

Intramolecular C–H Activation by Inferred Terminal Cobalt Imido Intermediates

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Terminal imido complexes of the late transition metals (group 9 and beyond) are rare, presumably due to the lack of empty $d\pi$ orbitals suitable for stabilization of the lone pairs of the NR^{2-} moiety.¹ We have previously considered the intermediacy of terminal cobalt oxo complexes of the type $Tp^{R,R}Co=O$ in various reactions,² and the investigation of isoelectronic imido derivatives $Tp^{R,R}Co=NR$ was expected to shed some light on the chemistry of the former. The observations reported herein afford a notable contrast to the seemingly related, but unusually stable, $[PhBP_3]Co=N-p\text{-tolyl}$.³

Coordination of organic azides followed by elimination of N_2 has been used as a preparative route to imido complexes.⁴ Accordingly, addition of 1 equiv of trimethylsilyl azide (Me_3SiN_3) to a pentane or THF solution of thermally stable $Tp^{t-Bu,Me}Co(N_2)$ at room temperature resulted in an immediate color change from brown to red and was accompanied by liberation of a gas (N_2).⁵ Standard workup of the reaction mixture yielded a paramagnetic cobalt complex (**1**, 70%), whose sharp, but isotropically shifted, 1H NMR resonances indicated loss of the three-fold symmetry of the Tp -ligand. The nature of this new complex was unveiled by an X-ray crystal structure determination; its molecular structure is shown in Figure 1.⁶

Complex **1** is a rare five-coordinate Co(III) complex adopting distorted trigonal bipyramidal coordination (N(5) and N(7) occupy the axial positions of the trigonal bipyramid). The cobalt atom is bound to three nitrogen atoms of the Tp -ligand, a trimethylsilylamido group ($N(H)SiMe_3^-$), and a methylene carbon stemming from one of the *tert*-butyl substituents of the scorpionate ligand. The metal–carbon bond is shorter than that of $Tp^{t-Bu}CoMe$ (2.115(14) Å),⁷ befitting the higher formal oxidation state of **1**. We note that the IR spectrum of **1** did not exhibit a discernible N–H stretch; however, the N-bound proton was located crystallographically. Besides, the length of the $Co(1)–N(7)$ single bond (1.839(3) Å) and the $Co–N(7)–Si(1)$ angle (146.6(3)°) leave little doubt about its presence. Moreover, a hypothetical assignment as an imido group (i.e., $NSiMe_3^{2-}$) would catapult cobalt into the formal oxidation state +IV, a rather unlikely scenario. The effective magnetic moment of **1** (μ_{eff} (295 K) = 3.9(1) μ_B) is rather high; most trigonal bipyramidal Co(III) complexes exhibit values in the range of 2.9–3.3 μ_B , consistent with an intermediate ($S = 1$) spin state.⁸ However, values as high as 3.6 and 4.4 μ_B have been reported, raising the possibility of spin equilibria.⁹ While **1** is not the desired $Tp^{t-Bu,Me}Co=NSiMe_3$, it is an isomer thereof, formally resulting from a hydrogen atom transfer from a *tert*-butyl group to the nitrogen of an imido intermediate, followed by stabilization of the resulting alkyl radical by formation of a cobalt–carbon bond. Indeed, we postulate such a series of events as part of the mechanism of the formation of **1** (Scheme 1).

Further evidence for the intervention of alkyl radical intermediates was provided by the outcome of an analogous reaction of

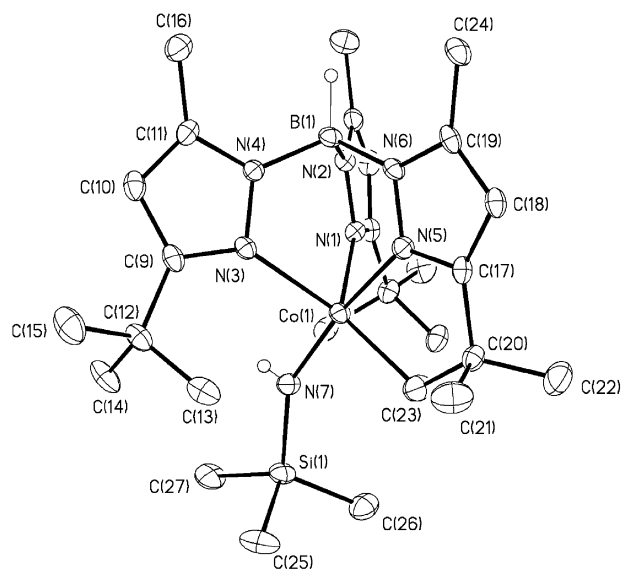


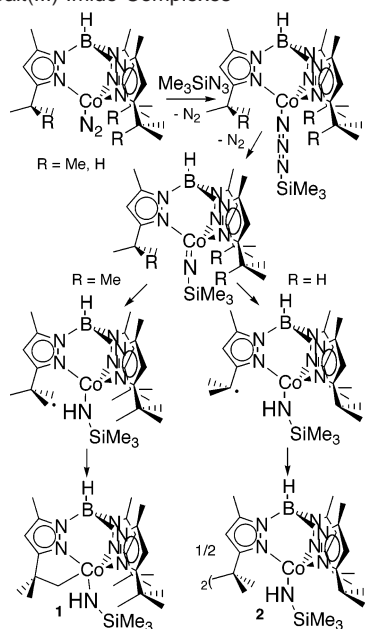
Figure 1. The molecular structure of **1**; selected distances [Å] and angles [deg]: $Co(1)–N(1)$, 2.203(3); $Co(1)–N(3)$, 2.210(4); $Co(1)–N(5)$, 1.914(3); $Co(1)–N(7)$, 1.839(3); $Co(1)–C(23)$, 2.029(5); $N(5)–Co(1)–N(7)$, 171.01(17); $C(23)–Co(1)–N(1)$, 127.75(19); $C(23)–Co(1)–N(3)$, 133.71(18); $N(1)–Co(1)–N(3)$, 91.96(12); $Si(1)–N(7)–Co(1)$, 146.6(3).

($Tp^{i-Pr,Me}Co$) $_2(\mu-N_2)$. Treatment of the latter with Me_3SiN_3 produced the dinuclear Co(II) amido complex **2**. The molecular structure of **2** is shown in Figure 2;¹⁰ the molecule consists of two independent four-coordinate cobalt fragments, which are joined via a newly formed C–C bond between two erstwhile isopropyl groups of the Tp -ligand. Each cobalt is coordinated by three nitrogen atoms of the functionalized scorpionate ligand and a fourth nitrogen atom of a trimethylsilylamido group ($N(H)SiMe_3^-$). Similar to **1**, no N–H stretch was discernible in the IR spectrum of **2**, but the N-bound hydrogen atom was located in an electron density map, and the $Co(1)–N(7)–Si(1)$ angle of 128.7(2)° as well as the long $Co(1)–N(7)$ distance (1.898(4) Å) indicate its presence. Furthermore, the $Co–N_{Tp}$ distances (average: 2.06 Å) and the effective magnetic moment of **2** (μ_{eff} (295K) = 4.4(1) μ_B/Co) are consistent with a formal oxidation state of Co(II).¹¹

We propose that the formation of **2** initially proceeds by the same mechanism as that of **1** (Scheme 1). However, the isopropyl radical shuns the formation of a tertiary metal alkyl and strained four-membered ring and opts for bimolecular recombination instead.

The isomeric relationship between **1** and hypothetical " $Tp^{t-Bu,Me}Co=NSiMe_3$ " inspired the question of whether hydrolysis of the amide might yield a structurally analogous Co(III) hydroxide isomer of the elusive " $Tp^{t-Bu,Me}Co=O$ ". However, reaction of **1** in THF with 1 equiv of H_2O yielded $Tp^{t-Bu,Me}CoN(H)SiMe_3$ (**3**) as the major product, along with several other minor products (notably, no

Scheme 1. Proposed Mechanism of Formation of **1** and **2** via Terminal Cobalt(III) Imido Complexes



$\text{Tp}^t\text{-Bu}_2\text{MeCoOH}$). The mechanism of this transformation is presently unclear; in particular, the reductant responsible for the transformation of Co(III) to Co(II) and/or its oxidized form remains elusive. In a related reaction of **1** with excess 2-propanol, formation of $\text{Tp}^t\text{-Bu}_2\text{MeCo}^i\text{Pr}$ (**4**) and acetone was observed. These products can be rationalized by assuming alcoholysis of the amide, followed by β -hydrogen atom transfer from coordinated iso-propoxide to the alkyl group and finally reaction of the resulting $\text{Tp}^t\text{-Bu}_2\text{MeCo}$ -

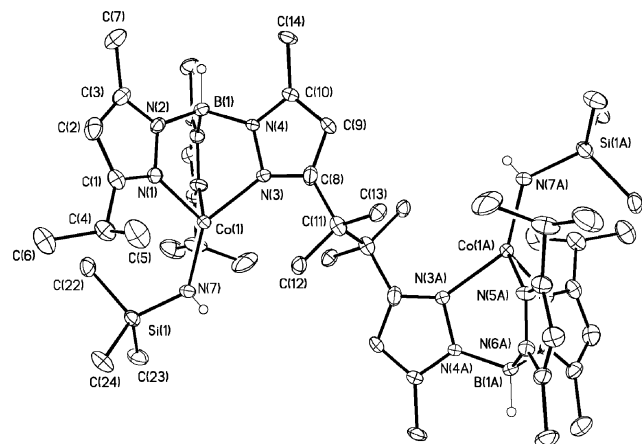


Figure 2. The molecular structure of **2**; selected distances [\AA] and angles [deg]: Co(1)–N(1), 2.043(3); Co(1)–N(3), 2.097(3); Co(1)–N(5), 2.030(3); Co(1)–N(7), 1.898(4); C(11)–C(11A), 1.566(7); N(1)–Co(1)–N(3), 87.75(13); N(1)–Co(1)–N(5), 95.73(13); N(3)–Co(1)–N(5), 91.26(14); N(1)–Co(1)–N(7), 116.57(16); N(3)–Co(1)–N(7), 138.58(14); N(5)–Co(1)–N(7), 116.87(16); Si(1)–N(7)–Co(1), 128.7(2).

($\text{O}=\text{CMe}_2$) with an additional equivalent of alcohol. We are continuing the investigation of the reactivity of **1** with other reagents.

Our results suggest that the terminal cobalt imido species $\text{Tp}^{\text{R,R}}\text{Co}=\text{NSiMe}_3$ may be highly reactive intermediates. They are apparently capable of abstracting hydrogen atoms from alkyl groups (including primary C–H bonds with $D_{\text{C-H}} = 98$ kcal/mol).¹² These observations also lend support to our assertion that isoelectronic $\text{Tp}^{\text{R,R}}\text{Co}=\text{O}$ is a very reactive species as well. Its generation from O_2 and use in productive transformations of external substrates remain a significant challenge.

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Supporting Information Available: Characterization and X-ray crystallographic files for **1** and **2** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5) Repeated Toepler pump experiments indicated the formation of 1.7(1) equiv of N_2 , consistent with the formation of **1** in 70% isolated yield and $\text{Tp}^t\text{-Bu}_2\text{MeCoN}_3$ as minor byproduct.
- (6) **1**: C_2H_{12} , $\text{C}_{32}\text{H}_{61}\text{BCoN}_7\text{Si}$, MW = 641.71, $T = 173(2)$ K, monoclinic space group $P2_1/c$, $a = 12.4593(13)$ \AA , $b = 10.4460(11)$ \AA , $c = 29.652(3)$ \AA , $\beta = 97.321(2)^\circ$, $V = 3827.8(7)$ \AA^3 , $Z = 4$, $R_1 = 0.0683$ [$I > 2\sigma(I)$], GOF = 1.334.
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- (10) **2**: $\text{C}_{62}\text{H}_{102}\text{B}_2\text{Co}_2\text{N}_{14}\text{Si}_2$, MW = 1239.24, $T = 173(2)$ K, triclinic space group $P-1$, $a = 11.7096(10)$ \AA , $b = 12.3659(11)$ \AA , $c = 12.3697(10)$ \AA , $\alpha = 88.925(2)^\circ$, $\beta = 79.172(2)^\circ$, $\gamma = 79.722(2)^\circ$, $V = 1730.8(3)$ \AA^3 , $Z = 1$, $R_1 = 0.0584$ [$I > 2\sigma(I)$], GOF = 1.187.
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