Synthesis, Characterization and Reactivity of Neutral Octahedral Alkyl-Cobalt(III) Complexes Bearing a Dianionic Pendentate Ligand.

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Abstract

A variety of neutral alkyl-cobalt(III) complexes bearing a dianionic tetrapodal pendentate ligand B_2Pz_4Py are reported. Compounds **2-R** ($R = CH_3$, CH_2SiMe_3 , CH_2SiMe_2Ph , iBu , $CH_2(c-C_5H_9)$ and $(CH_2)_4CH=CH_2$) are synthesized in 58-90% yield. These diamagnetic, octahedral complexes are thermally stable up to $110^\circ C$ and are also remarkably stable to ambient atmosphere. They were fully characterized by spectroscopic techniques, and in three cases, X-ray crystallography. Evidence for reversible homolytic cleavage of the Co-C bonds was found in their reactions with the hydrogen atom donor 1,4-cyclohexadiene and the radical trap TEMPO, as well as the observed cyclization of the 5-hexenyl group to the methylcyclopentyl derivative over the course of several hours. Despite these observations, it can be concluded that the diborate B_2Pz_4Py ligand provides a very stable platform for these Co(III) alkyls. Reduction by one electron to a Co(II) alkyl can accelerate bond homolysis, but in this instance, using cobaltocene as the reducing agent, leads to ejection of an alkide anion through bond heterolysis, an unusual reaction for Co(III) alkyls. Finally, protonation of compound **2-Me** with the strong acid $HNTf_2$ leads to divergent reactivity in which the major protonation site is the pyridyl nitrogen of the ligand as opposed to protonation of the methyl group. The produce of protonation at nitrogen is the dimeric species **4** which was prepared via separate synthesis and characterized by X-ray crystallography.

Introduction.

In Nature, two types of cobalamins, also known as Vitamin B12, exhibit a Co-C bond, methylcobalamin (MeCbl)¹ and adenosylcobalamin (AdoCbl),² featuring $-CH_3$ and $-CH_2R$ groups in the axial position, respectively (Figure 1). In both stable forms of Vitamin B12, the cobalt center bears a +III oxidation state. During catalysis, however, the Co-C bond of MeCbl, can undergo heterolytic cleavage to give Co(I) and CH_3^+ , while for AdoCbl the bond can cleave homolytically to provide a source of Co(II) and organic radical.³ Thus, the alkyl groups in these Co(III) alkyls exhibit divergent reactivity in the *in vivo* function of Vitamin B12. Although both MeCbl and AdoCbl bear the same functionalized corrin L_3X supporting

ligand, the side chain terminating in a benzimidazole function which serves as the second axial ligand⁴ can dissociate or bind during the catalytic transformations mediated by Vitamin B12, modulating the behavior of the Co-C bond.⁵

Since the discovery of the cobalamin coenzymes, many synthetic alkyl-cobalt(III) complexes have been reported in an effort to mimic and model the properties of Vitamin B12. A recent review by Detrembleur *et al.* codifies the main categories of reported synthetic alkyl-cobalt(III) complexes, sorting them according to the nature of the supporting ligand.⁶ While the bulk of the compounds reported enlist porphyrin, cobaloxime, Schiff base or *bis*-(acetylacetonate) multidentate supporting ligands, other systems are potentially of interest. For example, tetrapodal pentadentate ligands,^{7, 8} can provide a well-defined platform around the metal center that mimics the five coordinate

Figure 1. Schematic representation of alkyl-Co(III) complexes.

environment of the B12 cobalamin construct.⁹ Such ligands have been deployed across the transition series and used for a variety of small molecule activation and catalytic transformations such as the reduction of water to hydrogen¹⁰⁻¹³ or the oxidation of water

to oxygen.^{14, 15} Despite the extensive chemistry of such ligands, only a single example of a Co(III) alkyl species supported by a pentadentate ligand has been structurally characterized, the pyN₄ cobalt methyl complex **I** of Grohmann *et al.* shown in Figure 1.¹⁶ However, its reactivity was not investigated, and the effect of the rigidity imposed by the pentadentate platform around the cobalt center remains unclear.

Based on the well-known pentapyridyl (PY₅) system introduced 20 years ago,^{17, 18} and later on the work by Gardinier who substituted the equatorial pyridine arms with pyrazole donors,¹⁹ our group has reported the synthesis of a B₂Pz₄Py ligand which features two borate moieties.²⁰⁻²² The introduction of the borate linkers renders the ligand dianionic and therefore more electron-rich. This stabilizes higher oxidation state intermediates so they can be studied in more detail. For Co, the B₂Pz₄Py ligand moves the Co(II)/Co(III) couple more than 0.5 V to more positive potentials, suggesting that it is a suitable platform for octahedral Co(III) alkyls. Herein we report the synthesis and properties of a family of neutral Co(III) alkyl complexes of the general formula shown in Figure 1.

Results and Discussion.

Synthesis and Characterization of 2-R

The Co(III) bromide complex **1**²² is a convenient starting material for a family of Co(III) alkyls (Scheme 1). Treatment of **1** in toluene with the corresponding alkyllithium reagent

R	Yield	Cmpd	δC	δH	$^1\text{J}_{\text{CH}}$
			(ppm)		(Hz)
CH ₃	70%	2-Me	19.1	4.13	135
CH ₂ SiMe ₃	88%	2-CH ₂ SiMe ₃	16.6	4.10	119
CH ₂ SiMe ₂ Ph	71%	2-CH ₂ SiMe ₂ Ph	14.3	4.27	120
CH ₂ CH(CH ₃) ₂	58%	2- ⁱ Bu	43.7	4.88	133

Scheme 1. Synthesis of **2-R** by salt metathesis

in a 1:1 ratio affords the alkyl-Co(III) complexes **2-R** (Scheme 1) in moderate to excellent yield. Various alkyl groups can be introduced, ranging from methyl (**2-Me**), to bulkier groups (**2-CH₂SiMe₃** and **2-CH₂SiMe₂Ph**) and an alkyl group with a beta-hydrogen (**2-ⁱBu**). The reaction proceeds quickly at room temperature, as observed by a color change from dark orange (**1**) to light pink (**2-R**), accompanied by the formation of a white precipitate (LiBr). The products are all diamagnetic and fully characterizable by NMR spectroscopy (*vide infra*). Although these reactions proceed cleanly without reduction of **1**, the organometallic products *are* prone to reduction to Co(II) by excess RLi. Additional equivalents of RLi resulted in the disappearance of the diamagnetic peaks in the ¹H NMR spectrum and emergence of the distinct signal at + 75 ppm in the ¹¹B NMR spectrum, attributed to the previously reported Co(II) complex.²² Therefore, a strict 1:1 ratio of **1** and alkylolithium was used for the syntheses of compounds **2-R**.

The low spin, d⁶ octahedral alkyl-cobalt(III) complexes **2-R** are stable at room temperature under ambient atmosphere for a few hours, which is surprising since many alkyl-cobalt(III) complexes have been shown to react with oxygen to form alkylperoxo complexes.^{23, 24} In addition, **2-R** are thermally stable (tested up to 110 °C in toluene). They were fully characterized using multi-nuclei NMR spectroscopy, mass-spectrometry and elemental analysis, and all the characterization data can be found in the experimental section. Through spectral analysis of the 2D NMR spectra of **2-R**, the peaks ranging from 4.13 (**2-Me**) to 4.10 (**2-CH₂SiMe₃**), 4.27 (**2-CH₂SiMe₂Ph**) and 4.88 (**2-ⁱBu**) were assigned to the protons located on the α carbon of the ligating alkyl group (Table inset, Scheme 1), which are close to the range of chemical shift of reported peaks of other alkyl-Co(III) complexes.^{16, 25} The ¹J_{CH} coupling constants for the α C-H bonds are in good agreement with the values reported for the free alkanes,²⁶ consistent with classical, non-agostic structures for these compounds. In addition, three of the **2-R** derivatives were characterized using X-ray crystallography (Figure 2). From the structures, the complexes exhibit an overall octahedral geometry with a Co-C bond length similar to other alkyl-Co(III) complexes.^{16, 25, 27, 28} In particular, the metrical data of **2-Me** is comparable to that of MeCbl with a Co-C bond length of 1.987 (4) vs 1.99 for MeCbl and Co-N1 of 2.072 (3) vs 2.19 in MeCbl.²⁹ Notably, the axial Co-N1 bond of **2-Me** is shorter than the Co-N_{py} bond using the pyN₄

Figure 2. Thermal ellipsoid diagrams for **2-Me** (a), **2-CH₂SiMe₃** (b) and **2-CH₂SiMe₂Ph** (c). Hydrogen, boron, carbon, nitrogen, silicon and cobalt atoms are white, pink, grey, light blue, light yellow and dark blue respectively. Thermal ellipsoids are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity except the ones of the alpha carbon. Solvent molecules are omitted for clarity. Selected bond distances (Å) and bond angles (°): a. Co-C, 1.987(4); Co-N1, 2.072(3); Co-N2, 1.914(3); Co-N4, 1.927(3); N1-Co-C, 178.3(1); N1-Co1-N2, 90.6(1). b. Co-C, 2.017(3); Co-N1, 2.083(2); Co-N2, 1.957(4); Co-N4, 1.988(3); N1-Co-C, 177.8(2); N1-Co1-N2, 90.0(1). c. Co-C, 2.03(1); Co-N1, 2.098(8); Co-N2, 1.920(8); Co-N4, 1.978(7); N1-Co-C, 175.6(4); N1-Co1-N2, 88.1(3). Selected metrical data given in Table S1.

platform (2.018(2)), showing how the pyrazole arms impose a more rigid environment around the cobalt center in comparison to alkylamines. The Co-N1 bond length in **2-Me** is slightly elongated in comparison to the Co-N1 bond of **1** (2.005 (2)). This is attributed to the stronger trans influence of the alkyl group vs. the bromo ligand.³⁰ As in other structures involving this ligand environment,^{20-22,31,32} the bulkier silylalkyl groups orient themselves along the vector bisecting the narrower N-Co-N angle, which is more sterically open than the perpendicular vector bisecting the wider N-Co-N angles. Nevertheless, rotation about the Co-C bonds is rapid on the NMR timescale, averaging the environments of the four pyrazolyl rings at all accessible temperatures.

Properties of the Co-C bonds in 2-R

The relatively electron richness of the dianionic B₂Pz₄Py ligand environment contributes to the apparent stability of these octahedral Co(III) alkyl complexes. Co(III)-C bonds tend to be fairly weak (14-40 kcal mol⁻¹) and subject to thermal homolysis via *k*₁ (Scheme 2).^{6,33-36} Typically, the equilibrium lies towards the alkyl and *k*₋₁ is essentially diffusion controlled

such that the R• radical only slowly escapes the solvent cage; the presence of a radical trapping agent can accelerate this process by drawing the equilibrium to the right. Bond homolysis may also be accelerated by one electron reduction (via $k^{R\bullet}$) since addition of an electron populates an antibonding orbital and lowers the Co-C bond order. However, in situations where Co(I) is less accessible, loss of R• via $k^{R\bullet}$ (Scheme 2) becomes a possibility although this has not been directly observed to our knowledge. Therefore, given the historical importance of such compounds as models for the behavior of cobalamin alkyls, it is of interest to probe the reactivity of these species towards radical trapping agents, one-electron reducing agents and protons.

Scheme 2. Pathways for cleavage of the Co-C bond in alkyl-Co(III) complexes

The Co-C bond dissociation energies (BDE) for **2-R** were evaluated using DFT calculations with the B3PW91 functional (for details, see the Supporting Information) and result in values of 32.1 (**2-Me**, kcal mol⁻¹), 29.3 (**2-CH₂SiMe₃**), 31.6 (**2-CH₂SiMe₂Ph**) and 27.6 (**2-ⁱBu**) for the four synthesized compounds. These are consistent with experimental and computed values⁶ for other six coordinate Co(III)-C complexes (perhaps towards the high end of the range) but follow a general trend of weaker bonds for sterically more imposing R groups.³³

Based on these values, it might be expected that the homolytic bond cleavage equilibrium in Scheme 2 can be apprehended using radical trapping agents such as 1,4-cyclohexadiene (CHD) or 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), Scheme 3. While compounds **2-R** are stable towards bond homolysis up to 110°C, in the presence of the hydrogen atom donor CHD, (BDE = 71 kcal/mol),³⁷ all of the compounds except **2-Me** slowly released R-H

Scheme 3. Reactivity of **2-R** with R• trapping agents.

at 80°C, along with the known five coordinate (B₂Pz₄Py)Co(II) complex **3**, identifiable via its characteristic ¹¹B NMR chemical shift of 75 ppm (Figures S1-S7).²¹ Protio benzene was also detected in these reactions. This suggests that under these conditions, the R• formed via bond homolysis can be trapped when it is sterically large enough to escape the solvent cage; in the case of **2-Me**, this does not occur. More efficient trapping of R• from all of the cobalt (III) alkyls is seen when TEMPO is employed (Scheme 3, bottom). Here, the reactions occur smoothly at room temperature over ≈24 hrs to produce **3** and the TEMPO-R products in excellent NMR yields (Figures S8-S15). In these TEMPO trapping reactions, once bond cleavage and cage escape occurs, reaction of R• with TEMPO is essentially diffusion controlled, whereas when CHD is the trapping agent, there is an added barrier involving H atom transfer, accounting for the harsher conditions necessary to effect those reactions.

Both outcomes are consistent with a homolytic cleavage pathway as depicted in Scheme 2. Qualitatively, in comparison to other literature accounts, the thermal stability of **2-R** both in the absence and presence of $R^\bullet$ trapping agents indicate they are generally more robust towards thermal homolytic bond cleavage than most six coordinate Co(III) alkyl compounds.

Further evidence for the rapid and reversible cleavage of **2-R** was obtained by preparing alkyl derivative **2-(CH₂)₄CH=CH₂**, featuring the “radical clock” 5-hexenyl³⁸ group. If homolytic cleavage is occurring, conversion of this species to **2-CH₂(c-C₅H₉)** should be observed. A summary of this experiment is shown in Scheme 4. The 5-hexenyl lithium

Scheme 4. Radical clock experiment.

reagent was generated *in situ* from the requisite iodo-alkane and $^t\text{BuLi}$ and added to a solution of **1** in toluene; it was not possible to prevent some cyclization to methylcyclopentyl lithium even at low temperature³⁹ and so an 2:1 mixture of **2-(CH₂)₄CH=CH₂** and **2-CH₂(c-C₅H₉)** was produced in this synthesis (Figure S16). The

identity of **2-CH₂(c-C₅H₉)** was confirmed through separate synthesis (90% isolated yield) from **1** and methylcyclopentyl lithium. The 2:1 mixture converted fully to **2-CH₂(c-C₅H₉)** after 24 h at room temperature in C₆D₆ we observed its full consumption and the formation of **2-CH₂(c-C₅H₉)** (Figures S17-18). The cyclization is rather slow and a small amount of **3** is observed to form by ¹¹B NMR spectroscopy, suggesting that some R• escapes during this process. Nonetheless, the experiment indicates that reversible bond homolysis is occurring in this system.

The above observations suggest that for the K₁ equilibrium of Scheme 2, the ratio of k₁/k₋₁ is very low and that trapping of alkyl radicals by Co(II) complex **3** is rapid, contributing to the overall macroscopic stability of these alkyls. Martin and Finke have shown that one electron reduction of MeCbl results in significantly enhanced rates of bond homolysis.³⁴ Indeed, cyclic voltammetric measurements on compounds **2-R** indicate that all of them undergo an irreversible one-electron reduction at potentials of – 0.89 V (**2-Me**), –0.86 V (**2-CH₂SiMe₃**), –0.88 V (**2-CH₂SiMe₂Ph**) and –0.85 V (**2-ⁱBu**), all vs Fc/Fc⁺. Figure 3 shows the CV of **2-Me** at various scan rates and the data for the other **2-R** compounds are shown in

Figure 3. Cyclic voltammograms of **2-Me** in THF at different scan rates (0.02 to 0.5 V/s) under argon. Supporting electrolyte: TBAPF₆; working electrode: glassy carbon; counter electrode: Pt; reference electrode: Ag wire.

Figures S19-21). This suggests that the addition of one electron to **2-R** leads to a highly unstable radical anion $[\text{Co(II)-R}]^{\bullet-}$. However, interpretation of the cyclic voltammogram suggests that this radical anion does not decompose via bond *homolysis* (via $k^{\text{R}\bullet}$, Scheme 2) but rather via dissociative loss of R^- , i.e. *heterolytic* cleavage of Co-C. As seen in Figure 3, for **2-Me**, when scanned in the range of 0.1 to -1.6 V at variable scan rates (0.02 to 0.5 V s⁻¹), a reduction wave at -0.89 V (vs Fc/Fc⁺) is observed to be partially reversible at faster scan rates, but is essentially irreversible at slower scan rates. Anodic scanning shows a pseudo reversible oxidation at -0.33 V, which is identical to the potential observed for the Co(II)/Co(III) couple of five coordinate complex **3** under the same conditions,²² suggesting that **3** is the product of decomposition of the one electron reduction product of **2-Me**. If bond homolysis from $[\text{Co(II)-R}]^{\bullet-}$ occurred via $k^{\text{R}\bullet}$, the product would be the $[\text{Co(I)}]^-$ anion, that is the one electron reduction product of **3**. Electrochemical measurements on **3** itself show that the Co(I)/Co(II) couple in this compound occurs at very negative potentials ($\approx$ -2.54 V vs Fc/Fc⁺, see Figure S22) so this clearly is not the product of decomposition of $[\text{Co(II)-R}]^{\bullet-}$, which prefers to eject alkyl anions R^- .

This notion was supported by experiments that probe the one electron chemical reduction of compounds **2-R**. For those with larger alkyl groups than methyl, reduction with cobaltocene (Cp_2Co) in benzene proceeds cleanly as depicted in Scheme 5. These reactions occur essentially upon mixing and cleanly produce compound **3**, along with the CpCo(I) cyclopentadiene complexes **I-R** (Figures S23-28). These are the known products of the reactions of the cobalticenium cation with bulky alkide nucleophiles;⁴⁰ although these specific examples are new, we did not pursue isolation/characterization of these byproducts. They are formed in >90% NMR spectroscopic yield and exhibit characteristic resonances in the ¹H NMR spectra for the allylic cyclopentadienyl hydrogen and the CH_2 groups of the added alkyl group (shown in Scheme 5). Thus, it appears clear that the Cp_2Co reduces **2-R**, and the resulting radical anion ejects R^- that adds to the $[\text{Cp}_2\text{Co}]^+$ as encountered in well-established chemistry.

Interestingly, despite having a similar reduction potential to the others, the same reaction with **2-Me** appears to not to proceed; mixing **2-Me** with Cp_2Co results in no reaction at room temperature (Figure S29). We believe this stems from divergent reactivity of $[\text{Cp}_2\text{Co}]^+$ with the methide anion in comparison to the bulkier alkide anions discussed

Scheme 5. One electron reduction of **2-R** ($\text{R} \neq \text{Me}$)

above.⁴⁰ Rather than add to one of the Cp rings, $\text{Me}^\bullet$ reduces the cobalticinium cation back to cobaltocene, and the methyl radical that results dimerizes to ethane or scavenges a hydrogen atom to produce methane. Indeed, we reproduced this chemistry and observed only a trace of **I-Me** upon reaction of $[\text{Cp}_2\text{Co}]^+[\text{PF}_6]^-$ with MeLi, the major products being cobaltocene and ethane (Figures S30-31). In the case of reduction of **2-Me**, the $\text{Me}^\bullet$ produced is trapped rapidly by **3**, to regenerate **2-Me**, giving the *appearance* of no reaction (Scheme 6). Upon heating the benzene solutions of **2-Me** and Cp_2Co to 80°C for 24 hours, traces of **I-Me** were observed, but otherwise the sample was unchanged (Figure S32).

The relative electron richness of these neutral Co(III) alkyls (in comparison to cationic Co(III) alkyls) lead us to also explore the reactivity of alkyls **2-Me** and **2-CH₂SiMe₃** towards protic reagents. Both are relatively inert towards weaker acids like water and alcohols. The

stronger acid bis(trifluoromethanesulfonyl)imide acid (HNTf₂) did react with the alkyls, although for the bulkier compound the reaction was not clean, and indeed much of **2-CH₂SiMe₃** remained unreacted (Figure S33). However, when **2-Me** was treated with one equivalent of HNTf₂, a purple precipitate was rapidly formed and a new ¹H NMR spectrum recorded (Figures S34-35). In the ¹H NMR spectrum both ethane and methane were observed according to the chemical shifts referenced against C₆D₆ (Figure S37).⁴¹ Based on the ¹H NMR integration of C₂H₆ vs CH₄, a rough estimation of a 4:1 ratio of C₂H₆ : CH₄ was found (Figure S37). A small amount of the known diamagnetic compound [(B₂Pz₄Py)Co(III)]⁺[NTf₂]⁻ was identified by ¹H and ¹⁹F NMR spectroscopy,²² but the bulk of the cobalt containing product was the paramagnetic purple precipitate, which was identified to be the dimeric Co(II) complex **4** by X-ray crystallography (Figure 4, Scheme 7.)

Scheme 7. Divergent protonation pathways for **2-Me**.

The HOMO of **2-Me** (Figure S39) is primarily localized along the Py-Co-CH₃ vector and therefore has electron density associated with both the methyl group and the pyridyl nitrogen. We thus interpret these results in terms of two competing pathways involving protonation of the methyl group leading to CH₄ and the contact ion pair [(B₂Pz₄Py)Co(III)]⁺[NTf₂]⁻ (minor) and protonation of the pyridyl nitrogen, leading dimeric compound **4** and H₃C-CH₃ (major). Ethane has been observed to form upon photolysis of methyl cobaloximes and labeling experiments indicate that it forms from dimerization of methyl radicals.⁴² While it is not clear exactly how **4** forms, we note that protonation of the five coordinate Co(II) complex **3** with HNTf₂ gives **4** in good yield, suggesting that protonation of the pyridyl nitrogen in **2-Me** triggers the homolytic cleavage of the Co-C bond to release •CH₃, which dimerizes to ethane. The protonated Co(II) compound that

Figure 4. Thermal ellipsoid diagram for **4**. Thermal ellipsoids are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity except the ones of the protonated pyridines. The two NTf₂ anions are omitted for clarity. Selected bond distances (Å) and bond angles (°): Co1-N2, 1.980(6); Co1-N4, 1.981(7); Co1-Co1', 5.738(2); Co1'-N2', 1.977(7); Co1'-N4', 1.982(7). Further metrical data are given in Table S2.

results then dimerizes with ligand rearrangement to give the observed product **4**. The structure of **4** is reminiscent of the coordination mode found in the lithium salts of the ligands that we have observed previously;²² a thermal ellipsoid representation of its structure is given in Figure 4, along with some selected metrical parameters, which are

unremarkable. Interestingly, when **4** is treated with LiOⁱPr in THF, rapid reformation of **3-THF** is observed. Evidently the substitutional lability of Co(II) compounds enables facile conversion between dinuclear and mononuclear compounds in this system.

Conclusions.

Cobalt (III) alkyl derivatives have a place of significance in the history of bioorganometallic chemistry due to their role as models for vitamin B12 chemistry. We therefore were interested in preparing alkyl complexes using our recently reported dianionic, electron rich pentadentate diborate platform²⁰ to examine their properties in this context but also as potential synthons for incorporating (B₂Pz₄Py)Co units into dinuclear structures. The compounds **2-R** are straightforwardly synthesized in good to excellent yields via salt metathesis between Co(III) bromide **1** and alkyllithium reagents. The dianionic nature of the ligand stabilizes the Co(III) oxidation state and the alkyl compounds are remarkably robust, thermally and with respect to ambient atmosphere. Nonetheless, there is evidence for reversible bond homolysis in the reaction of compounds **2-R** with hydrogen atom donors like 1,4-cyclohexadiene or radical traps like TEMPO, and also in the observed slow cyclization of the “radical clock” 5-hexenyl group to the methylcyclopentyl derivative. Most interestingly, reduction of the Co(III) alkyls to Co(II) anions does not accelerate bond homolysis as previously observed,³⁴ but leads to ejection of R[•] through heterolytic cleavage of the Co-C bond. This is a rare, possibly unprecedented, reactivity mode for Co(III) alkyls and again reflects the unusually electron rich nature of the B₂Pz₄Py ligand framework, which is not prone to supporting Co(I) centers. This study underscores the utility of this ligand platform for stabilizing higher oxidation state complexes and intermediates in metals from across the transition series.

Experimental Section.

General Procedures. Unless mentioned otherwise, all manipulations were performed under an inert gas (argon) in gloveboxes or using standard Schlenk techniques. All anhydrous solvents were prepared by passing through Mbraun SP-800 solvent purification

system and were stored in 500 mL thick-walled vessels over sodium/benzophenone ketal or CaH_2 . All dried solvents were degassed, and vacuum distilled prior to use. Pentane, toluene and benzene solvents were dried over K/Na alloy and freshly distilled before use. Chemicals were obtained from common vendors and used as received. The syntheses of the dianionic pentadentate $\text{B}_2\text{Pz}_4\text{Py}$ ligand, **1**, **3** and $[(\text{B}_2\text{Pz}_4\text{Py})\text{Co}(\text{III})]^+[\text{NTf}_2]^-$ have previously been reported.²² $\text{LiCH}_2\text{SiMe}_3$,⁴³ and $\text{LiCH}_2\text{SiMe}_2\text{Ph}$,⁴⁴ were prepared according to literature procedures. Li^iBu was synthesized using the same procedure as for $\text{LiCH}_2\text{SiMe}_3$.

Synthesis of 2-Me. To a pressure tube equipped with a Teflon tap containing suspension of **1** (60 mg, 0.087 mmol) in 8 mL of toluene, LiCH_3 (2 mg, 0.087 mmol) was added as a solid all at once. The resulting orange reaction mixture was stirred for 4 h at room temperature. The solution was stored at -40°C overnight and passed through a syringe filter. The solvent was removed *in vacuo*. The orange solid was washed with 5 mL of pentane and dried *in vacuo* to afford 38 mg of **2-Me** (70%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane in saturated solution of **2-Me** in benzene. ^1H NMR (500 MHz, C_6D_6) δ 7.96 (4H, d, $^3J_{\text{HH}} = 7.6$ Hz, H5), 7.90 (2H, d, $^3J_{\text{HH}} = 7.5$ Hz, H2), 7.67 (4H, m, H9), 7.44 (4H, m, H11), 7.26 (4H, d, $^3J_{\text{HH}} = 7.5$ Hz, H6), 7.11 (1H, t, $^3J_{\text{HH}} = 7.5$ Hz, H3), 5.78 (4H, m, H10), 4.13 (3H, s, H12), 2.35 (6H, s, H8). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6) δ 172.4 (s, C1), 142.2 (s, C9), 139.9 (s, C4), 137.1 (s, C11), 136.8 (s, C7), 136.0 (s, C5), 133.8 (s, C3), 129.1 (s, C6), 126.8 (s, C2), 105.8 (s, C10), 21.4 (s, C8), 19.1 (s, C12). ^{11}B NMR (161 MHz, C_6D_6) δ -2.1 (s, 2B). Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{B}_2\text{CoN}_9$: C 61.67; H 5.18; N 20.23. Found: (%): C 60.25; H 4.78; N 19.82. HRMS (APCI) m/z calcd: 624.2372 ($\text{M}+\text{H}$) $^+$ m/z found: 624.2400 ($\text{M}+\text{H}$) $^+$.

Synthesis of 2-CH₂SiMe₃. To a pressure tube equipped with a Teflon tap containing suspension of **1** (60 mg, 0.087 mmol) in 8 mL of toluene, $\text{LiCH}_2\text{SiMe}_3$ (9 mg, 0.087 mmol) dissolved in 2 mL of toluene was added dropwise. The resulting pink reaction mixture was stirred for 1 h at room temperature. The solution was stored at -40°C overnight and passed through a syringe filter. The solvent was removed *in vacuo*. The pink solid was washed with

5 mL of pentane and dried *in vacuo* to afford 53 mg of **2-CH₂SiMe₃** (88%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane in saturated solution of **2-CH₂SiMe₃** in benzene. ¹H NMR (500 MHz, C₆D₆) δ 7.97 (4H, d, ³J_{HH} = 7.6 Hz, H5), 7.94 (2H, d, ³J_{HH} = 7.6 Hz, H2), 7.86 (4H, d, ³J_{HH} = 2.4 Hz, H9), 7.40 (4H, d, ³J_{HH} = 2.4 Hz, H11), 7.25 (4H, d, ³J_{HH} = 7.6 Hz, H6), 7.10 (1H, t, ³J_{HH} = 7.6 Hz, H3), 5.77 (4H, t, ³J_{HH} = 2.4 Hz, H10), 4.10 (2H, s, H12), 2.34 (6H, s, H8), -0.09 (9H, s, H13). ¹³C{¹H} NMR (151 MHz, C₆D₆) δ 172.5 (s, C1), 143.0 (s, C9), 139.7 (s, C4), 137.5 (s, C11), 136.9 (s, C5), 136.1 (s, C7), 133.7 (s, C3), 129.2 (s, C6), 126.5 (s, C2), 105.8 (s, C10), 21.4 (s, C8), 16.6 (s, C12), 1.53 (s, C13). ¹¹B NMR (161 MHz, C₆D₆) δ -1.6 (s, 2B). Anal. Calcd for C₃₅H₄₀B₂SiCoN₉: C 60.45; H 5.80; N 18.13. Found: (%): C 60.82; H 5.62; N 17.96.

Synthesis of 2-CH₂SiMe₂Ph. To a pressure tube equipped with a Teflon tap containing suspension of **1** (60 mg, 0.087 mmol) in 8 mL of toluene, LiCH₂SiMe₂Ph (14 mg, 0.087 mmol) dissolved in 2 mL of toluene was added dropwise. The resulting light pink reaction mixture was stirred for 1 h at room temperature. The solution was stored at -40°C overnight and passed through a syringe filter. The solvent was removed *in vacuo*. The pink solid was washed with 5 mL of pentane and dried *in vacuo* to afford 47 mg of **2-CH₂SiMe₂Ph** (71%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane in saturated solution of **2-CH₂SiMe₂Ph** in benzene. ¹H NMR (500 MHz, C₆D₆) δ 7.97 (4H, d, ³J_{HH} = 7.6 Hz, H5), 7.92 (2H, d, ³J_{HH} = 7.6 Hz, H2), 7.83 (2H, m, H15), 7.74 (4H, d, ³J_{HH} = 2.4 Hz, H9), 7.39 (4H, d, ³J_{HH} = 2.4 Hz, H11), 7.37 (2H, d, ³J_{HH} = 7.4 Hz, H16), 7.32 (1H, t, ³J_{HH} = 7.4 Hz, H17), 7.26 (4H, d, ³J_{HH} = 7.6 Hz, H6), 7.08 (1H, t, ³J_{HH} = 7.6 Hz, H3), 5.72 (4H, t, ³J_{HH} = 2.4 Hz, H10), 4.27 (2H, s, H12), 2.34 (6H, s, H8), -0.17 (6H, s, H13). ¹³C{¹H} NMR (151 MHz, C₆D₆) δ 144.6 (s, C14), 143.3 (s, C9), 137.5 (s, C11), 136.9 (s, C7), 136.0 (s, C5), 134.5 (s, C15), 133.7 (s, C3), 129.2 (s, C6), 128.7 (s, C16), 128.4 (s, C17), 126.5 (s, C2), 105.8 (s, C10), 21.4 (s, C8), 14.3 (s, C12), -1.2 (s, C13). C1 and C4 not observed. ¹¹B NMR (161 MHz, C₆D₆) δ -1.5 (s, 2B). Anal. Calcd for C₄₀H₄₂B₂CoN₉Si: C 63.43; H 5.59; N 16.64. Found: (%): C 62.58; H 5.25; N 16.40.

Synthesis of 2-ⁱBu. To a pressure tube equipped with a Teflon tap containing suspension of **1** (60 mg, 0.087 mmol) in 8 mL of toluene, Li^{*i*}Bu (9 mg, 0.087 mmol) dissolved in 2 mL of toluene was added dropwise. The resulting pink reaction mixture was stirred for 1 h at room temperature. The solution was stored at -40°C overnight and passed through a syringe filter. The solvent was removed *in vacuo*. The pink solid was washed with 5 mL of pentane and dried *in vacuo* to afford 35 mg of **2-ⁱBu** (58%). ¹H NMR (500 MHz, C₆D₆) δ 7.98 (4H, d, ³J_{HH} = 7.6 Hz, H5), 7.92 (2H, d, ³J_{HH} = 7.6 Hz, H2), 7.67 (4H, d, ³J_{HH} = 2.4 Hz, H9), 7.44 (4H, d, ³J_{HH} = 2.4 Hz, H11), 7.26 (4H, d, ³J_{HH} = 7.6 Hz, H6), 7.12 (1H, t, ³J_{HH} = 7.6 Hz, H3), 5.77 (4H, t, ³J_{HH} = 2.4 Hz, H10), 4.88 (2H, d, ³J_{HH} = 7.0 Hz, H12), 2.58 (1H, m, H13), 2.34 (6H, s, H8), 0.98 (6H, d, ³J_{HH} = 6.3 Hz, H14). ¹³C{¹H} NMR (151 MHz, C₆D₆) δ 172.5 (s, C1), 142.5 (s, C9), 140.1 (s, C4), 137.4 (s, C11), 136.8 (s, C7), 136.1 (s, C5), 133.6 (s, C3), 129.1 (s, C6), 126.5 (s, C2), 105.6 (s, C10), 43.7 (s, C12), 32.9 (s, C13), 23.7 (c, C14), 21.4 (s, C8). ¹¹B NMR (161 MHz, C₆D₆) δ -1.6 (s, 2B). Anal. Calcd for C₃₅H₃₈B₂CoN₉: C 63.19; H 5.76; N 18.95. Found: (%): C 63.06; H 5.84; N 18.58. HRMS (APCI) *m/z* calcd: 666.2841 (M+H)⁺ *m/z* found: 666.2823 (M+H)⁺.

Synthesis of 2-CH₂(*c*-C₅H₉). A suspension of **1** (60 mg, 0.087 mmol) in 8 mL of toluene in a swivel frit apparatus was cooled to -78°C using an acetone/dry ice bath. 272 μL of (cyclopentylmethyl)lithium (0.32 M, 0.087 mmol) in 3:2 ratio of pentane:diethyl ether was added dropwise at -78 °C under a flow of Ar. The acetone/dry ice bath was removed. The resulting brown reaction mixture was stirred for 1 h at room temperature. The solution was filtered to remove lithium salts. The solvent was removed *in vacuo*. The brown solid was washed with 5 mL of pentane and dried *in vacuo* to afford 54 mg of **2-CH₂(*c*-C₅H₉)** (90%). ¹H NMR (500 MHz, C₆D₆) δ 7.98 (4H, d, ³J_{HH} = 7.6 Hz, H5), 7.92 (2H, d, ³J_{HH} = 7.6 Hz, H2), 7.70 (4H, d, ³J_{HH} = 2.4 Hz, H9), 7.45 (4H, d, ³J_{HH} = 2.4 Hz, H11), 7.25 (4H, d, ³J_{HH} = 7.6 Hz, H6), 7.12 (1H, t, ³J_{HH} = 7.6 Hz, H3), 5.78 (4H, t, ³J_{HH} = 2.4 Hz, H10), 5.04 (2H, d, ³J_{HH} = 7.3 Hz, H12), 2.70 (1H, m, H13), 2.34 (6H, s, H8), 1.75 (2H, m, H15), 1.57 (2H, m, H16), 1.51 (2H, m,

H14), 1.39 (2H, m, H17). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6) δ 172.6 (s, C1), 142.5 (s, C9), 139.1 (s, C4), 137.3 (s, C11), 136.8 (s, C7), 136.1 (s, C5), 133.6 (s, C3), 129.1 (s, C6), 126.5 (s, C2), 105.6 (s, C10), 46.2 (s, C13), 40.8 (s, C12), 34.2 (s, C14 and C17), 26.1 (s, C15 and C16), 21.4 (s, C8). ^{11}B NMR (161 MHz, C_6D_6) δ -1.6 (s, 2B). Anal. Calcd for $\text{C}_{37}\text{H}_{40}\text{B}_2\text{CoN}_9$: C 64.28; H 5.83; N 18.23. Found: (%): C 62.55; H 5.37; N 18.22.

Generation of $2\text{-(CH}_2)_4\text{CH=CH}_2$. A suspension of **1** (60 mg, 0.087 mmol) in 8 mL of toluene in a swivel frit apparatus was cooled to -78°C using an acetone/dry ice bath. 272 μL of 5-Hexenyllithium (0.32 M, 0.087 mmol) in 3:2 ratio of pentane:diethyl ether was added dropwise at -78°C under a flow of Ar. The resulting brown reaction mixture was stirred for 1 h at -78°C . The solution was filtered to remove lithium salts. The solvent was removed *in vacuo*. The brown solid was washed with 5 mL of pentane and dried *in vacuo* to afford 41 mg of a mixture of the desired product **2-(CH₂)₄CH=CH₂** and **2-CH₂(c-C₅H₉)** (68%). The formation of **2-CH₂(c-C₅H₉)** is arising from the generation of cyclo(pentylmethyl)lithium *in situ* (see Figure S16 for assignment from the mixture). ^1H NMR (500 MHz, C_6D_6) δ 7.98 (4H, d, $^3J_{\text{HH}} = 7.6$ Hz, H5), 7.95 (2H, d, $^3J_{\text{HH}} = 7.6$ Hz, H2), 7.75 (4H, d, $^3J_{\text{HH}} = 2.4$ Hz, H9), 7.39 (4H, d, $^3J_{\text{HH}} = 2.4$ Hz, H11), 7.25 (4H, d, $^3J_{\text{HH}} = 7.6$ Hz, H6), 7.12 (1H, t, $^3J_{\text{HH}} = 7.6$ Hz, H3), 5.95 (2H, m, H12), 5.79 (4H, t, $^3J_{\text{HH}} = 2.4$ Hz, H10), 5.10 (2H, m, H17), 2.67 (1H, m, H16), 2.34 (6H, s, H8), 2.25 (2H, m, H15), 1.93 (2H, m, H14), 1.72 (2H, m, H13). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6) δ 142.6 (s, C9), 139.9 (s, C4), 137.3 (s, C11), 136.8 (s, C7), 136.2 (s, C5), 133.6 (s, C3), 129.1 (s, C6), 126.4 (s, C2), 105.7 (s, C10), 46.2 (s, C12), 34.5 (s, C17), 34.2 (s, C15), 31.4 (s, C14), 26.1, (s, C13), 21.4 (s, C8). C1 not observed. ^{11}B NMR (161 MHz, C_6D_6) δ -1.7 (s, 2B). Anal. Calcd for $\text{C}_{37}\text{H}_{40}\text{B}_2\text{CoN}_9$: C 64.28; H 5.83; N 18.23. Found: (%): C 62.57; H 5.44; N 17.49.

Generation of **4.** To a pressure tube equipped with a Teflon tap containing suspension of **3** (60 mg, 0.099 mmol) in 10 mL of bromobenzene, HNTf₂ (28 mg, 0.099 mmol) was added as a solid all at once at room temperature. The reaction was immediate, resulting in the

formation of a deep purple precipitate. The solvent was removed *in vacuo* to afford 75 mg of **4** (85%). Crystals suitable for X-ray diffraction were obtained from the precipitate formed in bromobenzene. ¹H NMR (500 MHz, *o*-Cl₂-C₆D₄) δ 47.5, 35.0, 31.8, 27.2, 24.5, 22.3, 16.0, 13.8, 10.2, 6.0, 1.3, 0.9, -35.7, -39.6. ¹⁹F NMR (471 MHz, *o*-Cl₂-C₆D₄) δ -79.4 (s, 12F) No ¹¹B signal. Anal. Calcd for C₆₆H₆₀B₄Co₂N₂₀F₁₂O₈S₄: C 44.57; H 3.40; N 15.75. Found: (%): C 45.05; H 3.68; N 15.17. Note: **4** is sparingly soluble in *o*-Cl₂-C₆D₄.

Supporting Information Available.

The following files are available free of charge.

Experimental and characterization details for all new compounds, including spectroscopic data, X-ray crystallographic data and computational details with the cartesian coordinates for calculated structures (PDF).

CCDC codes 1993721-1993724 contain the crystallographic data for compounds **2-Me**, **2-CH₂SiMe₃**, **2-CH₂SiMe₂Ph** and **4**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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Synthesis, Characterization and Reactivity of Neutral Octahedral Alkyl-Cobalt(III) Complexes
Bearing a Dianionic Pendentate Ligand

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Supporting Information

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Experimental Details.

Physical Methods

^1H , $^{13}\text{C}\{^1\text{H}\}$ chemical shifts are referenced to the residual solvent signals of C_6D_6 (^1H , 7.16 ppm; $^{13}\text{C}\{^1\text{H}\}$, 128.06 ppm), THF- d_8 (^1H , 3.58, 1.72 ppm; $^{13}\text{C}\{^1\text{H}\}$, 67.21, 25.31 ppm) and toluene- d_8 (^1H , 7.09, 7.01, 6.97, 2.08 ppm; $^{13}\text{C}\{^1\text{H}\}$, 137.48, 128.87, 127.96, 125.13, 20.43 ppm). ^1H , ^{11}B , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F , $^{29}\text{Si}\{^1\text{H}\}$, ^1H - ^1H -COSY, ^1H - ^{13}C -HSQC and ^1H - ^{13}C -HMBC NMR experiments were performed at room temperature on Bruker RDQ-400, or Ascend-500 or Avance-600 MHz spectrometers and analyzed with MestReNova software (v8.1, Mestrelab Research S.L.). All ^{11}B chemical shifts are relative to $\text{BF}_3\cdot\text{OEt}_2$, all ^{19}F chemical shifts are relative to hexafluorobenzene. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass loop. Diffraction experiments were performed on a Bruker Smart diffractometer equipped with an Incoatec Microfocus (Cu $\text{K}\alpha$, $\lambda = 1.54178 \text{ \AA}$) and an APEX II CCD detector. The crystals were kept at 173 K during data collection. Diffractions spots were integrated and scaled with SAINT (Bruker-AXS. SAINT; Madison, Wisconsin, USA, 2017) and the space group was determined with XPREP (Bruker-AXS. XPREP; Madison, Wisconsin, USA, 2017.) Using Olex2¹, the structures were solved with the ShelXT² structure solution program using Intrinsic Phasing and refined with the ShelXL³ refinement package using Least Squares minimization. Full crystallography details can be found in independently uploaded .cif files. Elemental analysis was performed on site by Johnson Li using a Perkin Elmer Model 2400 series II analyzer. Solution high resolution-mass spectrometry experiments were performed on a Kratos MS-80 spectrometer by Wade White (direct ESI-MS or APCI-MS) on samples prepared in the glovebox in a gas tight syringe. Cyclic voltammetry experiments were carried out using a CH instrument potentiostat and C-3 cell stand. A glassy carbon working electrode, a platinum counter electrode and a silver wire pseudo reference electrode were used for cyclic experiments in THF with 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ electrolyte in a glovebox. Ferrocene ($E_{\text{Fc}^+/\text{Fc}} = 0.64 \text{ V vs SHE}$) was added during each experiment as an internal reference.

Computational Details

All the quantum-chemical calculations were conducted using the Gaussian16 program suite.⁴ As functional we have used the Becke's 3-parameter hybrid one,⁵ combined with the non-

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⁴ Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang,

local correlation functional provided by Perdew/Wang, denoted as B3PW91.⁶ For Co, the relativistic energy-consistent pseudopotential of the Stuttgart-Köln ECP library was used in combination with its adapted segmented basis.⁷ For all other atoms, a standard 6-31G** basis set was used.^{8,9} All stationary points have been identified as minima (number of imaginary frequencies Nimag=0).

Further Synthetic Details.

Generation of (Cyclopentylmethyl)lithium

This procedure was done according to a modified literature procedure under Ar.¹⁰

In a two-neck round bottom flask equipped with a Y-Joint was added iodo(methyl)cyclopentane (90 mg, 0.43 mmol). A 3:2 ratio of pentane (500 μ L) and diethyl ether (340 μ L) was added to the flask to have an overall 0.5 M solution of iodo(methyl)cyclopentane. The solution was cooled to -78 °C using an acetone/dry ice bath and ^tBuLi (1.7M, 500 μ L, 0.86 mmol) was added dropwise under vigorous stirring. The solution was stirred at -78 °C for 1 h and the concentration of 0.32 M was found assuming 100 % yield.

Generation of 5-Hexenyllithium

This procedure was done according to a modified literature procedure under Ar.¹⁰

In a two-neck round bottom flask equipped with a Y-Joint was added 6-iodo-1-hexene (90 mg, 0.43 mmol). A 3:2 ratio of pentane (500 μ L) and diethyl ether (340 μ L) was added to the flask to have an overall 0.5 M solution of 6-iodo-1-hexene. The solution was cooled to -78 °C using an acetone/dry ice bath and ^tBuLi (1.7M, 500 μ L, 0.86 mmol) was added dropwise under vigorous stirring. The solution was stirred at -78 °C for 1 h and the concentration of 0.32 M was found assuming 100 % yield.

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⁹ Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, 28 (3), 213.

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Generation of CpCo(I) cyclopentadiene complexes I-R

Note: [CoCp₂][PF₆] has a very poor solubility in C₆D₆. Therefore even though a 1:1 ratio of [CoCp₂][PF₆] and LiR was used, some unreacted LiR remains in solution (See Figures S30-31 and S52-57).

Generation of I-CH₃. To a J-Young tube equipped with a Teflon tap, [CoCp₂][PF₆] (30.4 mg, 0.091 mmol) and LiCH₃ (2.0 mg, 0.091 mmol) were added as solids and THF-*d*8 was added (~0.5 mL). Two ¹H NMR spectra were taken 30 mins after addition of THF-*d*8. One spectrum in the diamagnetic region to detect I-CH₃ and one spectrum with a bigger window to detect CoCp₂. CoCp₂, along with ethane and methane were detected (Figures S30-31). ¹H NMR (500 MHz, THF-*d*8) δ 5.14 (2H, m, H4), 4.67 (5H, s, H1), 2.63 (3H, m, H3 & H2 overlapping), 0.12 (6H, d, ³J_{HH} = 5.9 Hz, H5). C₂H₆ detected at 0.85 ppm; CH₄ detected at 0.19 ppm; CoCp₂ detected at -51.3 ppm.

Note: Due to the very poor solubility of both [CoCp₂][PF₆] and LiCH₃ in C₆D₆, this reaction was done in THF.

Generation of I-CH₂SiMe₃. To a J-Young tube equipped with a Teflon tap, [CoCp₂][PF₆] (25.0 mg, 0.075 mmol) and LiCH₂SiMe₃ (7.0 mg, 0.075 mmol) were added as solids and C₆D₆ was added (~0.5 mL). Two ¹H NMR spectra were taken 30 mins after addition of C₆D₆. One spectrum in the diamagnetic region to detect I-CH₂SiMe₃ and one spectrum with a bigger window to detect CoCp₂ (Figures S52-53). No CoCp₂ was detected. ¹H NMR (500 MHz, C₆D₆) δ 5.02 (2H, m, H4), 4.60 (5H, s, H1), 2.73 (3H, m, H3 & H2 overlapping), 0.00 (2H, br, H5), -0.02 (9H, s, H6).

Generation of I-CH₂SiMe₂Ph. To a J-Young tube equipped with a Teflon tap, [CoCp₂][PF₆] (20.0 mg, 0.060 mmol) and LiCH₂SiMe₂Ph (9.4 mg, 0.060 mmol) were added as solids and then C₆D₆ was added (~0.5 mL). Two ¹H NMR spectra were taken 30 mins after addition of C₆D₆. One spectrum in the diamagnetic region to detect I-CH₂SiMe₂Ph and one spectrum with a bigger window to detect CoCp₂ (Figures S54-55). No CoCp₂ was detected. ¹H NMR (500 MHz, C₆D₆) δ 7.44 (2H, m, H7), 7.20 (3H, m, H8 & H9), 4.98 (2H, m, H4), 4.54 (5H, s, H1), 2.76 (1H, m, H2), 2.66 (2H, m, H3), 0.30 (2H, d, ³J_{HH} = 6.7 Hz, H5), 0.20 (6H, s, H6).

Generation of I-CH₂CH(CH₃)₂. To a J-Young tube equipped with a Teflon tap, [CoCp₂][PF₆] (20.0 mg, 0.060 mmol) and Li^{*i*}Bu (3.8 mg, 0.060 mmol) were added as solids and C₆D₆ was added (~0.5 mL). Two ¹H NMR spectra were taken 30 mins after addition of C₆D₆. One spectrum in the diamagnetic region to detect I-^{*i*}Bu and one spectrum with a bigger window to detect CoCp₂ (Figures S56-57). No CoCp₂ was detected. ¹H NMR (500 MHz, C₆D₆) δ 5.04 (2H, dd, J = 2.5, 1.5 Hz, H4), 4.60 (5H, s, H1), 2.67 (3H, m, H3 & H2 overlapping), 1.42 (1H, m, H6), 0.78 (6H, d, ³J_{HH} = 6.6 Hz, H7), 0.48 (2H, dd, J = 6.6 Hz, H5).

Numbering schemes for ^1H NMR assignments for compounds **I-R**:

Figures S1-S39:

Procedure for the reactivity of **2-R** in the presence of 1,4-cyclohexadiene (CHD) in Toluene-d8.

A J-Young tube equipped with a Teflon tap was charged with 5.0 mg of **2-R** in toluene-d8. A ^1H NMR spectrum was recorded. CHD (5 eq) was added at room temperature and another ^1H NMR spectrum was recorded. The Y-Young tube was then heated at 80 °C for 24 h and another ^1H NMR spectrum was recorded. If any reactivity was observed, a ^{11}B NMR spectrum was recorded to detect complex **3**.

Figure S1. ^1H stack NMR spectra of **2-Me** (spectrum 1), **2-Me + CHD** at RT (spectrum 2) and **2-Me + CHD** at 80 °C (spectrum 3) in toluene-d8.

Figure S2. ^1H stack NMR spectra of $2\text{-CH}_2\text{SiMe}_3$ (spectrum 1), $2\text{-CH}_2\text{SiMe}_3 + \text{CHD}$ at RT (spectrum 2) and $2\text{-CH}_2\text{SiMe}_3 + \text{CHD}$ at 80°C (spectrum 3) in toluene- d_8 . Protio benzene and SiMe_4 are detected in spectrum 3.

Figure S3. ^{11}B NMR spectrum of $2\text{-CH}_2\text{SiMe}_3 + \text{CHD}$ at 80°C in toluene- d_8 . The broad peak corresponds to complex 3.

Figure S4. ^1H stack NMR spectra of $2\text{-CH}_2\text{SiMe}_2\text{Ph}$ (spectrum 1), $2\text{-CH}_2\text{SiMe}_2\text{Ph} + \text{CHD}$ at RT (spectrum 2) and $2\text{-CH}_2\text{SiMe}_2\text{Ph} + \text{CHD}$ at $80\text{ }^\circ\text{C}$ (spectrum 3) in toluene- d_8 . Protio benzene and SiMe_3Ph are detected in spectrum 3.

Figure S5. ^{11}B NMR spectrum of $2\text{-CH}_2\text{SiMe}_2\text{Ph} + \text{CHD}$ at $80\text{ }^\circ\text{C}$ in toluene- d_8 . The broad peak corresponds to complex **3**.

Figure S6. ^1H stack NMR spectra of **2- i Bu** (spectrum 2), **2- i Bu + CHD** at RT (spectrum 2) and **2- i Bu + CHD** at 80 °C (spectrum 3) in toluene- d_8 . Protio benzene is detected in spectrum 3.

Figure S7. ^{11}B NMR spectrum of **2- i Bu + CHD** at 80 °C in toluene- d_8 . The broad peak corresponds to complex **3**.

Procedure for the reactivity of **2-R** with TEMPO in C_6D_6 .

A J-Young tube equipped with a Teflon tap was charged with 5.0 mg of **2-R** in C_6D_6 . A 1H NMR spectrum was recorded. TEMPO (1.1 eq) was added as a solid at room temperature and another 1H NMR spectrum was recorded after 24 h. If any reactivity was observed, a ^{11}B NMR spectrum was recorded to detect complex **3**.

Figure S8. 1H stack NMR spectra of **2-Me** (spectrum 1) and **2-Me** + TEMPO (spectrum 2) in C_6D_6 .

Figure S9. ^{11}B NMR spectrum of **2-Me** + TEMPO in C_6D_6 .

Figure S10. ^1H stack NMR spectra of **2-CH₂SiMe₃** (spectrum 1) and **2-CH₂SiMe₃ + TEMPO** (spectrum 2) in C₆D₆.

Figure S11. ^{11}B NMR spectrum of **2-CH₂SiMe₃ + TEMPO** in C₆D₆.

Figure S12. ^1H stack NMR spectra of **2-CH₂SiMe₂Ph** (spectrum 1) and **2-CH₂SiMe₂Ph + TEMPO** (spectrum 2) in C₆D₆.

Figure S13. ^{11}B NMR spectrum of **2-CH₂SiMe₂Ph + TEMPO** in C₆D₆.

Figure S14. ^1H stack NMR spectra of **2-ⁱBu** (spectrum 1) and **2-ⁱBu + TEMPO** (spectrum 2) in C_6D_6 .

Figure S15. ^{11}B NMR spectrum of **2-ⁱBu + TEMPO** in C_6D_6 .

Figure S16. Stack ^1H NMR spectra of $2\text{-CH}_2(\text{c-C}_5\text{H}_9)$ (top) and the mixture of $2\text{-(CH}_2)_4\text{CH=CH}_2$ (green dots, bottom) and $2\text{-CH}_2(\text{c-C}_5\text{H}_9)$ (orange dots, bottom) in C_6D_6 . A 2:1 ratio was determined by ^1H integration of the peaks corresponding to $2\text{-(CH}_2)_4\text{CH=CH}_2$ vs $2\text{-CH}_2(\text{c-C}_5\text{H}_9)$.

Procedure for the reactivity of 2-(CH₂)₄CH=CH₂ in C₆D₆.

A J-Young tube equipped with a Teflon tap was charged with 5.0 mg of 2-(CH₂)₄CH=CH₂ in C₆D₆. A ¹H NMR spectrum was recorded. The J-Young tube was stirred for 16 h and 24 h at room temperature and two ¹H NMR spectra were recorded. A ¹¹B NMR spectrum was recorded at room temperature after 24 h of stirring.

Figure S17. ¹H stack NMR spectra of 2-(CH₂)₄CH=CH₂ (spectrum 1), 2-(CH₂)₄CH=CH₂ at room temperature after 16 h in solution (spectrum 2), 2-(CH₂)₄CH=CH₂ at room temperature after 24 h in solution (spectrum 3) and 2-CH₂(c-C₅H₉) synthesized independently (spectrum 4) in C₆D₆.

Figure S18. ^{11}B NMR spectra of $2\text{-(CH}_2)_4\text{CH=CH}_2$ at room temperature after 24 h in solution in C_6D_6 . The broad peak corresponds to complex **3**.

Figure S19. Refer to physical method for general information. Cyclic voltammogram of $2\text{-CH}_2\text{SiMe}_3$ in THF at different scan rates (from 0.02 to 0.5 V.s^{-1}). Concentration of $2\text{-CH}_2\text{SiMe}_3$: 0.1 mM .

Figure S20. Refer to physical method for general information. Cyclic voltammogram of **2-CH₂SiMe₂Ph** in THF at different scan rates (from 0.02 to 0.5 V.s⁻¹). Concentration of **2-CH₂SiMe₂Ph**: 0.1 mM.

Figure S21. Refer to physical method for general information. Cyclic voltammogram of **2-ⁱBu** in THF at different scan rates (from 0.02 to 0.5 V.s⁻¹). Concentration of **2-ⁱBu**: 0.1 mM.

Figure S22. Refer to physical method for general information. Cyclic voltammogram of **3** in THF with a scan rate of 0.1 V.s⁻¹. The background is shown in black. Concentration of **3**: 0.1 mM.

Procedure for the reactivity of 2-R with CoCp₂ in C₆D₆.

A J-Young tube equipped with a Teflon tap was charged with 5.0 mg of **2-R** in C₆D₆. A ¹H NMR spectrum was recorded. CoCp₂ (1.1 eq) was added at room temperature and another ¹H NMR spectrum was recorded 15 mins after the addition of CoCp₂. A ¹¹B NMR spectrum was recorded to detect complex **3**.

Figure S23. ¹H stack NMR spectra of **2-CH₂SiMe₃** (spectrum 1), **2-CH₂SiMe₃ + CoCp₂** (spectrum 2) and **I-CH₂SiMe₃** (spectrum 3) in C₆D₆.

Figure S24. ¹¹B NMR spectrum of **2-CH₂SiMe₃ + CoCp₂** in C₆D₆.

Figure S25. ^1H stack NMR spectra of **2-CH₂SiMe₂Ph** (spectrum 1), **2-CH₂SiMe₂Ph + CoCp₂** (spectrum 2) and **I-CH₂SiMe₂Ph** (spectrum 3) in C_6D_6 .

Figure S26. ^{11}B NMR spectrum of **2-CH₂SiMe₂Ph + CoCp₂** in C_6D_6 .

Figure S27. ^1H stack NMR spectra of $2\text{-}^i\text{Bu}$ (spectrum 1), $2\text{-}^i\text{Bu} + \text{CoCp}_2$ (spectrum 2) and $\text{I-CH}_2\text{CH}(\text{CH}_3)_2$ (spectrum 3) in C_6D_6 .

Figure S28. ^{11}B NMR spectrum of $2\text{-}^i\text{Bu} + \text{CoCp}_2$ in C_6D_6 .

Figure S29. ^1H stack NMR spectra of **2-Me** (spectrum 1) and **2-Me + CoCp₂** (spectrum 2) in C_6D_6 .

Figure S30. ¹H NMR spectrum (diamagnetic window) of [Cp₂Co][PF₆] + LiCH₃ in THF-d₈. The CH₄ peak is overlapping with the -CH₃ protons (H5).

Figure S31. ¹H NMR spectrum (large window) of [Cp₂Co][PF₆] + LiCH₃ in THF-d₈. Cp₂Co is detected in this reaction at -51.3 ppm.

Figure S32. ^1H stack NMR spectra of **2-Me** (spectrum 1) and **2-Me + CoCp₂** at 80 °C (spectrum 2) in C_6D_6 .

Procedure for the reactivity of 2-R with HNTf₂ in C₆D₆.

A J-Young tube equipped with a Teflon tap was charged with 5.0 mg of **2-R** in C₆D₆. A ¹H NMR spectrum was recorded. A stock solution of HNTf₂ in C₆D₆ was prepared and 1 eq of HNTf₂ was added to the J-Young tube. A ¹H NMR spectrum was recorded at room temperature.

Figure S33. ¹H stack NMR spectra of **2-CH₂SiMe₃** (spectrum 1) and **2-CH₂SiMe₃ + HNTf₂** at room temperature (spectrum 2) in C₆D₆.

Figure S34. Picture of the purple precipitate formed by the reaction of **2-Me** with HNTf₂ in a J-Young tube.

Figure S35. ^1H stack NMR spectra of **2-Me** (spectrum 1), **2-Me** + HNTf_2 (spectrum 2) and $[(\text{B}_2\text{Pz}_4\text{Py})\text{Co}(\text{III})]^+[\text{NTf}_2]^-$ (spectrum 3) in C_6D_6 . The zoomed section is shown in Figure S34.

Figure S36. Zoomed section from ^1H stack NMR spectra of **2-Me** (spectrum 1), **2-Me** + HNTf_2 (spectrum 2) and $[(\text{B}_2\text{Pz}_4\text{Py})\text{Co}(\text{III})]^+[\text{NTf}_2]^-$ (spectrum 3) in C_6D_6 . The zoomed section shows the formation of ethane and methane.

Figure S37. Zoomed section from ^1H NMR spectrum of **2-Me** + HNTf_2 with integrations.

Figure S38. ^{19}F NMR spectrum of **2-Me** + HNTf_2 in C_6D_6 .

Figure S39. Depiction of the HOMO of **2-Me**.

NMR spectra of characterized compounds

Figure S40. ^1H NMR spectrum of **2-Me** in C_6D_6 .

Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-Me** in C_6D_6 .

Figure S42. ¹H NMR spectrum of **2-CH₂SiMe₃** in C₆D₆.

Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-CH₂SiMe₃** in C_6D_6 .

Figure S44. ¹H NMR spectrum of **2-CH₂SiMe₂Ph** in C₆D₆.

Figure S45. ¹³C{¹H} NMR spectrum of **2-CH₂SiMe₂Ph** in C₆D₆.

Figure S46. ^1H NMR spectrum of **2-ⁱBu** in C_6D_6 .

Figure S47. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-iBu in C_6D_6 .

Figure S48. ^1H NMR spectrum of $2\text{-CH}_2(\text{c-C}_5\text{H}_9)$ in C_6D_6 .

Figure S49. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-CH₂(c-C₅H₉)** in C_6D_6 .

Figure S50. ^1H NMR spectrum of $2\text{-(CH}_2)_4\text{CH=CH}_2$ in C_6D_6 .

Figure S51. ¹³C{¹H} NMR spectrum of **2**-(CH₂)₄CH=CH₂ in C₆D₆.

Figure S52. ¹H NMR spectrum (diamagnetic window) of **I-CH₂SiMe₃** in C₆D₆.

Figure S53. ¹H NMR spectrum (large window) of **I-CH₂SiMe₃** in C₆D₆. No Cp₂Co is detected.

Figure S56. ^1H NMR spectrum (diamagnetic window) of $\text{I-CH}_2\text{CH}(\text{CH}_3)_2$ in C_6D_6 . *Leftover $\text{LiCH}_2\text{CH}(\text{CH}_3)_2$ due to the poor solubility of $[\text{Cp}_2\text{Co}][\text{PF}_6]$ in C_6D_6 .

Figure S57. ^1H NMR spectrum (large window) of $\text{I-CH}_2\text{CH}(\text{CH}_3)_2$ in C_6D_6 . No Cp_2Co is detected.

Figure S58. ^1H NMR spectrum of **4** in $o\text{-Cl}_2\text{-C}_6\text{D}_4$.

Figure S59. ¹⁹F NMR spectrum of **4** in *o*-Cl₂-C₆D₄.

Additional crystallographic data of 4:

During the refinement, it was noticed that there was a large amount of residual electron density located between the Co atoms and the ellipsoids for Co were elongated in the same direction. Given the synthetic and recrystallization conditions used, the residual electron density was attributed to bromine from bromobenzene, the recrystallization solvent. Based on the bromine present and the elongated Co ellipsoids, the Co atom was split in to Co1A and Co1B. Initially, the occupancies of bromine and Co atoms were refined independently with the occupancy refining to 0.1326(19) and 0.12(3) for Br and Co1B, respectively. Based on their similar occupancies, Co1B is assumed be the oxidized to Co(III) and charge balanced by Br(-I). For consistency, the occupancy of Br and Co1B were set equal and allowed to refine, reaching occupancies of 0.1325(19).

Figure S60. Unit cell contents of **4**. Hydrogen, boron, carbon, nitrogen, oxygen, fluorine, sulfur, cobalt, and bromine atoms are white, pink, grey, light blue, red, green, yellow, dark blue, and gold, respectively. Ellipsoid probability set at 20%. Organic hydrogen atoms and the minor components of disorder have been omitted for clarity.

Figure S61. Structure of the Co(III) dimer present in the crystal structure of **4** due to the use of bromobenzene as the recrystallization solvent. Boron, carbon, nitrogen, cobalt, and bromine atoms are pink, grey, light blue, dark blue, and gold, respectively. Ellipsoid probability set at 50%. Hydrogen atoms, one of the disordered bromine atoms, solvent molecules, and NTf₂ anions have been omitted for clarity.

Table S1

	2-Me	2-CH₂SiMe₃	2-CH₂SiMe₂Ph
chemical formula	C ₃₂ H ₃₂ B ₂ CoN ₉	C ₃₅ H ₄₀ B ₂ CoN ₉ Si	2(C ₄₀ H ₄₃ B ₂ CoN ₉ Si), C ₆ H ₆
crystal colour	Orange	Orange	Orange
<i>F</i>w; <i>F</i>(000)	623.21; 1296	695.40; 2912.0	1595.05, 1672.0
<i>T</i> (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	1.54178
space group	P 21/c	C 2/c	P -1
<i>a</i> (Å)	20.0211(17)	39.0465(14)	15.0959(5)
<i>b</i> (Å)	17.4573(11)	8.3423(2)	17.0864(5)
<i>c</i> (Å)	8.3874(6)	26.7224(10)	17.5752(5)
α (deg)	90	90	107.220(2)
β (deg)	97.808(5)	126.921(2)	94.154(2)
γ (deg)	90	90	109.589(2)
<i>Z</i>	4	8	2
<i>V</i> (Å³)	2904.3(4)	6958.9(4)	4004.5(2)
ρ_{calcd} (g·cm⁻³)	1.425	1.327	1.323
μ (mm⁻¹)	0.632	0.568	3.986
θ range (deg); completeness	2.549– 25.999; 0.993	2.991 – 27.512; 0.996	2.681 – 72.392; 0.957
collected reflections; <i>R</i>_σ	5679; 0.0548	7969; 0.1003	15179; 0.0287
unique reflections; <i>R</i>_{int}	3259; 0.1146	4761; 0.1278	7546; 0.0512
<i>R</i>1^a; <i>wR</i>2^b [<i>I</i> > 2σ(<i>I</i>)]	0.0548; 0.0990	0.0579; 0.1210	0.2429; 0.3112
<i>R</i>1; <i>wR</i>2 [all data]	0.1223; 0.1220	0.1204; 0.1471	0.1314; 0.4058
GOF	1.005	1.012	1.001
largest diff peak and hole	0.320 and -0.491	0.456 and -0.522	0.889 and -0.707

$$^a R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$$

$$^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$$

Table S2

	4
chemical formula	C ₇₈ H ₇₀ B ₄ Br _{2.27} Co ₂ F ₁₂ N ₂₀ O ₈ S ₄
crystal colour	Pink
<i>F</i>_w; <i>F</i>(000)	2114.27; 1067.0
<i>T</i> (K)	173.0
wavelength (Å)	1.54178
space group	P-1
<i>a</i> (Å)	13.3026(2)
<i>b</i> (Å)	13.3777(2)
<i>c</i> (Å)	15.0410(3)
α (deg)	90.2900(10)
β (deg)	113.8510(10)
γ (deg)	113.6130(10)
<i>Z</i>	1
<i>V</i> (Å³)	2198.10(7)
ρ_{calcd} (g·cm⁻³)	1.597
μ (mm⁻¹)	5.849
θ range (deg); completeness	6.556 – 130.454; 0.994
collected reflections; <i>R</i>_σ	7496; 0.0311
unique reflections; <i>R</i>_{int}	7496; 0.0440
<i>R</i>₁^a; <i>wR</i>₂^b [<i>I</i> > 2σ(<i>I</i>)]	0.0598; 0.1718
<i>R</i>₁; <i>wR</i>₂ [all data]	0.0698; 0.1810
GOF	1.042
largest diff peak and hole	0.82 and -0.75

$$^a R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$$

$$^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$$

Cartesian Coordinates for calculated structures

3

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scf done: -1886.819075

H	-2.143641	2.318587	-1.858290
H	0.002175	3.276748	-2.675048
H	2.146402	2.343737	-1.826422
H	-1.091647	-2.087445	3.684324
H	-3.351205	-0.745157	4.504068
H	-4.179541	0.541013	2.226583
H	-1.141549	-3.953786	-1.808111
H	-3.206552	-3.265016	-3.487261
H	-4.075865	-0.868316	-2.461787
H	-5.228270	-0.780141	-0.489681
H	-7.323623	0.477011	-0.450723
H	-5.137925	4.102217	0.235082
H	-3.038684	2.849555	0.176589
H	-7.942985	3.510537	-1.140292
H	-7.614744	4.059004	0.504431
H	-8.518241	2.559522	0.230077
H	1.193266	-2.270188	3.599700
H	3.452195	-0.935282	4.437346
H	4.212857	0.472395	2.208784
H	1.008899	-3.816666	-2.006609
H	3.077605	-3.104106	-3.667458
H	4.045004	-0.804860	-2.514289
H	5.223091	-0.777453	-0.556036
H	7.322651	0.474400	-0.501252
H	5.151271	4.083628	0.304965
H	3.047761	2.837157	0.228480
H	8.530867	2.528863	0.211892
H	7.635373	4.014751	0.572441
H	7.932904	3.544063	-1.101796
B	-2.557478	0.089532	-0.133020
B	2.560370	0.087929	-0.143599
C	-1.189908	0.864333	-0.591326
C	-1.198208	1.932027	-1.494512
C	0.001500	2.464827	-1.951294
C	1.200258	1.945879	-1.476889
C	1.191086	0.872348	-0.580268
C	-1.750801	-1.447331	3.115862
C	-2.898381	-0.763568	3.523761
C	-3.330710	-0.106108	2.381821
C	-1.774723	-3.078906	-1.783959
C	-2.828708	-2.725890	-2.631076
C	-3.286699	-1.520311	-2.120357
C	-3.932259	0.931601	-0.250226
C	-5.181911	0.300772	-0.382691
C	-6.380795	1.009543	-0.339914
C	-6.393898	2.394141	-0.139062
C	-5.162130	3.031111	0.043089
C	-3.967263	2.314901	-0.006562
C	-7.683345	3.169399	-0.129871

C	1.828737	-1.588659	3.052138
C	2.976447	-0.910214	3.468130
C	3.374417	-0.191060	2.350965
C	1.677942	-2.972579	-1.932543
C	2.732823	-2.606079	-2.773243
C	3.241172	-1.451475	-2.197707
C	3.934724	0.929824	-0.255134
C	5.181155	0.300199	-0.418058
C	6.381961	1.005218	-0.366651
C	6.399823	2.383440	-0.126085
C	5.171109	3.018100	0.083643
C	3.974207	2.306090	0.024482
C	7.690899	3.155809	-0.104104
N	0.000719	0.343651	-0.205075
N	-2.485443	-0.393326	1.369508
N	-1.511587	-1.215507	1.822202
N	-2.557572	-1.208914	-1.030248
N	-1.604592	-2.151001	-0.836710
N	2.509967	-0.439067	1.344531
N	1.557021	-1.294698	1.777516
N	2.539551	-1.182903	-1.078161
N	1.556230	-2.101968	-0.925627
Co	-0.000870	-1.621121	0.488284

2-Me

76

scf done: -1926.703864

H	-2.113650	2.665743	-1.696078
H	0.039100	3.686690	-2.436232
H	2.175367	2.650081	-1.671164
H	-1.055515	-2.465830	3.207255
H	-3.281615	-1.250418	4.249728
H	-4.079000	0.441321	2.232293
H	-1.037212	-3.710661	-1.921205
H	-3.198547	-3.118124	-3.495627
H	-4.077749	-0.715752	-2.480771
H	-5.167458	-0.635096	-0.544248
H	-7.284460	0.568394	-0.373358
H	-5.159975	4.184254	0.520735
H	-3.037844	2.987840	0.325229
H	-7.987519	3.623548	-0.833344
H	-7.626970	4.069408	0.835601
H	-8.504985	2.570675	0.484577
H	0.914337	-2.275047	3.323641
H	3.121756	-1.047347	4.365611
H	4.052472	0.473119	2.267932
H	0.886191	-3.552175	-2.145550
H	3.039409	-2.927379	-3.702020
H	4.060981	-0.672366	-2.496125
H	5.164702	-0.721218	-0.516564
H	7.313460	0.429997	-0.345179
H	5.278310	4.105016	0.516021
H	3.126387	2.960072	0.325872
H	8.578895	2.408881	0.513074

H	7.738117	3.935931	0.831463
H	8.099783	3.452133	-0.826713
H	-1.091453	-3.774154	0.867128
H	0.506561	-3.653773	1.659630
H	0.411348	-4.051275	-0.054754
B	-2.501825	0.280024	-0.193683
B	2.530965	0.253239	-0.176002
C	-1.159687	1.085804	-0.596358
C	-1.166380	2.240944	-1.383582
C	0.032082	2.808857	-1.794388
C	1.221615	2.232233	-1.369240
C	1.197960	1.076174	-0.584194
C	-1.671017	-1.694292	2.775502
C	-2.816468	-1.082918	3.289735
C	-3.229785	-0.221371	2.287131
C	-1.669848	-2.839322	-1.898916
C	-2.784273	-2.539274	-2.683670
C	-3.245951	-1.332984	-2.179308
C	-3.899584	1.085407	-0.221579
C	-5.138810	0.437066	-0.368104
C	-6.350785	1.113574	-0.247841
C	-6.388475	2.479941	0.051185
C	-5.166512	3.129682	0.251641
C	-3.958264	2.446394	0.122986
C	-7.693545	3.222543	0.145144
C	1.576209	-1.570457	2.850198
C	2.709013	-0.944946	3.373087
C	3.189719	-0.171150	2.330293
C	1.572263	-2.730330	-2.038049
C	2.678250	-2.409862	-2.825827
C	3.211723	-1.280312	-2.225737
C	3.942603	1.033064	-0.203582
C	5.164981	0.352168	-0.343648
C	6.393248	0.998850	-0.225364
C	6.464182	2.366123	0.063992
C	5.258616	3.048382	0.255769
C	4.033684	2.394743	0.129597
C	7.787588	3.075935	0.155984
C	-0.051762	-3.457380	0.739254
N	0.014594	0.500510	-0.266995
N	-2.369848	-0.320854	1.252247
N	-1.405206	-1.212062	1.558993
N	-2.456446	-0.965857	-1.153004
N	-1.460073	-1.869214	-1.003183
N	2.378758	-0.335482	1.265631
N	1.383070	-1.187596	1.584004
N	2.469990	-0.978666	-1.144054
N	1.438834	-1.849368	-1.039894
Co	-0.005933	-1.551792	0.284914

-CH₃ fragment

4
 scf done: -39.825672
 H -1.137742 -3.680641 0.849137

H	0.533977	-3.549929	1.692907
H	0.434915	-3.972383	-0.133425
C	-0.056256	-3.733658	0.802709

2-CH₂SiMe₃

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scf done: -2335.315467

B	-2.161505	-1.139239	0.207204
B	2.821847	-0.444096	0.172490
C	5.838416	-2.751614	-0.821472
C	6.964593	-1.984886	-0.506301
C	4.552004	-2.283075	-0.558301
C	-0.712952	-1.815804	0.475036
C	4.317601	-1.033724	0.040040
C	1.821661	-2.757900	1.007027
C	3.408083	0.624977	-2.155901
C	1.624080	-1.496162	0.437307
C	-0.545465	-3.075753	1.054639
C	0.729496	-3.545204	1.344701
C	5.459258	-0.256228	0.304006
C	2.881049	1.632955	-2.945528
C	-2.826639	-0.506341	-2.253151
C	-3.466702	-2.079740	0.104346
C	3.387347	0.785975	2.451404
C	2.767715	1.746653	3.234502
C	6.748421	-0.719422	0.050573
C	-4.754475	-1.537178	0.270083
C	-1.604938	1.614811	2.521781
C	1.687201	1.983878	-2.312761
C	-2.383034	0.393204	-3.208668
C	-1.355400	1.096197	-2.577543
C	-3.412834	-3.402462	-0.362844
C	-5.908763	-2.284529	0.049709
C	-5.835556	-3.617289	-0.371453
C	1.602668	2.062715	2.535414
C	-3.049079	-0.040835	2.446861
C	-2.669614	1.045126	3.220932
C	8.356054	-2.503380	-0.748256
C	-4.563946	-4.156319	-0.589705
C	-7.078681	-4.440359	-0.573424
C	-0.305396	3.013724	-0.003134
C	-3.527581	2.658932	-0.216591
C	-2.235964	5.188722	0.844114
C	-2.032063	4.519439	-2.120535
Co	0.072356	1.064868	0.061763
H	5.969091	-3.726438	-1.287545
H	3.708922	-2.901700	-0.855015
H	2.830764	-3.095097	1.215433
H	4.329315	0.070882	-2.242399
H	-1.419598	-3.665353	1.306443
H	0.868769	-4.510241	1.826185
H	5.344258	0.755630	0.684348
H	3.304600	2.060092	-3.842224
H	-3.605681	-1.251173	-2.290439

H	4.305818	0.240283	2.601270
H	3.111365	2.160877	4.170591
H	7.601579	-0.081853	0.274868
H	-4.862545	-0.490320	0.544536
H	-1.046667	2.503711	2.755525
H	0.981868	2.757561	-2.571522
H	-2.751973	0.524529	-4.214837
H	-0.744815	1.893156	-2.959958
H	-2.450791	-3.853890	-0.589135
H	-6.883619	-1.822110	0.192840
H	0.849778	2.790411	2.784899
H	-3.818015	-0.782174	2.598095
H	-3.104093	1.378924	4.151302
H	9.057296	-1.690808	-0.963947
H	8.384196	-3.207493	-1.585969
H	8.735686	-3.033540	0.134613
H	-4.472398	-5.178486	-0.952199
H	-7.366556	-4.949471	0.355355
H	-6.931754	-5.213507	-1.334355
H	-7.927681	-3.820313	-0.878832
H	-0.037351	3.380357	0.994902
H	0.437113	3.477922	-0.663782
H	-3.629491	2.250509	0.793247
H	-3.527552	1.827457	-0.925563
H	-4.420308	3.264846	-0.418575
H	-3.162330	5.741320	0.645015
H	-1.404354	5.901931	0.794274
H	-2.291422	4.815088	1.874035
H	-2.131784	3.762152	-2.904587
H	-1.125858	5.103118	-2.322872
H	-2.887568	5.199035	-2.219582
N	0.369359	-1.034392	0.241556
N	2.563788	0.396671	-1.128376
N	-2.099279	-0.330531	-1.130710
N	-2.261788	-0.082377	1.355917
N	1.499325	1.218403	-1.232946
N	1.513790	1.332880	1.417405
N	-1.351732	0.913586	1.410187
N	2.635712	0.574666	1.355428
N	-1.196486	0.649759	-1.327928
Si	-2.002840	3.759580	-0.383264

-CH₂SiMe₃ fragment

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scf done: -448.442707

C	-0.003384	-0.003552	-0.005745
H	0.056289	0.135275	-1.091523
H	-0.429987	-0.994990	0.182773
H	-0.704006	0.742592	0.386549
Si	1.698894	0.173621	0.789011
C	2.869667	-1.145017	0.117250
H	3.001707	-1.034951	-0.965431
H	2.485551	-2.153334	0.307595
H	3.859636	-1.070540	0.581912

C	2.395408	1.881286	0.367147
H	2.488966	1.999733	-0.719198
H	1.743402	2.680162	0.737516
H	3.387903	2.026801	0.807905
C	1.541815	-0.023337	2.630393
H	0.649318	0.268356	3.184192
H	2.347481	-0.406411	3.256880

2-CH₂SiMe₂Ph

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scf done: -2526.995456

B	-3.043756	-0.543557	0.078110
B	1.808056	-1.890947	0.054292
C	0.272457	-2.409922	0.010315
C	-0.089860	-3.756787	0.089365
C	-1.431104	-4.116222	0.131449
C	-2.391204	-3.117012	0.050709
C	-2.000598	-1.775780	-0.012362
C	-1.738043	0.706166	3.254032
C	-2.989224	0.327147	3.740682
C	-3.654463	-0.165680	2.629571
C	-1.412984	2.426108	-1.290160
C	-2.579691	2.502467	-2.053354
C	-3.294363	1.366159	-1.712288
C	-4.580474	-0.832136	-0.317416
C	-5.640783	-0.047682	0.170494
C	-6.949345	-0.204317	-0.280594
C	-7.264998	-1.144840	-1.267684
C	-6.214348	-1.898495	-1.800050
C	-4.908386	-1.739721	-1.338183
C	-8.682886	-1.342541	-1.730487
C	1.416993	-0.066912	3.179259
C	2.352823	-0.983364	3.659099
C	2.651746	-1.776607	2.561983
C	1.478818	1.256748	-1.786530
C	2.466415	0.683234	-2.588975
C	2.734036	-0.538191	-1.994165
C	2.994415	-2.910267	-0.338919
C	4.321579	-2.650882	0.050446
C	5.389582	-3.431450	-0.384949
C	5.187981	-4.507650	-1.256817
C	3.881864	-4.747048	-1.694771
C	2.817507	-3.962884	-1.250835
C	6.333252	-5.377680	-1.698539
C	0.419195	2.280800	1.320954
C	2.481489	4.066863	2.637901
C	3.577665	1.718228	1.048191
C	2.241980	4.086514	-0.396963
C	1.226729	5.030357	-0.630937
C	1.234570	5.847639	-1.761889
C	2.272082	5.742726	-2.688409
C	3.299018	4.823984	-2.471133
C	3.280294	4.009008	-1.339182
Co	-0.141276	0.503237	0.636484

H	0.684756	-4.512745	0.150205
H	-1.722771	-5.159639	0.224874
H	-3.446793	-3.362853	0.076291
H	-0.923572	1.161610	3.789636
H	-3.357222	0.404834	4.752859
H	-4.642801	-0.586276	2.529375
H	-0.594682	3.126024	-1.220530
H	-2.864683	3.279336	-2.747006
H	-4.264180	1.019783	-2.032990
H	-5.439540	0.734858	0.897874
H	-7.737544	0.424340	0.129590
H	-6.419058	-2.614578	-2.593696
H	-4.121630	-2.323564	-1.809054
H	-9.257214	-0.411829	-1.679191
H	-9.201197	-2.078005	-1.101905
H	-8.723758	-1.710253	-2.760690
H	0.958342	0.756260	3.697598
H	2.756600	-1.055215	4.657918
H	3.312603	-2.623334	2.462084
H	1.008211	2.217011	-1.884474
H	3.423301	-1.321890	-2.265864
H	4.535260	-1.793963	0.685206
H	6.398941	-3.193441	-0.054416
H	3.695064	-5.553090	-2.401870
H	1.829210	-4.162984	-1.655295
H	7.271386	-4.815341	-1.746878
H	6.149794	-5.817295	-2.684104
H	6.488472	-6.206979	-0.996510
H	-0.299493	3.021465	0.949281
H	0.230930	2.246030	2.400558
H	1.699951	4.827757	2.746427
H	3.444068	4.585270	2.556720
H	2.498172	3.471853	3.559534
H	3.551215	1.051440	1.915965
H	4.539785	2.244415	1.069474
H	3.549321	1.098556	0.148761
H	0.406779	5.129145	0.078961
H	0.432668	6.564735	-1.920315
H	2.280727	6.373914	-3.573390
H	4.112051	4.737956	-3.188136
H	4.077878	3.282932	-1.201902
H	2.923666	1.107838	-3.469800
N	-0.688355	-1.454486	0.028692
N	-2.843961	-0.058364	1.560782
N	-1.646097	0.446979	1.944604
N	-2.579263	0.663339	-0.809143
N	-1.419303	1.304749	-0.562239
N	1.944012	-1.330445	1.508032
N	1.158872	-0.298797	1.886040
N	1.949918	-0.663334	-0.903078
N	1.179521	0.437119	-0.773837
Si	2.164580	2.962375	1.129259

-CH₂SiMe₂Ph fragment

23

scf done: -640.118980

C	0.795575	-0.862290	13.276839
C	0.880940	-1.448489	16.266108
C	2.637435	0.797538	15.120481
C	-0.425521	1.142930	15.195995
C	-1.724131	0.825407	14.762552
C	-2.787700	1.705730	14.952260
C	-2.572515	2.931908	15.581466
C	-1.292044	3.270447	16.016279
C	-0.232630	2.383881	15.823332
H	0.416198	-0.313641	12.415265
H	1.095914	-1.887042	13.058358
H	-0.085385	-1.963057	16.230183
H	0.999093	-1.028339	17.271238
H	1.668157	-2.197393	16.119383
H	3.463915	0.106588	14.920273
H	2.776587	1.191788	16.133943
H	2.718921	1.631639	14.415533
H	-1.906281	-0.124149	14.261697
H	-3.783337	1.438397	14.607277
H	-3.399287	3.621809	15.729466
H	-1.117955	4.226670	16.503231
H	0.759499	2.670303	16.165364
Si	0.981551	-0.094632	14.957480

2-ⁱBu

85

scf done: -2044.623394

B	-2.617304	-0.499030	0.185235
B	2.410776	-0.726308	0.198101
C	-1.326197	-1.431763	0.459380
C	-1.402980	-2.693832	1.057083
C	-0.239897	-3.367238	1.404995
C	0.984480	-2.786895	1.097828
C	1.030736	-1.530058	0.488919
C	-1.743420	2.017999	-2.314136
C	-2.909623	1.561644	-2.932781
C	-3.328385	0.502237	-2.144607
C	-1.642295	2.187542	2.468616
C	-2.772812	1.784884	3.180162
C	-3.291294	0.736995	2.436111
C	-4.052710	-1.226941	0.073062
C	-5.261546	-0.557123	0.332268
C	-6.502382	-1.144388	0.094734
C	-6.600450	-2.433419	-0.440645
C	-5.408164	-3.094925	-0.751625
C	-4.170764	-2.502343	-0.504492
C	-7.937280	-3.086512	-0.664104
C	1.321134	1.253389	-2.677349
C	2.406234	0.626882	-3.291051
C	2.979538	-0.134478	-2.287522

C	1.603595	1.977846	2.489364
C	2.710178	1.506958	3.195773
C	3.193998	0.464851	2.421552
C	3.789597	-1.558801	0.104068
C	5.033305	-0.922608	0.270353
C	6.240590	-1.582312	0.053028
C	6.267754	-2.917667	-0.365141
C	5.040033	-3.550725	-0.581962
C	3.835949	-2.883926	-0.358295
C	7.569660	-3.644700	-0.565559
C	0.064824	3.243386	-0.043848
C	1.121757	3.965319	-0.874851
C	0.842709	5.476046	-0.851139
C	2.549504	3.688740	-0.403498
Co	-0.030498	1.261572	0.026565
H	-2.374906	-3.120044	1.279201
H	-0.285972	-4.330313	1.907942
H	1.910748	-3.287068	1.357171
H	-1.111524	2.855532	-2.567671
H	-3.385649	1.953426	-3.819293
H	-4.196019	-0.133772	-2.222173
H	-0.969010	3.000011	2.681975
H	-3.159393	2.199377	4.099244
H	-4.151772	0.109622	2.608415
H	-5.241250	0.467185	0.695593
H	-7.410940	-0.586973	0.315005
H	-5.448186	-4.085237	-1.201351
H	-3.274009	-3.043027	-0.796081
H	-8.246037	-3.659327	0.219764
H	-7.909865	-3.783471	-1.507905
H	-8.720116	-2.346789	-0.860138
H	0.601067	1.925003	-3.108589
H	2.724953	0.715588	-4.318894
H	3.834628	-0.791551	-2.299955
H	0.958798	2.803253	2.732688
H	3.102483	1.874400	4.132247
H	4.024119	-0.205951	2.578969
H	5.064242	0.128809	0.546228
H	7.178148	-1.048320	0.196593
H	5.025014	-4.578097	-0.940955
H	2.910376	-3.406576	-0.583669
H	8.359337	-2.969412	-0.910843
H	7.471722	-4.453969	-1.296085
H	7.916230	-4.094437	0.373739
H	-0.939968	3.566903	-0.340320
H	0.193888	3.560649	0.997354
H	1.047464	3.644252	-1.921078
H	0.903252	5.867467	0.172504
H	1.571387	6.026299	-1.459552
H	-0.157959	5.707470	-1.234511
H	3.279399	4.223621	-1.022546
H	2.684155	4.020632	0.633377
H	2.786741	2.623522	-0.438723
N	-0.120979	-0.860148	0.245099
N	-2.450097	0.344350	-1.131721

N	-1.469329	1.261356	-1.247971
N	-2.518765	0.557363	1.348943
N	-1.476528	1.423922	1.382838
N	2.268931	0.044416	-1.155177
N	1.252332	0.902208	-1.388770
N	2.422436	0.354922	1.324244
N	1.423177	1.264635	1.371120

-CH₂ⁱPr fragment

13
 scf done: -157.752819

C	0.138181	-1.408402	0.176199
C	0.714233	-0.593539	1.285127
C	2.247225	-0.616485	1.261279
C	0.181696	0.844169	1.260939
H	0.648199	-2.298172	-0.182938
H	-0.870630	-1.224149	-0.183160
H	0.397118	-1.041758	2.246707
H	2.664318	-0.060045	2.107860
H	2.631807	-1.641282	1.311541
H	2.626056	-0.161827	0.338532
H	-0.912697	0.865230	1.310931
H	0.567107	1.422990	2.107530
H	0.484332	1.352736	0.338193