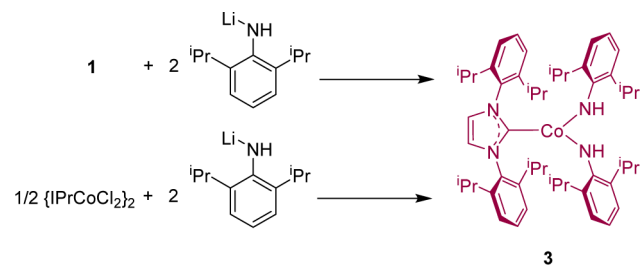


Figure 3. Molecular structure of **3**. Hydrogen atoms, except the N–H (H2N) and short-contact CHMe_2 (H9) hydrogen atoms, are omitted. The structure contains half a unique molecule per asymmetric unit. The NHC ligand diisopropylphenyl group is disordered over two positions, only one of which is shown. Selected metrical parameters (Å and deg): Co1–C1 2.061(2), Co1–N2 1.8934(13), Co1–H9 2.235(22), C9–H9 1.00(2); N2–Co1–N2 126.15(8), N2–Co1–C1 116.93(4).

contrast to **1** and **2**, however, the $\text{N}_{\text{amide}}\text{-Co-N}_{\text{amide}}$ plane is nearly parallel to the NHC plane [angle between planes = $5.98(7)^\circ$]. The reduction of the torsion angle from 90° with increasing steric demand is in agreement with Layfield's observations from $(\text{NHC})\text{Co}\{\text{N}(\text{SiMe}_3)_2\}$ compounds.¹³ This geometry accommodates the bulky anilides by minimizing steric interactions between the isopropylmethyl groups of the NHC and anilide ligands. The solid-state structure of **3** also exhibits short contacts between the cobalt center and two CHMe_2 methine hydrogen atoms of the anilide ligand, rendering the cobalt center pseudo-trigonal-bipyramidal [$\text{Co}\cdots\text{H} = 2.235(22)\text{ Å}$]. The hydrogen atoms with close contacts were located in the difference map and refined isotropically. However, the FTIR spectrum of **3** did not display reduced-frequency C–H stretching bands that could be conclusively assigned to the agostic $\text{Co}\cdots\text{H-C}$ units. A related compound, $(\text{IMes}'\text{-NDIPP})\text{Co}(\text{NHDIPP})$, has been prepared and displays similar structural parameters, including a close $\text{Co}\cdots\text{H}$ contact.²⁰

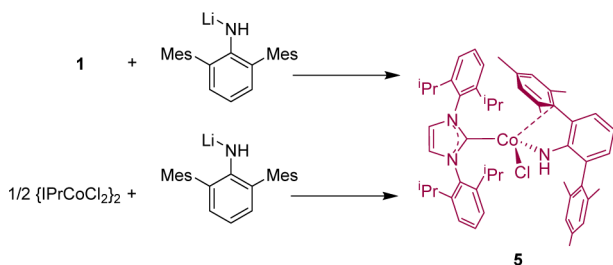
Compound **3** exhibits a solution magnetic moment of $4.5(1)\mu_{\text{B}}$, as measured by the Evans method in CD_2Cl_2 . A similar value, $4.27\mu_{\text{B}}$, was observed for **3** in the solid state by SQUID magnetometry (see the SI). The related compound $\text{IPrCo}(\text{CH}_2\text{SiMe}_3)_2$ has the same ligand orientation around the cobalt center but has a solution magnetic moment of $5.1\mu_{\text{B}}$.¹⁸ The low magnetic moment for **3** may result from the short $\text{Co}\cdots\text{H}$ contacts. Other high-spin cobalt(II) species in pseudo-trigonal-

bipyramidal geometries have been shown to exhibit similar magnetic moments.²¹ At 300 K, the solid-state magnetic moment of **3** is somewhat lower than the solution value although still higher than the $S = 3/2$ spin-only value. The small difference in the solid-state and solution μ_{eff} values may reflect differences in the strength of the Co---H interactions resulting from packing forces or solvation. The μ_{eff} value determined by variable-temperature SQUID magnetometry is relatively constant between 100 and 300 K, indicating that there are no significant structural changes over this temperature range.

Compound **3** is thermally stable up to 85 °C in solution for several days before eventually beginning to slowly plate out black solid. Compound **3** reacts readily with an excess of dry oxygen to form IPr=O, NH₂DIPP, and bis(2,6-diisopropyl)azobenzene, as established by ¹H NMR and electrospray ionization mass spectrometry (ESI-MS).

Synthesis and Structure of IPrCoCl(NHDMP) (5). To avoid the instability of **4** toward disproportionation, we utilized a more sterically encumbering anilide ligand. The reaction of 2 equiv of lithium 2,6-dimesitylanilide (Li[NHDMP]) with {IPrCoCl₂}₂ in diethyl ether at -35 °C and subsequent warming afford **5**, which was isolated in 78% yield as a dark-purple air-sensitive solid (Scheme 5). The reaction of **1** with 1 equiv of

Scheme 5



Li[NHDMP] gives the same product. Thus, as observed for the reaction of **1** with Li[NH(DIPP)], net amide exchange instead of salt metathesis is the favored pathway.

Single crystals of **5** were obtained from a concentrated toluene solution at -35 °C as dark-purple blocks. The solid-state structure of **5** is shown in Figure 4. The cobalt center of **5** exhibits

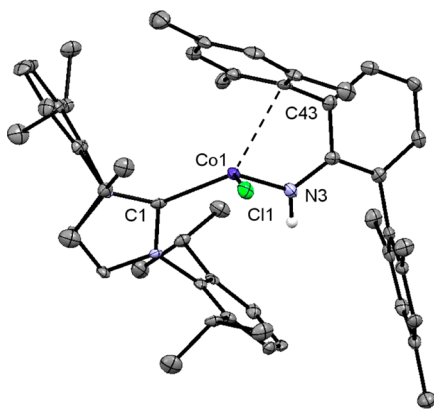


Figure 4. Molecular structure of **5**·2toluene. Solvent and hydrogen atoms, except the amide N-H (H3N) hydrogen atom, are omitted. Selected metrical parameters (Å and deg): Co1–C1 2.070(4), Co1–N3 1.901(3), Co1–Cl1 2.2391(12), Co1–C43 2.577(3); N3–Co1–C1 116.85(17), N3–Co1–Cl1 118.61(11), C1–Co1–Cl1 105.82(12).

a distorted tetrahedral geometry due to a cobalt–arene interaction with a mesityl group of the anilide ligand, resulting in pyramidalization of the cobalt center. The Co–C_{ipso} distance [2.577(3) Å] is well within the sum of the van der Waals radii (4.17 Å)²² but is longer than those observed in cobalt η^6 -arene complexes (ca. 2.15–2.20 Å).²³ Power observed a similar Co–arene interaction in the cobalt(II) arylamide species {2,6-(2,6-ⁱPr₂Ph)₂Ph}Co(NHDMP).^{23f} The Co–C_{ipso} distance in that case (2.393 Å) is 0.184 Å shorter than that in **5**, most likely because of the lower coordination number, and both distances are significantly longer than those in cobalt η^6 -arene complexes. The pseudo-four-coordinate homoleptic cobalt(II) diamide species Co(NHDMP)₂ and Co{NH-2,6-(2,4,6-ⁱPr₂Ph)₂Ph}₂ also display short Co–arene contacts of 2.56 and 2.61 Å (avg), respectively, which are comparable to that of pseudo-four-coordinate **5**.²⁴

Compound **5** exhibits a solution magnetic moment of 3.7(1) μ_{B} , as measured by the Evans method, which is close to the spin-only value for high-spin cobalt(II) in a tetrahedral environment. Thus, the low magnetic moment compared to those of **1–3** is likely a result of pyramidalization of the cobalt center. Magnetic moments close to the spin-only value were observed in other pseudotetrahedral neutral NHC cobalt compounds such as (IMes'-NDipp)Co(NHDipp) [3.9(1) μ_{B}],²⁰ (IMes)₂CoCl₂ [3.9(1) μ_{B}],^{1g} {PhB(^tBuIm)₃}CoCl [3.9(3) μ_{B}],²⁵ and {PhB(^tBuIm)₃}CoNH^tBu [4.0(3) μ_{B}].²⁶

CONCLUSIONS

The three-coordinate (NHC)Co complex **1** is a useful starting material for the synthesis of other low-coordinate (NHC)Co species by protonolysis and displacement of the -N(SiMe₃)₂ group. The protonolysis reaction of **1** with BHT-H results in the clean formation of three-coordinate species **2**. The reaction of **1** with NH₂DIPP or 1 equiv of Li[NH(DIPP)] generates **4**, which is unstable toward disproportionation to an equilibrium mixture of **4**, **3**, and {IPrCoCl₂}₂. The reaction of **1** with 2 equiv of Li[NH(DIPP)] yields **3** as the only product. The reaction of **1** with Li[NHDMP] yields a stable mixed anilide chloride complex, **5**, which displays a short contact between cobalt and a flanking aryl *ipso*-carbon of the terphenylamide in the solid state, rendering the compound pseudotetrahedral. In contrast to the instability of **4**, the sterics of the bulkier anilide and possible additional stabilization afforded by arene coordination in **5** stabilize this species against disproportionation to {IPrCoCl₂}₂ and IPrCo(NHDMP)₂. The rigorously three-coordinate compounds **1** and **2** display solution magnetic moments of 5.0(1) and 5.1(1) μ_{B} , respectively. Conversely, **3** and **5** display solution magnetic moments of 4.5(1) and 3.7(1) μ_{B} , respectively. The reduced magnetic moments relative to **1** and **2** are consistent with the cobalt–ligand interactions observed in the solid state being maintained in solution.³⁷

EXPERIMENTAL SECTION

General Considerations. Unless noted otherwise, all operations were performed under a purified nitrogen atmosphere in a standard MBraun Lab Master 130 drybox or under an argon atmosphere using high-vacuum and Schlenk techniques. Hexanes, pentane, and toluene were dried by passage through activated alumina and Q-5 columns under nitrogen. Q-5 was activated by heating at 200 °C under 5% H₂ in a dinitrogen atmosphere. CH₂Cl₂ was dried by passage through two activated alumina columns under nitrogen. THF was distilled from a dark-purple THF solution of sodium benzophenone ketyl and stored over 4 Å molecular sieves. Diethyl ether, benzene, and bis(trimethylsilyl) ether were stirred for 24 h over metallic sodium and filtered under

nitrogen through a plug of activated alumina. CD_2Cl_2 and C_6D_6 were purchased from Cambridge Isotope Laboratory, degassed, dried over CaH_2 , transferred under vacuum, and stored over 4 Å molecular sieves. Molecular sieves, alumina, silica, and Celite were dried under dynamic vacuum overnight at 180 °C. Unless noted, chemicals were purchased from commercial sources and used without further purification. 2,6-Diisopropylaniline (NH_2DIPP) was distilled under vacuum and lithiated with *n*-BuLi at –35 °C in pentane. $[\text{IPrH}]\text{Cl}$,²⁷ $\{\text{Co}(\mu\text{-N}(\text{SiMe}_3)_2)\text{N}(\text{SiMe}_3)_2\}_2$,^{9–12} $\{\text{IPrCoCl}_2\}_2$,^{16,g} $\text{Na}[\text{BHT}]$,²⁸ and $\text{Li}[\text{NHDMP}]$ ²⁹ were prepared by literature methods.

All NMR spectra were recorded using a Bruker DRX-400 or DRX-500 spectrometer. ¹H NMR spectra were referenced to solvent residual resonances at δ 7.16 for C_6D_6 and δ 5.32 for CD_2Cl_2 . Solution magnetic susceptibilities were calculated using the Evans method with bis-(trimethylsilyl) ether as an internal standard.³⁰ Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ). Fourier transform infrared (FTIR) spectra were recorded using a Thermo Nicolet NEXUS 670 spectrometer. Mass spectra were recorded using an Agilent 6130 Quadrupole LC/MS with electrospray ionization.

IPrCoCl(N(SiMe₃)₂) (1). *Route A.* A suspension of $\{\text{IPrCoCl}_2\}_2$ (0.500 g, 0.482 mmol, 1 equiv) in 5 mL of Et_2O was cooled to –35 °C and stirred. A solution of $\text{NaN}(\text{SiMe}_3)_2$ (173.0 mg, 0.955 mmol, 1.98 equiv) in 10 mL of Et_2O was cooled to –35 °C and added dropwise to the stirred suspension of $\{\text{IPrCoCl}_2\}_2$. The mixture was allowed to warm to ambient temperature, resulting in dissolution of $\{\text{IPrCoCl}_2\}_2$ (<5 min) and a color change from blue to green. A white precipitate formed within ca. 15 min. The mixture was stirred overnight, filtered through a fine frit, and evaporated to dryness. The residue was extracted with toluene and filtered through Celite. The solvent was evaporated under vacuum to yield 0.5720 g (93% yield) of **1** as a bright-green solid. Crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of **1** in 1:1 hexanes/toluene to –35 °C.

Route B. $[\text{IPrH}]\text{Cl}$ (223.9 mg, 0.527 mmol, 2 equiv) was suspended in 5 mL of toluene. $\{\text{Co}(\mu\text{-N}(\text{SiMe}_3)_2)\text{N}(\text{SiMe}_3)_2\}_2$ (200 mg, 0.263 mmol, 1 equiv) was dissolved in 3 mL of toluene and added to the stirred suspension of $[\text{IPrH}]\text{Cl}$. $[\text{IPrH}]\text{Cl}$ rapidly dissolved, and the mixture darkened from green to green-brown (ca. 10 min). After stirring overnight, the mixture was filtered through Celite, and the solvent was removed under vacuum. Washing of the green-brown waxy solid with hexanes afforded 203.4 mg of **1** (60% yield). ¹H NMR (C_6D_6): δ 93.5 (br s, 2H, $\text{CH}=\text{CH}$, NHC backbone), 72.4 (br s, 4H, CHMe_2), 18.3 (br s, 12H, CHMe_2), –2.3 (br s, 18H, SiMe_3), –29.0 (br s, 4H, *m*-Ar), –29.8 (br s, 2H, *p*-Ar), –43.4 (br s, 12H, CHMe_2). $\mu_{\text{eff}} = 5.0(1) \mu_{\text{B}}$ (C_6D_6 , Evans Method). Elemental analyses of multiple crystalline samples returned results consistently low in carbon. Elem anal. Calcd for $\text{C}_{34}\text{H}_{54}\text{N}_3\text{Si}_2\text{ClCo}$: C, 61.61; H, 8.46; N, 6.53. Found: C, 58.47; H, 8.60; N, 6.25.

IPrCoCl(BHT) (2). *Route A.* Separate solutions of compound **1** (359.1 mg, 0.558 mmol, 1 equiv) and BHT-H (129.1 mg, 0.586 mmol, 1.05 equiv) in 5 mL of Et_2O were prepared. The solution of **1** was stirred, and the solution of BHT-H was added dropwise, resulting in a rapid color change from green to dark red. Some product begins to precipitate from the reaction mixture within ca. 30 min. The mixture was allowed to stir for 3 h. The mixture was concentrated to 2 mL, to which 8 mL of hexanes was added and stored at –35 °C overnight, resulting in the formation of a red solid. Filtration of the reaction mixture on a fine frit and washing of the red solid with 3×1 mL of cold hexanes yielded 307.6 mg of **2** (78.5% yield) as a red powder. Crystals suitable for X-ray diffraction were obtained by diffusion of hexanes into a dilute ether solution at –35 °C over the course of 1 week.

Route B. A solution of NaBHT (47.9 mg, 0.192 mmol, 2 equiv) in 3 mL of THF was cooled to –35 °C. A solution of $\{\text{IPrCoCl}_2\}_2$ (100.0 mg, 0.096 mmol, 1 equiv) in 5 mL of THF was cooled to –35 °C and stirred. The solution of NaBHT was added dropwise to the stirred solution of $\{\text{IPrCoCl}_2\}_2$, resulting in a color change from blue to brown and finally dark red (ca. 1 h). The solution was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was filtered through a fine frit to remove an off-white solid, and the solvent was evaporated. The residue was extracted with 15 mL of toluene and filtered through Celite. The filtrate was concentrated and stored in the freezer at

–35 °C overnight to yield a red solid, which was collected on a glass frit and washed with cold hexanes. Further concentration of the mother liquor yielded additional product. Total yield from three crops: 80.8 mg (65% yield). Note: This product was contaminated by small amounts of impurities, one of which was identified by single-crystal X-ray diffraction as the green salt $[\text{IPrH}][\text{Co}(\text{BHT})_3]$. See the SI. ¹H NMR (C_6D_6): δ 110.6 (br s, 4H, CHMe_2), 93.4 (br s, 2H), 88.4 (br s, 2H, $\text{CH}=\text{CH}$ NHC backbone and phenoxide *m*-Ar), 61.1 (br s, 3H, phenoxide *p*-Me), 14.8 (br s, 12H, CHMe_2), –27.6, –27.7 (two overlapping broad resonances, 6H total, NHC *m*-Ar and *p*-Ar), –37.7 (br s, 12H, CHMe_2), –66.1 (br s, 18H, ¹Bu). $\mu_{\text{eff}} = 5.1(1) \mu_{\text{B}}$ (C_6D_6 , Evans method). Elem anal. Calcd for $\text{C}_{42}\text{H}_{59}\text{N}_2\text{OClCo}$: C, 71.83; H, 8.47; N, 3.99. Found: C, 71.74; H, 8.61; N, 3.99.

IPrCo(NHDIPP)₂ (3). A solution of $\{\text{IPrCoCl}_2\}_2$ (220.0 mg, 0.212 mmol, 1 equiv) in 6 mL of THF was cooled to –35 °C and stirred. A solution of $\text{Li}[\text{NH}(\text{DIPP})]$ (155.5 mg, 0.848 mmol, 4 equiv) in 6 mL of THF was cooled to –35 °C. The solution of $\text{Li}[\text{NH}(\text{DIPP})]$ was added dropwise to the stirred solution of $\{\text{IPrCoCl}_2\}_2$, and the mixture was allowed to warm to ambient temperature, resulting in a rapid color change from blue to dark violet. After stirring overnight, the solvent was removed, and the residue was extracted with 10 mL of CH_2Cl_2 . The CH_2Cl_2 solution was filtered through Celite. Removal of the solvent under vacuum yielded 319.7 mg (94% yield) of **3** as a dark-violet solid. Crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of **3** in pentane.

From 1. $\text{Li}[\text{NHDIPP}]$ (57.0 mg, 0.311 mmol, 2 equiv) was dissolved in 3 mL of THF, and the solution was cooled to –35 °C. Compound **1** (100 mg, 0.155 mmol, 1 equiv) was dissolved in 5 mL of THF, and the solution was cooled to –35 °C. The solution of $\text{Li}[\text{NH}(\text{DIPP})]$ was added rapidly to the cold stirred solution of **1**. The color changed quickly from green to brown to dark violet. After stirring overnight, the reaction mixture was filtered through Celite, and the solvent was removed under vacuum. Extraction of the residue with dichloromethane and filtration through Celite to remove a dark solid afforded a dark-violet solution. The solution was concentrated, layered with bis(trimethylsilyl) ether, and cooled to –35 °C to afford 57.0 mg (46% yield) of **3** as a dark-violet solid. ¹H NMR (CD_2Cl_2): δ 57.2 (br s, 4H), 54.2 (br s, 2H), 27.5 (br s, 4H, CHMe_2), 6.5 (two overlapping broad resonances, 18H total, 12H, CHMe_2 + 6H), 1.2 (br s, 6H), –5.8, –6.2 (two overlapping broad resonances, 6H total, *m*-Ar and *p*-Ar), –11.7 (br s, 12H, CHMe_2), –90.1 (br s, 2H, $\text{CH}=\text{CH}$ NHC backbone). N–H resonances not observed. ¹H NMR (C_6D_6): δ 58.1 (br s, 4H), 54.0 (br s, 2H), 28.0 (br s, 4H), 6.5 (two overlapping broad resonances, 18H total, 12H + 6H), 1.2 (br s, 6H), –5.5, –5.7 (two overlapping broad resonances, 6H total), –11.7 (br s, 12H), –94.9 (br s, 2H). $\mu_{\text{eff}} = 4.5(1) \mu_{\text{B}}$ (CD_2Cl_2 , Evans method). FTIR (KBr pellet): 3368 cm^{-1} (N–H stretch). C–H stretches associated with close Co...H contacts were not conclusively observed. Elem anal. Calcd for $\text{C}_{51}\text{H}_{72}\text{N}_4\text{Co}$: C, 76.56; H, 9.07; N, 7.00. Found: C, 76.32; H, 9.32; N, 6.81.

NMR Data for IPrCoCl(NHDIPP) (4). ¹H NMR (C_6D_6): δ 86.0, 58.8, 9.2, 6.3, 4.7, –13.8, –16.9, –112.1.

Reaction of 1 with NH₂DIPP. *At Ambient Conditions.* NH_2DIPP (12.9 μL , 13.8 mg, 0.0777 mmol, 1 equiv) was added via micropipette to a solution of **1** (50 mg, 0.0777 mmol, 1 equiv) in 5 mL of toluene. The reaction was stirred for 3 days at ambient conditions, over which time the color gradually turned from green to brown. A 1 mL aliquot was filtered through Celite and the solvent removed under vacuum. An NMR sample was prepared in C_6D_6 , which showed that a mixture of $\{\text{IPrCoCl}_2\}_2$, **3**, **4**, and unreacted starting materials was present.

At 70 °C. NH_2DIPP (3.1 μL , 2.9 mg, 0.0163 mmol, 1.05 equiv) was added via micropipette to a solution of **1** (10 mg, 0.0155 mmol, 1 equiv) in ca. 700 μL of toluene-*d*⁸ in a J. Young NMR tube. The tube was sealed, heated in an oil bath at 70 °C, and monitored by ¹H NMR. After 36 h, the reaction had essentially gone to completion and the ¹H NMR spectrum displayed resonances for $\{\text{IPrCoCl}_2\}_2$, **3**, and **4**, as well as $\text{HN}(\text{SiMe}_3)_2$. The color rapidly changed from green to brown and then gradually to deep violet during the course of the reaction. After completion, the volatile materials were vacuum-transferred to a second J. Young NMR tube and analyzed by ¹H NMR, which showed that only $\text{HN}(\text{SiMe}_3)_2$ and trace NH_2DIPP were present. ¹H NMR data of **3**

(toluene- d^8): δ 58.3, 55.9, 28.0, 6.5 (overlaps with 4), 1.1, -4.7, -10.3, -95.6. ^1H NMR data of 4 (toluene- d^8): δ 86.0, 60.1, 59.9 (two overlapping peaks), 9.2, 6.5 (overlaps with 3), -14.2, -14.3 (two overlapping peaks), -17.3, -107.0. ^1H NMR data of $\{\text{IPrCoCl}_2\}_2$ (toluene- d^8): δ 36.6, 16.1, 4.4, -0.0, -0.6, -1.4. An assigned spectrum of the reaction mixture is available in the SI.

Reaction of 1 with 1 equiv of Li[NH(DIPP)]. A solution of 1 (50 mg, 0.0777 mmol, 1 equiv) in 5 mL of THF was cooled to -35°C and stirred. A solution of Li[NH(DIPP)] (14.2 mg, 0.0777 mmol, 1 equiv) in 3 mL of THF was cooled to -35°C and added rapidly to the cold stirring solution of 1. The color changed quickly from green to brown to dark violet. After stirring for 3 h, the reaction mixture was filtered through Celite, and the solvent was removed under vacuum. ^1H NMR analysis of a sample prepared in C_6D_6 showed that a mixture of $\{\text{IPrCoCl}_2\}_2$, 3, and 4 was present.

Reaction of 3 with $\{\text{IPrCoCl}_2\}_2$. A solution of 1 (7.7 mg, 0.0096 mmol, 2 equiv) in 1 mL of C_6D_6 was added to solid $\{\text{IPrCoCl}_2\}_2$ (5.0 mg, 0.0048 mmol, 1 equiv), and the mixture was stirred overnight. The violet solution was filtered into an NMR tube. A small amount of 4 was generated and observed in the NMR spectrum, along with 3 and $\{\text{IPrCoCl}_2\}_2$.

Reaction of 3 with Oxygen. Compound 3 (5.0 mg, 0.00625 mmol) was added to an NMR tube with a J. Young tap and dissolved in 700 μL of C_6D_6 . The tube was attached to a high-vacuum line, the solution was frozen, and the headspace was evacuated. The headspace was refilled with an atmosphere of dry oxygen. The J. Young tap was closed, and the solution was allowed to thaw. The color rapidly changed from dark violet to brown, with concomitant disappearance of 3 from the NMR spectrum. The sample was left at room temperature overnight, and a dark solid deposited on the walls and bottom of the NMR tube. The sample was filtered on the benchtop through a glass filter into a clean NMR tube. The ^1H NMR spectrum contained only diamagnetic compounds, identified as $\text{IPr}=\text{O}$, NH_2DIPP , and bis(2,6-diisopropylphenyl)azobenzene. The identities of these products were confirmed by a comparison of the ^1H NMR data to the NMR data of authentic samples and by ESI-MS analysis.

IPrCoCl(NHDMP) (5). A suspension of $\{\text{IPrCoCl}_2\}_2$ (200 mg, 0.193 mmol, 1 equiv) in 4 mL of Et_2O was cooled to -35°C and stirred. A solution of Li[NHDMP] (128.1 mg, 0.386 mmol, 2 equiv) in 8 mL of Et_2O was cooled to -35°C . The solution of Li[NHDMP] was added dropwise to the stirring suspension of $\{\text{IPrCoCl}_2\}_2$ and allowed to warm to ambient temperature, resulting in a color change from blue to dark purple. The reaction was allowed to stir overnight. The reaction mixture was filtered through a fine frit to remove a white solid, and the solvent was removed under vacuum. The resulting dark-purple residue was extracted with pentane (ca. 40 mL) and filtered through Celite. Removal of the solvent under vacuum yielded 240 mg (77% yield) of 5 as a dark-purple solid. Crystals suitable for X-ray diffraction were obtained by cooling a concentrated toluene solution to -35°C .

From 1. 1 (10 mg, 0.015 mmol, 1 equiv) was dissolved in ca. 800 μL of C_6D_6 and added to solid Li[NHDMP] (5.2 mg, 0.015 mmol, 1 equiv) with stirring. The color changed quickly from green to brown to dark purple. The reaction was stirred overnight. The solution was filtered through a pipet filter containing Celite into an NMR tube. The NMR spectrum showed the formation of 5 along with a $-\text{N}(\text{SiMe}_3)_2$ resonance at δ 0.12. The ^1H NMR spectrum cannot be assigned with confidence, but characteristic resonances are reported. ^1H NMR (C_6D_6): δ 50.6 (br s), 38.7 (br s), 6.8 (br s), 5.7 (br s), 3.5 (br s), -1.8 (br s), -5.3 (br s), -10.3 (br s), -17.8 (br s), -82.4 (br s). $\mu_{\text{eff}} = 3.7(1) \mu_{\text{B}}$ (C_6D_6 ; Evans method). Elem anal. Calcd for $\text{C}_{34}\text{H}_{54}\text{N}_3\text{ClCo}$: C, 75.49; H, 7.70; N, 5.18. Found: C, 75.15; H, 7.36; N, 5.02.

Single-Crystal X-ray Diffraction. Crystals were loaded onto a glass slide in the glovebox and covered with STP oil or fluorolube. Suitable crystals were selected using stereo and polarizing microscopes under oil blanketed with a stream of nitrogen, attached to the tip of a glass fiber, mounted in a stream of cold dry nitrogen at 100(2) K, and centered in the X-ray beam using a video camera. X-ray diffraction data were collected on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a microfocus molybdenum-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$). All data were collected at 100(2) K using a routine

of ϕ and ω scans to survey an entire sphere of reciprocal space and were indexed using the APEX2 program suite.³¹ Data were corrected for absorption effects using the empirical and multiscan methods, as implemented in SADABS.³² Space groups were determined based on systematic absences and intensity statistics. The structures were solved using Patterson or direct methods and refined by full-matrix least-squares refinement on F^2 using the Bruker SHELXTL (version 6.14) software package.³³ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions, unless specified otherwise. For further details on refinement, disorder modeling, tables with atomic coordinates, and an extensive list of geometric parameters, see the SI. All figures in the text are drawn at the 50% thermal ellipsoid probability level. Compound 3: Crystallized with half a unique molecule per asymmetric unit. Short-contact CHMe_2 (H9) hydrogen atoms were located in the difference map and refined isotropically. The anilide N-H hydrogen atoms (H2N) were located in the difference map, restrained to a typical N-H bond distance (0.88 \AA), and refined isotropically. The 2,6-diisopropylphenyl groups of the NHC ligand were disordered over two positions, which converged to 55:45 occupancy. Compound 5: Crystallized with two molecules of toluene per molecule of 5 in the asymmetric unit. The amide N-H hydrogen atom (H3N) was located in the difference map, restrained to a typical N-H bond distance (0.88 \AA), and allowed to refine isotropically. The data were restricted to 0.95 \AA because of a lack of high-angle diffraction. This may be a result of crystallization as thin plates or decomposition of the crystal during data collection. The solution included in CIF was solved in the *Pbca* space group ($R_1 = 4.99\%$, $wR_2 = 10.69\%$, and $\text{GOF} = 1.140$). A suitable solution in the monoclinic space group *P21/c* with $\beta \approx 90^\circ$ was able to be obtained but resulted in poorer refinement parameters ($R_1 = 5.87\%$, $wR_2 = 12.93\%$, and $\text{GOF} = 1.214$). $[\text{IPrH}][\text{Co}(\text{BHT})_3]$: Crystallized with three molecules of toluene and half a molecule of hexane per asymmetric unit. The identities of the solvent molecules could be determined; however, they exhibited heavy disorder and very large thermal ellipsoids. This was treated by application of the program SQUEEZE,³⁴ as implemented in Platon³⁵ using the "fab" file construct and ABIN command in XL. This construct allows the use of a solvent density distribution to be added to calculation of the structure factors rather than modifying the observed intensities through subtraction of a solvent contribution. The SQUEEZE algorithm located a void, centered at (0, 0.002, -0.056), with a volume of 2794 \AA^3 (ca. 32% of the unit cell volume) and an electron count of 581 e^- . The disordered solvent was expected to contain 700 e^- of electron density. This discrepancy may result from the partial occupancy of some of the sites. Two isopropyl groups from the $[\text{IPrH}]$ cation are disordered over two positions each.

Magnetic Measurements. Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Measurements for 3 were performed on a polycrystalline sample sealed in a polyethylene bag under a dinitrogen atmosphere. Direct-current (dc) susceptibility measurements were collected in the temperature range of 1.8–300 K under an applied dc field of 1.0 T. dc susceptibility data were corrected for diamagnetic contributions from the sample holder and for the core diamagnetism of the sample. The core diamagnetism was estimated to be $-769 \times 10^{-6} \text{ emu/mol}$ using Pascal's constants.³⁶

■ ASSOCIATED CONTENT

📄 Supporting Information

^1H NMR spectra for 1–3 and 5, the reaction of 1 with NH_2DIPP , dc susceptibility data and fitting for 3, FTIR spectrum of 3, and CIF files giving crystallographic data for 1–3, 5, and $[\text{IPrH}][\text{Co}(\text{BHT})_3]$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chansen6@uchicago.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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NOTE ADDED IN PROOF

After submission of this manuscript, a publication reporting similar work, including the synthesis of **3** was published.