Articles

Paramagnetic Alkyl, Hydride, and Alkene Complexes of the $Tp^{t-Bu,Me}Co$ Moiety

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The paramagnetic 15-electron alkyls $Tp^{t-Bu,Me}Co(R)$ (R = Me, Et, *n*-Bu) have been prepared, and the closely related $Tp^{t-Bu}Co(Me)$ has been structurally characterized. Hydrogenation of $Tp^{t-Bu,Me}Co(N_2)$ produced the analogous hydride, $Tp^{t-Bu,Me}Co(H)$, the crystal structure of which has been determined. Reactions of $Tp^{t-Bu,Me}Co(N_2)$ with ethylene and propene yielded the corresponding olefin complexes $Tp^{t-Bu,Me}Co(C_2H_3R)$ (R = H, Me). $Tp^{t-Bu,Me}Co(C_2H_4)$ has been structurally characterized by X-ray diffraction as well. The alkyls are thermally stable and show no tendency to β-eliminate; upon exposure to CO homolytic cleavage of the Co−C bond is observed rather than migratory insertion.

Introduction

Hindered tris(pyrazolyl)borate ligands (i.e. $Tp^{R,R'}$ = hydridotris(3-R-5-R′-pyrazolyl)borate) have been used extensively as ancillary ligands in bioinorganic and coordination chemistry.[1] The formal analogy between the Tp and Cp moieties (Cp = η^5-cyclopentadienyl) and the unique steric adaptability of the former are now driving a crossover of bulky Tp ligands into transition-metal organometallic chemistry,[2] where the ability to stabilize coordinatively unsaturated, low-coordinate molecules is especially prized, in anticipation of heightened reactivity. Whereas we originally began investigating $Tp^{R,R'}M$ chemistry with a view toward dioxygen activation,[3] we have also found uses for this class of ligands in organometallic chemistry.[4] Herein we describe the synthesis and characterization of a variety of archetypal organometallic molecules containing the $Tp^{t-Bu,Me}Co$ moiety. The results indicate that the $Tp^{t-Bu,Me}$ ligand deserves the appellation "tetrahedral enforcer",[5] in that it has allowed the preparation of 4-coordinate open-shell molecules with 15- and 16-electron configurations, i.e., organometallic compounds escaping the strictures of the 18-electron rule.

Results and Discussion

Synthesis and Structure. Addition of lithium alkyls to THF solutions of $Tp^{t-Bu,Me}Co(I)$ produced cobalt alkyls of the type $Tp^{t-Bu,Me}Co(R)$ in fair yields (55−60%; see Scheme 1). These paramagnetic complexes are thermally rather stable but decompose upon exposure to air and/or moisture. Despite repeated attempts, none of the alkyls containing the $Tp^{t-Bu,Me}$ ligand afforded crystals suitable for an X-ray structure determination. Finally, preparation of $Tp^{t-Bu}Co(Me)$ (**1b**), i.e., a derivative lacking methyl substituents in the 5-position of the pyrazole rings, allowed the determination of its structure. The result is shown in Figure 1 (see Table 1 for selected interatomic distances and angles); presumably this molecule is representative of the whole series.

Consistent with the intense blue color of the alkyls, **1b** features four-coordinate cobalt(II) in a pseudotetrahedral coordination environment. Notably, the methyl carbon atom sits essentially on the 3-fold symmetry axis of the TpCo fragment defined by the B−Co vector (B−Co−C angle β = 177.3°). While intuitively expected, this C_{3v} symmetric structure differs significantly from the cis-divacant octahedral geometry of analogous chromium alkyls—i.e., $Tp^{t-Bu,Me}Cr(R)$ (R = Et, CH_2SiMe_3, Ph; β = 131−136°)[4c]—and similarly distorted Co^I complexes of the type $Tp^{R,R'}Co(L)$ (L = CO, N_2; β = 142−153°).[4b] However, we have traced the electronic origin of these distortions theoretically, and the d^7 electronic configuration of Co^{II} is not susceptible to it.[4b] The Co−N distances of $Tp^{t-Bu}Co(Me)$ (Co−N_{av} = 2.11 Å, range

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10.1021/om980844f CCC: $18.00

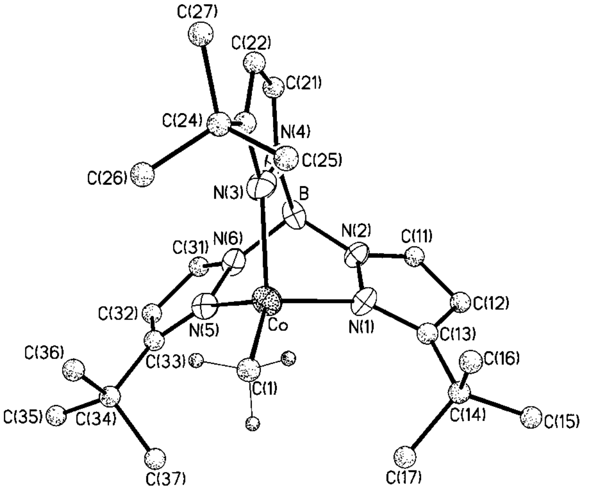

Figure 1. Molecular structure of Tp$^{t\text{-Bu}}$Co(Me)·C_7H_8 (**1b**). Hydrogen atoms, except for the methyl hydrogens, and the solvent molecule are omitted for clarity. Selected interatomic distances and angles are listed in Table 1.

2.097(14)−2.122(13) Å) are slightly longer than those of "inorganic" TpCo^{II} complexes with sterically hindered Tp ligands (2.02−2.04 Å);[3a,b,d] this may reflect the "reduced" nature of the more electron rich organometallic compound. However, even the Co−C distance of 2.12 Å appears relatively long when compared to those of other structurally characterized Co^{II} alkyls—e.g. (TMEDA)Co(CH_2SiMe_3)$_2$ (Co−C = 2.02−2.03 Å), (TMEDA)Co(CH_2CMe_3)$_2$ (Co−C = 2.04 Å), [Li(TMEDA)$_2$]-[CoCl(C(SiMe$_3$)$_2$)$_2$] (Co−C = 2.03−2.04 Å), and [Li(TMEDA)]$_2$[Co(CH_2SiMe_3)$_4$] (Co−C = 2.15 Å).[6] Aryl complexes such as (η^6-C_6H_5Me)Co(C_6F_5)$_2$ (Co−C = 1.93 Å)[7] and [Co(mesityl)$_2$]$_2$ (Co−C =, 1.98−1.99 Å)[8] feature much shorter cobalt−carbon bonds.

The stability of the simple alkyls raised the question of accessibility of the corresponding hydride. Indeed, Tp$^{t\text{-Bu,Me}}$Co(H) (**4**) could be prepared via several different routes, including treatment of Tp$^{t\text{-Bu,Me}}$Co(I) with hydride reagents and reaction of Tp$^{t\text{-Bu,Me}}$Co(BH_4) with 4-(dimethylamino)pyridine. However, the most convenient preparation involved heating the dinitrogen complex Tp$^{t\text{-Bu,Me}}$Co(N_2)[3a] with H_2 (see Scheme 1). This reaction yielded X-ray-quality crystals, and the result of the structure determination is shown in Figure 2 (see Table 2 for selected interatomic distances and angles). The hydrogen atom bonded to cobalt was located from a difference map, and its position was refined. Much like the related alkyls, **4** adopts approximate C_{3v} symmetry (β = 175.1°). The average Co−N distance of 2.04 Å (range 2.035(4)−2.043(4) Å) is a bit shorter than for the methyl complex **1b**, but this may at least partially reflect a steric interaction between the methyl substituents in the 5-position of the pyrazole rings, which affords the Tp$^{t\text{-Bu,Me}}$ ligand a marginally tighter bite angle. The Co−H distance of 1.69(4) Å is in the accepted range for terminal metal hydrides.[9] Subtracting the difference between the covalent radii of carbon (0.77 Å) and hydrogen (0.32 Å) from the Co−C bond distance of **1b** yields a predicted Co−H distance of 1.67 Å, rather close to the experimental value as well. Apparently, no terminal cobalt hydride has had its structure determined by neutron diffraction. However, extrapolation of the available data would suggest an average Co−H distance of ca. 1.54 Å,[10] much shorter than the value found here. Given the inherent uncertainty of the X-ray determination, we do not wish to overinterpret this discrepancy, only to suggest that the Co−H bond of Tp$^{t\text{-Bu,Me}}$Co(H)—much like the Co−C bond of Tp$^{t\text{-Bu}}$Co(Me)—may be unusually long.

Olefin π-complexes constitute one of the defining compound classes of organometallic chemistry. It was therefore of interest to explore the binding of olefins to the Tp$^{t\text{-Bu,Me}}$Co fragment. Exposure of hydrocarbon solutions of Tp$^{t\text{-Bu,Me}}$Co(N_2) to an excess of ethylene resulted in an immediate color change from brown to blue-green. Concentration of the solution and cooling to −30 °C yielded the 16-electron alkene complex Tp$^{t\text{-Bu,Me}}$Co(C_2H_4) (**5**) in quantitative yield. A similar reaction of the dinitrogen complex with propene yielded the spectroscopically observable Tp$^{t\text{-Bu,Me}}$Co(C_3H_6) (**6**); however, attempts to isolate this complex were frustrated by reversibility of the reaction—i.e., removal of excess propene and exposure to N_2 resulted in re-formation of Tp$^{t\text{-Bu,Me}}$Co(N_2). We suggest that steric interactions with the extremely hindered Tp$^{t\text{-Bu,Me}}$ ligand are responsible for this remarkable selectivity. The result of an X-ray crystal structure determination of **5** is shown in Figure 3, and selected interatomic distances and angles are listed in Table 3. The most remarkable structural feature of **5** is its deviation from pseudo-3-fold symmetry; i.e., the midpoint of the ethylene ligand does not lie on the B−Co axis, being bent away from it to reach β = 154.3°. As mentioned before, Co^{I} (d^8) complexes of the type Tp$^{R,R'}$Co(L) suffer an electronically driven distortion toward this "bent" geometry, and **5** provides yet another example of this well-understood phenomenon.

The metric parameters of the ethylene coordination are ordinary. The short C═C bond (1.294(12) Å, i.e., shorter than the 1.33 Å of free ethylene) is thought to be a crystallographic artifact, due at least in part to rotational oscillation of the ethylene ligand.[11] The Co−C distances are similar to those of other cobalt ethylene complexes.[12] Finally, we note that the pyrazolyl rings close to the ethylene ligand feature longer Co−N distances (2.153(5) and 2.156(5) Å) than the "trans" pyrazole (Co−N(5) = 2.024(4) Å); at the same time the N(1)−Co−N(3) angle is widened significantly (101.1(2)°). We propose that these structural features are due to steric interactions between the olefin and the ^{t}Bu substituents of the proximal pyrazolyl rings. It is apparent that addition of a methyl substituent to the olefin would create a significant steric problem, thus explaining the ephemeral nature of the propene complex.

Physical Properties and Reactivity. None of the

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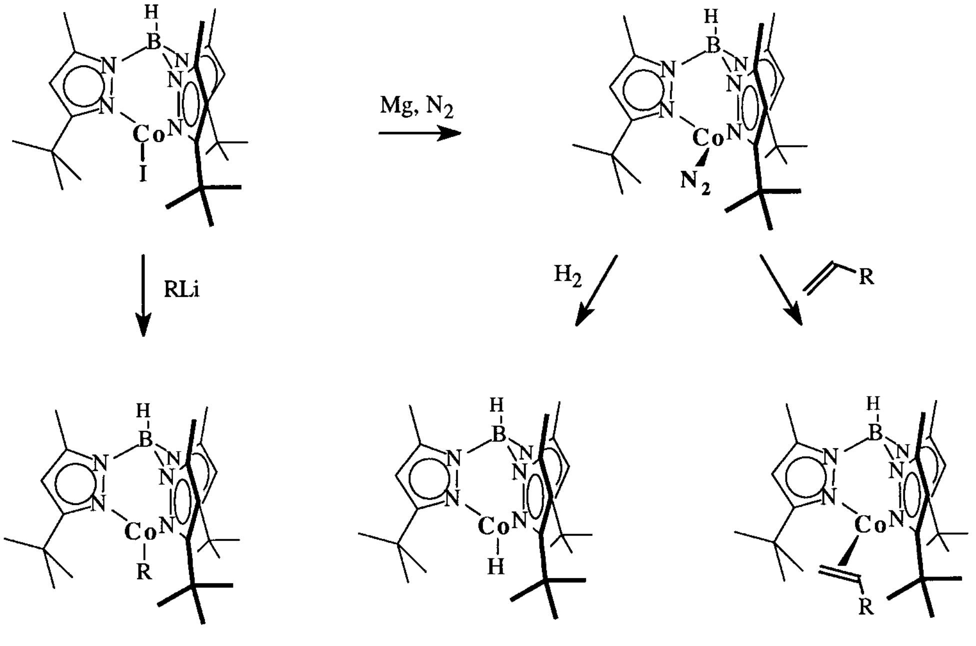
Scheme 1



1a: R = Me, **2**: R = Et, **3**: R = *n*-Bu

4

5: R = H, **6**: R = Me

Table 1. Selected Interatomic Distances and Angles for Tp$^{t\text{-Bu}}$Co(Me) (1b)

Distances (Å)			
Co−N(1)	2.112(23)	Co−N(3)	2.099(13)
Co−N(5)	2.097(5)	Co−C(1)	2.115(14)
Angles (deg)			
N(1)−Co−N(3)	93.5(7)	N(1)−Co−N(5)	93.8(6)
N(3)−Co−N(5)	92.0(5)	N(1)−Co−C(1)	122.6(6)
N(3)−Co−C(1)	122.2(7)	N(5)−Co−C(1)	124.3(6)

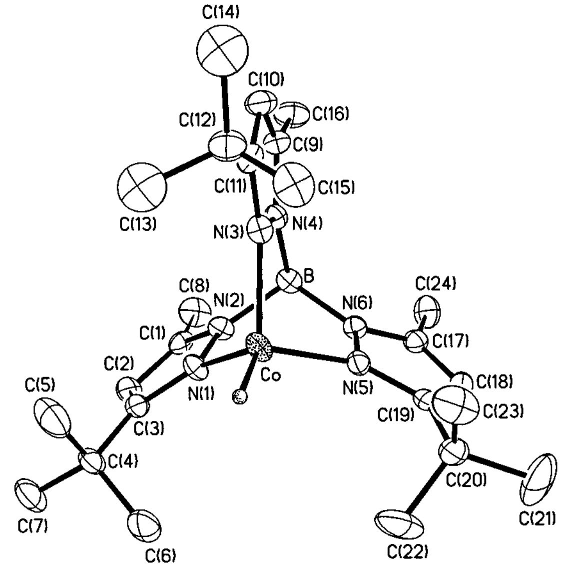


Figure 2. Molecular structure of Tp$^{t\text{-Bu,Me}}$Co(H) (**4**). Hydrogen atoms, except for the hydride, are omitted for clarity. Selected interatomic distances and angles are listed in Table 2.

new organometallic compounds described herein satisfy the 18-electron rule, and they are all paramagnetic. The alkyls and the hydride each have 15 electrons in their valence shell, and their effective magnetic moments (μ_{eff} = 4.3(1)−4.9(1) μ_B at 295 K) are consistent with the three unpaired electrons of a Co^{II} (d^7) ion in tetrahedral coordination. The magnetic moments of such complexes are well-known to exceed the spin-only moment (i.e. 3.89 μ_B for $S = {}^3/_2$), due to an orbital angular momentum contribution.[13] Tp$^{t\text{-Bu,Me}}$Co(C_2H_4) is a 16-electron species, but despite its even number of valence electrons

Table 2. Selected Interatomic Distances and Angles for Tp$^{t\text{-Bu,Me}}$Co(H) (4)

Distances (Å)			
Co−N(1)	2.038(4)	Co−N(3)	2.043(4)
Co−N(5)	2.035(4)	Co−H	1.69(4)
Angles (deg)			
N(1)−Co−N(3)	93.95(16)	N(1)−Co−N(5)	93.63(16)
N(3)−Co−N(5)	93.42(17)		

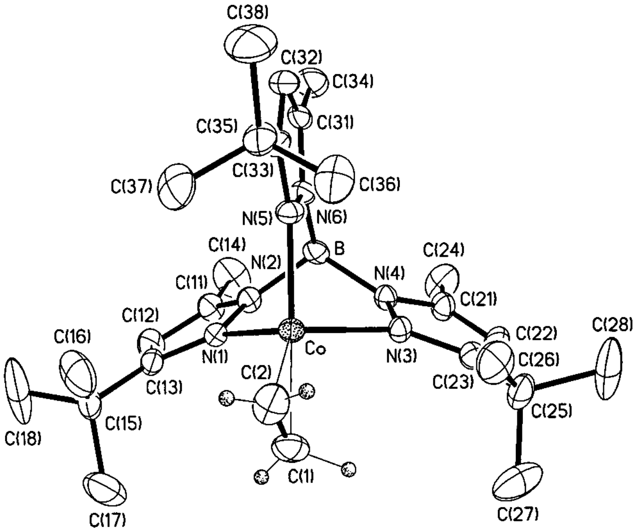


Figure 3. Molecular structure of Tp$^{t\text{-Bu,Me}}$Co(C_2H_4) (**5**). Hydrogen atoms, except for the ylene hydrogens, are omitted for clarity. Selected interatomic distances and angles are listed in Table 3.

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Table 3. Selected Interatomic Distances and Angles for $Tp^{t-Bu,Me}Co(C_2H_4)$ (5)

Distances (Å)			
Co−N(1)	2.156(5)	Co−N(3)	2.153(5)
Co−N(5)	2.024(4)	Co−C(1)	2.033(6)
Co−C(2)	2.004(7)	C(1)−C(2)	1.294(12)
Angles (deg)			
N(1)−Co−N(3)	101.1(2)	N(1)−Co−N(5)	88.6(2)
N(3)−Co−N(5)	88.4(2)	N(1)−Co−C(1)	100.5(3)
N(3)−Co−C(1)	98.8(3)	N(5)−Co−C(1)	167.0(2)
N(1)−Co−C(2)	119.3(3)	N(3)−Co−C(2)	121.4(3)
N(5)−Co−C(2)	129.8(3)	C(1)−Co−C(2)	37.4(3)

(Co^I, d^8) and its low symmetry its magnetic moment (μ_{eff} = 3.8(1) μ_B at 295 K) indicates the presence of two unpaired electrons.

The ^1H NMR spectra of the complexes exhibited isotropically shifted and broadened resonances. However, within the class of $Tp^{t-Bu,Me}Co(R)$ the chemical shifts were consistent and changed very little; they also showed the expected dependence on temperature (i.e. $\delta_{iso} \propto 1/T$). Resonances for the hydride and for hydrogen atoms bonded directly to an α- or β-carbon atom were not detected. However, $Tp^{t-Bu,Me}Co(n\text{-}Bu)$ (**3**) exhibited two alkyl resonances at 18.47 (2H) and 13.99 (3H) ppm. To our surprise, we have observed a resonance at 146.5 ppm in the ^1H NMR spectrum of **5**, which we attribute to the hydrogen atoms of the ethylene ligand. Similarly, the propene complex **6** exhibited four resonances attributed to the alkene ligand at $\delta = 110.7$ (1H), 25.0 (3H), −117.5 (1H), and −142.3 (1H) ppm.

The infrared spectrum of **4** showed a strong cobalt−hydrogen stretching vibration at $\nu_{Co-H} = 1669\ cm^{-1}$; substitution of deuterium shifted this band to $\nu_{Co-D} = 1201\ cm^{-1}$, in accord with a predicted shift to 1190 cm^{-1}. Stretching vibrations of metal hydrides are variously expected in the region 2250−1700 cm^{-1} or 1900 ± 300 cm^{-1}.[14] More specifically, ν_{Co-H} typically falls in the range 1967−1745 cm^{-1}.[15] Considering these numbers, it is apparent that the Co−H stretch of **4** appears at unusually low frequency. This observation is consistent with our inference of an unusually long Co−H distance, and both would indicate a relatively weak bond.

The Co^{II} alkyls $Tp^{t-Bu,Me}Co(R)$ are remarkably stable when protected from air and protic substances. Heating of **1a** or **3** in C_6D_6 to 90 °C for weeks did not result in any signs of decomposition. It is thus fair to say that β-hydrogen elimination is not a facile reaction pathway for these electronically unsaturated complexes. Nor did the alkyls succumb to hydrogenolysis. Heating **1a** in the presence of H_2 (1 atm, 90 °C, 1 week) had no discernible effect; in particular, no **4** was formed under these conditions. Reactions with small ligands did eventually proceed, albeit sluggishly. Thus, exposure of $Tp^{t-Bu,Me}Co(Me)$ to CO (1 atm) at ambient temperature had no effect, but upon heating the solution to 50 °C for 1 day quantitative conversion to $Tp^{t-Bu,Me}Co(CO)$ was observed. Interestingly, a similar mixture of **1b** with CO produced $Tp^{t-Bu}Co(CO)$ within minutes at room temperature. We have noted before that the steric encumbrance of the fourth coordination site—as expressed by the cone angles—differs significantly for $Tp^{t-Bu,Me}Co$ and $Tp^{t-Bu}Co$ complexes. The $Tp^{t-Bu,Me}$ ligand in particular seems to be so bulky as to completely shut down any further reactions. **1a** did not react with ethylene (1 atm, 90 °C, 2 weeks). However, it catalyzed the polymerization of methyl methacrylate; heating a solution of 50 mg of **1a** and 25 g (2500 equiv) of dry methyl methacrylate in benzene to 70 °C produced 19 g of polymer (M_w = 931 000, M_n = 196 000, M_w/M_n = 4.74). A control experiment established that the cobalt complex was required for the polymerization to occur under these conditions. We believe that this reaction may be a radical polymerization intiated by methyl radicals resulting from homolysis of the cobalt−carbon bond.

While **4** is not produced by β-hydrogen elimination from an alkyl, its reaction with ethylene at elevated temperature yielded a 7:1 mixture of $Tp^{t-Bu,Me}Co(Et)$ (**2**) and **5**. We wondered whether this reaction might proceed via initial formation of $Tp^{t-Bu,Me}Co(C_2H_4)$ followed by reaction of the latter with hydride. However, an independent control experiment showed that the ethylene complex does not react with the hydride. Thus, **3** may be formed by a migratory insertion. As expected, the reaction of **4** with CO produced $Tp^{t-Bu,Me}Co(CO)$. The reaction of **5** with H_2 was a viable route to **4**, giving ethane as the byproduct.

Conclusions

The sterically hindered $Tp^{t-Bu,Me}$ ligand facilitates the preparation of a variety of paramagnetic organocobalt complexes containing both di- and monovalent cobalt. While coordinatively unsaturated in a formal sense (15- and 16-electron configurations), the compounds exhibit only modest reactivity, probably due to steric protection of the metal−carbon and metal−hydrogen bonds. Several lines of evidence suggest that these bonds may be relatively weak and susceptible to homolytic cleavage. The design and realization of catalytic cycles depending on $Tp^{R,R'}Co$ complexes (e.g. hydroformylation, polymerization) will likely require the use of less hindered tris(pyrazolyl)borate ligands.

Experimental Section

General Considerations. Commercial reagents were used as supplied. $Tp^{t-Bu,Me}Co(I)$ and $Tp^{t-Bu,Me}Co(N_2)$ were prepared as previously described.[3a] All manipulations of air-sensitive compounds were carried out under an inert atmosphere in a Vacuum Atmospheres inert-atmosphere drybox or using standard Schlenk and/or high-vacuum techniques. Solvents were purified by distillation from sodium benzophenone ketyl. Toluene-d_8 and benzene-d_6 were dried with Na and stored over Na/K. ^1H NMR spectra were collected on a Bruker WM 250 spectrometer, using a Bruker VT 1000 variable-temperature unit as required. UV/vis/near-IR spectra were obtained on a Bruins Instruments Omega 20 spectrophotometer. Solid-state IR spectra (KBr) were obtained with a Mattson Instruments Alpha Centauri FTIR. Magnetic moments (at room temperature) were measured using a Johnson-Matthey Magnetic Susceptibilities balance.

Methyl(hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato)cobalt(II), $Tp^{t-Bu,Me}Co(CH_3)$ (1a). To a solution of 500 mg of $Tp^{t-Bu,Me}Co(I)$ (0.82 mmol) in THF was added 0.41 mL of a 3.0 M solution of MeLi in THF (1.5 equiv) at −10 °C. The reaction mixture was stirred for 7 h at −10 °C. The solution was brought into the drybox and filtered. The solvent was removed in vacuo. The residue was recrystallized from toluene after filtering the solution through a silica gel plug to remove

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any unreacted lithium reagent; yield 230 mg (56%) of blue crystals. ^{1}H NMR (C_6D_6): −4.35 (27H), 16.28 (9H), 57.14 (3H) ppm. IR (KBr): 2955 (s), 2928 (s), 2865 (m), 2560 (m), 1539 (m), 1471 (w), 1431 (m), 1351 (m), 1242 (m), 1187 (sm) 1067 (m), 1020 (w), 784 (m), 650 (m), 511 (w) cm^{-1}. UV−vis (THF): 580 (ϵ = 235 M^{-1} cm^{-1}), 614 (ϵ = 293 M^{-1} cm^{-1}), 685 (ϵ = 499 M^{-1} cm^{-1}), 1004 (ϵ = 25 M^{-1} cm^{-1}), 1515 (ϵ = 70 M^{-1} cm^{-1}) nm. Mp: 284−286 °C. μ_{eff} = 4.3(1) μ_B (295 K). Anal. Calcd for $C_{25}H_{43}BCoN_6$: C, 61.06; H, 8.61; N, 16.44. Found: C, 59.75; H, 8.66; N, 16.31. MS (*m/e*): 482 (100%), 368 (41%), 256 (21%), 236 (14%), 185 (94%).

Methyl(hydridotris(3-*tert*-butylpyrazolyl)borato)cobalt(II), Tp$^{t-\mathrm{Bu}}$Co(CH$_3$) (1b). To a solution of 525 mg of Tp$^{t-\mathrm{Bu}}$Co(I) (0.926 mmol) in THF was added 0.46 mL of a 3.0 M solution of MeLi in THF (1.5 equiv) at −10 °C. The mixture was stirred for 7 h at −10 °C. The solution was brought into the drybox and filtered. The solvent was removed in vacuo. The residue was recrystallized from toluene after filtering the solution through a silica gel plug to remove any unreacted lithium reagent; yield 253 mg (60%). ^{1}H NMR (C_6D_6): −5.02 (27H), 53.39 (3H), 57.17 (3H) ppm. IR (KBr): 2955 (s), 2922 (s), 2889 (m), 2500 (m), 1502 (m), 1461 (w), 1362 (m), 1258 (m), 1196 (s) 1089 (m), 1055 (s), 782 (s), 737 (s), 599 (m), 495 (m) cm^{-1}. UV−vis (THF): 577 (ϵ = 277 M^{-1} cm^{-1}), 611 (ϵ = 374 M^{-1} cm^{-1}), 688 (ϵ = 839 M^{-1} cm^{-1}) nm. Mp: 218−220 °C. μ_{eff} = 4.9(1) μ_B (295 K). Anal. Calcd for $C_{22}H_{37}BCoN_6$: C, 58.04; H, 8.19; N, 18.45. Found: C, 57.92; H, 8.18; N, 18.76. MS (*m/e*): 440 (100%), 260 (12%), 212 (12%), 109 (19%).

Author: Is the value of 2955 in the IR data above correct?

Ethyl(hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato)cobalt(II), Tp$^{t-\mathrm{Bu,Me}}$Co(CH$_2$CH$_3$) (2). To a solution of 700 mg of Tp$^{t-\mathrm{Bu,Me}}$Co(I) (1.15 mmol) in THF was added 0.86 mL of a 2.0 M solution of CH_3CH_2Li in THF (1.5 equiv) at −10 °C, and the reaction mixture was stirred for 7 h at −10 °C. The solution was brought into the drybox and filtered, and the solvent was removed in vacuo. The residue was recrystallized from toluene after filtering the solution through a silica gel plug to remove any unreacted lithium reagent; yield 325 mg (55%) of blue crystals. ^{1}H NMR (C_6D_6): −6.62 (27H), 16.61 (9H), 53.78 (3H) ppm. IR (KBr): 2955 (s), 2928 (s), 2865 (m), 2560 (m), 1539 (m), 1471 (w), 1431 (m), 1351 (m), 1242 (m), 1187 (sm) 1067 (m), 1020 (w), 784 (m), 650 (m), 511 (w) cm^{-1}. UV−vis (THF): 581 (ϵ = 220 M^{-1} cm^{-1}), 617 (ϵ = 275 M^{-1} cm^{-1}), 688 (ϵ = 510 M^{-1} cm^{-1}), 1023 (ϵ = 24 M^{-1} cm^{-1}), 1526 (ϵ = 52 M^{-1} cm^{-1}) nm. Mp: 260−261 °C. μ_{eff} = 4.4(1) μ_B (295 K). MS (*m/e*): 482 (100%), 368 (42%), 256 (21%), 236 (15%), 185 (94%).

***n*-Butyl(hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato)cobalt(II), Tp$^{t-\mathrm{Bu,Me}}$Co((CH$_2$)$_3$CH$_3$) (3).** To a solution of 500 mg of Tp$^{t-\mathrm{Bu,Me}}$Co(I) (0.821 mmol) in THF was added 0.493 mL of a 2.5 M solution of *n*-BuLi in THF (1.5 equiv) at −10 °C, and the reaction mixture was stirred for 7 h at −10 °C. The solution was brought into the drybox and filtered. The solvent was removed in vacuo. The residue was recrystallized from toluene after filtering the solution through a silica gel plug to remove any unreacted lithium reagent; yield 270 mg (61%) of blue crystals. ^{1}H NMR (C_6D_6): −6.51 (27H), 13.99 (3H), 16.56 (9H), 18.47 (2H), 53.87 (3H) ppm. IR (KBr): 2959 (s), 2928 (s), 2865 (s), 2552 (m), 1542 (m), 1463 (w), 1431 (m), 1361 (m), 1196 (s) 1066 (m), 1025 (m), 985 (m), 771 (m), 645 (m), 555 (w) cm^{-1}. UV−vis (THF): 582 (ϵ = 214 M^{-1} cm^{-1}), 620 (ϵ = 265 M^{-1} cm^{-1}), 692 (ϵ = 553 M^{-1} cm^{-1}), 711 (ϵ = 556 M^{-1} cm^{-1}), 1041 (ϵ = 22 M^{-1} cm^{-1}), 1546 (ϵ = 60 M^{-1} cm^{-1}) nm. Mp.: 185−190 °C. μ_{eff} = 4.7(1) μ_B (295 K). Anal. Calcd for $C_{28}H_{49}BCoN_6$: C, 62.34; H, 9.09; N, 15.58. Found: C, 62.79; H, 9.39; N, 15.05. MS (*m/e*): 482 (100%), 344 (15%), 293 (45%), 288 (12%), 123 (23%), 41 (14%), 28 (46%).

Hydrido(hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato)cobalt(II), Tp$^{t-\mathrm{Bu,Me}}$Co(H) (4). A solution of 450 mg of Tp$^{t-\mathrm{Bu,Me}}$Co(N$_2$) (0.884 mmol) in 25 mL of toluene in an ampule was freeze−pump−thawed five times. To the solution was added an excess of H$_2$, and the ampule was heated overnight to 60 °C. The solution was filtered to remove Co metal and the solvent removed in vacuo. The residue was recrystallized from toluene to yield blue crystals; yield 250 mg (59%). ^{1}H NMR (C_6D_6): −2.56 (27H), 19.24 (9H), 61.53 (3H) ppm. IR (KBr): 2962 (s), 2930 (s), 2904 (s), 2882 (s), 2541 (m), Co−H 1669 (s), 1539 (m), 1471 (m), 1431 (m), 1363 (m), 1247 (w), 1161 (s) 1065 (m), 1030 (m), 986 (m), 970 (w), 862 (w), 774 (m), 728 (w), 646 (m), 527 (m), 490 (w) cm^{-1}. UV−vis (THF): 594 (ϵ = 452 M^{-1} cm^{-1}), 630 (ϵ = 635 M^{-1} cm^{-1}), 668 (ϵ = 582 M^{-1} cm^{-1}), 982 (ϵ = 82 M^{-1} cm^{-1}), 1456 (ϵ = 111 M^{-1} cm^{-1}) nm. Mp: 237−240 °C. μ_{eff} = 4.9(1)μ_B (295 K). Anal. Calc′d for $C_{24}H_{41}BCoN_6$: C, 59.63; H, 8.49; N, 17.39. Found: C, 59.75; H, 8.66; N, 17.13. MS (*m/e*): 482 (64%), 380 (28%), 345 (29%), 288 (33%), 203 (22%), 160 (12%), 123 (100%), 91 (40%), 69 (48%).

Deuterido(hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato)cobalt(II), Tp$^{t-\mathrm{Bu,Me}}$Co(D) (4-*d*). A solution of 200 mg of Tp$^{t-\mathrm{Bu,Me}}$Co(N$_2$) (0.392 mmol) in toluene-d_8 in an ampule was freeze−pump−thawed five times. To the solution was added an excess of D$_2$, and the ampule was heated overnight at 60 °C. The solution was filtered and the solvent removed in vacuo. The residue was recrystallized from toluene; yield 110 mg (58%) of blue crystals. ^{1}H NMR (C_6D_6): −2.59 (27H), 19.25 (9H), 61.57 (3H) ppm. IR (KBr): 2958 (s), 2930 (w), 2905 (w), 2863 (w), 2541 (w), 1539 (m), 1465 (m), 1430 (w), 1373 (m), Co−D 1201 (w), 1182 (s) 1084 (s), 1030 (w), 784 (m), 728 (w), 646 (w) cm^{-1}. UV−vis (THF): 593 (ϵ = 815 M^{-1} cm^{-1}), 632 (ϵ = 1155 M^{-1} cm^{-1}), 668 (ϵ = 1080 M^{-1} cm^{-1}), 999 (ϵ = 119 M^{-1} cm^{-1}), 1472 (ϵ = 206 M^{-1} cm^{-1}) nm. Mp: 238−241 °C. MS (*m/e*): 482 (35%), 380 (14%), 345 (30%), 288 (26%), 123 (100%), 83 (16%).

Ethylene(hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato)cobalt(I), Tp$^{t-\mathrm{Bu,Me}}$Co(C$_2$H$_4$) (5). To a stirred solution of 530 mg of Tp$^{t-\mathrm{Bu,Me}}$Co(N$_2$) (1.13 mmol) in pentane in an ampule was added an excess of ethylene. A color change from brown to blue-green occurred immediately. The solution was filtered and concentrated for recrystallization; yield 530 mg (100%). ^{1}H NMR (C_6D_6): −9.07 (27H), 14.18 (9H), 32.13 (3H), 146.50 (4H) ppm. IR (KBr): 2955 (s), 2925 (m), 2864 (m), 1544 (m), 1468 (w), 1425 (m), 1360 (m), 1191 (s), 1066 (m), 1026 (w), 781 (vs), 647 (m) cm$^{-1.}$ UV−vis (THF): 660 (ϵ = 313 M^{-1} cm^{-1}), 1237 (ϵ = 288 M^{-1} cm^{-1}) nm. Mp: 202−204 °C. μ_{eff} = 3.8(1) μ_B (295 K). Anal. Calcd for $C_{26}H_{44}BCoN_6$: C, 61.06; H, 8.61; N, 16.44. Found: C, 59.75; H, 8.66; N, 16.31. MS (*m/e*): 482 (100%), 481 (41%), 138 (21%), 123 (94%).

Propene(hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato)cobalt(I), Tp$^{t-\mathrm{Bu,Me}}$Co(C$_3$H$_6$) (6). An NMR tube was charged with 20 mg of Tp$^{t-\mathrm{Bu,Me}}$Co(N$_2$) (0.039 mmol) in toluene-d_8; to this was added an excess of propylene. A color change from brown to green occurred immediately. ^{1}H NMR (C_7D_8): −142.26 (1H), −117.48 (1H), −20.36 (27H), 15.24 (9H), 24.70 (3H), 24.97 (3H), 110.72 (1H) ppm. UV−vis (pentane): 618 (ϵ = 219 M^{-1} cm^{-1}), 659 (ϵ = 236 M^{-1} cm^{-1}), 818 (ϵ = 158 M^{-1} cm^{-1}), 961 (ϵ = 158 M^{-1} cm^{-1}), 1250 (ϵ = 197 M^{-1} cm^{-1}) nm. Due to the extreme sensitivity of this complex, further characterization was not attempted.

Crystal Structure Determinations. Crystal, data collection, and refinement parameters are given in Table 4. Single crystals of **1b**, **4**, and **5** were sealed in glass capillaries under N$_2$. The photographic data and the crystal symmetry indicated an orthorhombic crystal system for **1b** and a monoclinic crystal system for **4** and **5**. The systematic absences in the diffraction data were consistent with the space groups *Pna*2$_1$ and *Pnma* for **1b** and were uniquely consistent with the reported space groups for **4** and **5**. Although the molecule of **1b** possessed a mirror plane, it was not aligned perpendicular to the *z* axis, as would be required for the centrosymmetric option. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. A molecule of toluene (solvent

Table 4. Crystallographic Data for Tp^{t-Bu}Co(Me)·C_7H_8 (1b), Tp$^{t-Bu,Me}$Co(H) (4), and Tp$^{t-Bu,Me}$Co(C_2H_4) (5)

	1b	4	5
formula	$C_{29}H_{45}BCoN_6$	$C_{24}H_{41}BCoN_6$	$C_{26}H_{44}BCoN_6$
fw	547.45	483.37	510.4
space group	$Pna2_1$	$P2_1/n$	$P2_1/c$
a, Å	19.24(3)	9.5563(14)	9.213(2)
b, Å	16.19(3)	30.615(3)	17.334(4)
c, Å	10.303(11)	9.5639(9)	18.526(5)
β, deg		102.450(9)	102.51(2)
V, Å^3	3210(8)	2732.3(5)	1888.4(12)
Z	4	4	4
cryst color, habit	blue plate	blue block	green block
D(calcd), g cm^{-3}	1.133	1.l175	1.174
μ(Mo Kα), cm^{-1}	5.60	6.49	6.18
temp, K	293(2)	248(2)	298(2)
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)		
$R(F)$, %	8.06[a]	5.37[a]	5.21[b]
$R_w(F)$, %	15.99[a]	11.54[a]	5.93[b,c]

[a] Quantity minimized $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. [b] Quantity minimized $\sum\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R_w = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$. [c] $R_w(F^2)$, %.

of recrystallization) was located in the asymmetric unit of **1b**, but the methyl carbon atom could not be located from the difference map, because it was disordered over six positions. The phenyl carbon atoms were refined as rigid planar group, to preserve a reasonable data-to-parameter ratio, and the hydrogen atoms were omitted. The absolute configuration of the molecule of **1b** in the solid state has been determined (Flack parameter 0.04(7)). The carbon atoms of **1b** were refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bound to the cobalt and boron atoms of **4** were located from the difference map, and their thermal parameters were idealized. All other hydrogen atoms were treated as idealized contributions.

All software and sources of scattering factors are contained in either the SHEXTL PLUS (PC version) or SHELXTL (Versions 5.03, 5.10) program libraries (G. Sheldrick, Siemens XRD, Madison, WI). Thermal ellipsoids in Figures 1−3 are drawn at the 30% probability level.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and H-atom coordinates for **1b**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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