

[Me₂NN]Co(η⁶-toluene): O=O, N=N, and O=N Bond Cleavage Provides β-Diketiminato Cobalt μ-Oxo and Imido Complexes

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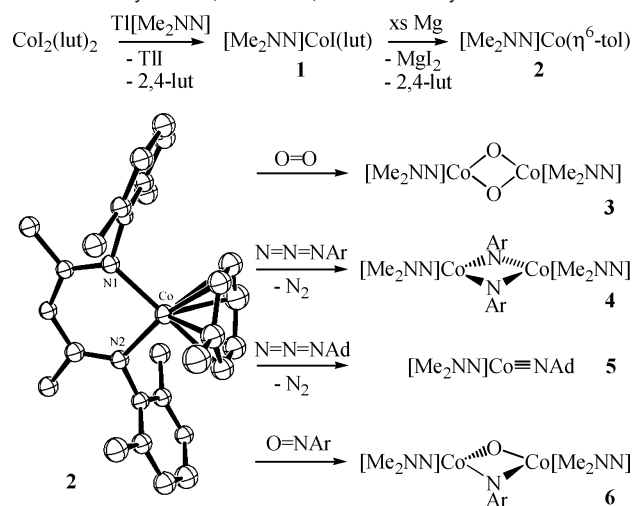
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Oxo (O²⁻) and imido (NR²⁻) functionalities bound to later first row transition metals attract interest as active agents in atom¹ and group transfer² reactions to alkenes as well as in C–H bond functionalization.³ Due to their important biological roles (especially for Fe),⁴ such oxo complexes have commanded considerably more attention than isoelectronic imido counterparts. Despite cobalt's seminal role in synthetic metal–dioxygen chemistry,⁵ species bearing oxo functionalities have been established only recently. The bulky tris(pyrazolyl)borates {Me³TpCo}₂(μ-OH)₂ react with H₂O₂ to provide {Me³TpCo}₂(μ-O)₂ species that are susceptible to intramolecular C–H bond abstraction by the oxo ligand.^{6,7} {ⁱ-PrMeTpCo}₂(μ-N₂) directly reduces O₂ by 4 electrons to produce a related, but especially thermally sensitive, bis(μ-oxo)dicobalt(III) complex.^{7,8} Furthermore, a square-planar [Co^{III}₂(μ-O)₂]²⁻ species was isolated in the disproportionation of the Co(II) complex [Co(H₂L)₂]²⁻ (H₂L = bis[(*tert*-butyl)aminocarbonyl]-1,2-diamidoethane) in the presence of O₂.⁹ Imido functionalities bound to later first row metals are beginning to exhibit reactivity patterns reminiscent of oxo species. For instance, Theopold observed intramolecular C–H bond abstraction by inferred Tp'Co=NTMS intermediates in the reaction of Tp'Co(N₂) with N₃TMS.¹⁰ Hillhouse showed that the terminal (dtbpe)Ni=NAr undergoes imido group transfer to CO to provide an isocyanate,¹¹ a reaction also observed by Peters with tris(phosphino)borate complexes [P₃B]M≡N(*p*-tolyl) (M = Fe,^{12a} Co^{12b}). Exploring relationships between oxo and imido functionalities in later first row chemistry, we describe herein the synthesis of a β-diketiminato Co(I) arene adduct and its reactivity with dioxygen, organoazides, and a nitrosobenzene to provide a family of structurally diverse μ-oxo and imido complexes.¹³

The paramagnetic, tetrahedral Co(II) β-diketiminato¹⁴ [Me₂NN]-Co(I)(2,4-lutidine) (**1**) may be prepared in 90% yield from reaction of Tl[Me₂NN]¹⁵ with CoI₂(2,4-lutidine)₂ as teal crystals. Reduction of this species with Mg powder in toluene provides air-sensitive, red crystals of [Me₂NN]Co(η⁶-toluene) (**2**) in 60–70% yield on a gram scale (Scheme 1). This d⁸ Co(I)-arene adduct is high-spin as evidenced by its room-temperature magnetic moment of 2.7 μ_B in toluene-*d*₈. While diamagnetic [Me₂NN]Rh(arene) and {[Me₂NN]-Rh}₂(arene) complexes favor η⁴-arene coordination,¹⁶ the X-ray structure of **2** reveals an η⁶-toluene ligand (Co–C = 2.207(6)–2.288(5) Å) bound to the [Me₂NN]Co fragment (Scheme 1).

Addition of several equivalents of dry oxygen to **2** in ether at room temperature results in an immediate color change from red to violet, signaling the formation of {[Me₂NN]Co}₂(μ-O)₂ (**3**) that may be isolated in 75% yield as maroon crystals (Scheme 1). The X-ray structure of **3** obtained at –90 °C consists of two [Me₂NN]-Co fragments related by inversion separated by 2.716(4) Å. Final refinement suggested positional disorder for the bridging oxygen atoms. The predominant orientation (86% occupancy; Figure 1) consists of oxo atoms related by inversion that appear in roughly square-planar sites⁹ (22.2° and 23.0° twist angles between the N–Co–N and O1–Co–O1' planes) with nearly identical Co–O1

Scheme 1. Synthesis, Structure, and Reactivity of **2**



and Co–O1' bond distances of 1.784(3) and 1.793(4) Å. The minor orientation consists of two inequivalent oxo atoms that symmetrically bridge in a tetrahedral disposition and exhibit somewhat lengthened Co–O distances.¹⁷ The short metal–metal and metal–oxo distances found in **3** compare favorably to those in related “diamond core” M₂(μ-O)₂ (M = Fe–Cu) structures.^{3c,9}

In contrast to Borovik's square-planar [Co^{III}₂(μ-O)₂]²⁻ complex that exhibits strong antiferromagnetic coupling, solid-state magnetic susceptibility data for **3** follow Curie–Weiss behavior from 50 to 200 K for which an average μ_{eff} = 3.5 ± 0.2 μ_B was determined.¹⁷ A plot of 1/χ versus *T* reveals a deviation from 200 to 300 K, mirrored by the reversible increase of the solution magnetic moment from 3.9 to 4.3 μ_B (toluene-*d*₈) over the range 200–350 K. Coupled with an upward inflection at ca. 300 K in both solid state and solution μ_{eff} versus *T* plots, these observations suggest population of a higher spin state at elevated temperatures.

Aiming to prepare related imido complexes, we explored the reactivity of **2** with organoazides (Scheme 1). Reaction of **2** with N₃Ar (Ar = 3,5-Me₂C₆H₃) in ether results in rapid effervescence and formation of the tetrahedral Co(III)-imido bridged dimer {[Me₂NN]Co}₂(μ-NAr)₂ (**4**). Its solution magnetic moment of 8.8 μ_B at room temperature (benzene-*d*₆) is consistent with two noninteracting, high-spin d⁶ centers. In addition, solid-state magnetic susceptibility data reveal antiferromagnetic coupling with a Neel temperature of 25 K.¹⁷ The X-ray structure of **4** (Figure 1) exhibits a considerably longer Co–Co separation (3.067(3) Å) than found in **3** with Co–N(imido) bond distances of 1.983(3) and 1.988(3) Å. In contrast, reaction of **2** with the more sterically demanding N₃Ad (Ad = 1-adamantyl) leads to the formation of the three-coordinate terminal imide [Me₂NN]Co≡NAd (**5**) that may be isolated in 50% yield as red crystals. The X-ray structure of **5** (Figure 1) reveals a Co–N(imide) bond distance of 1.624(4) Å

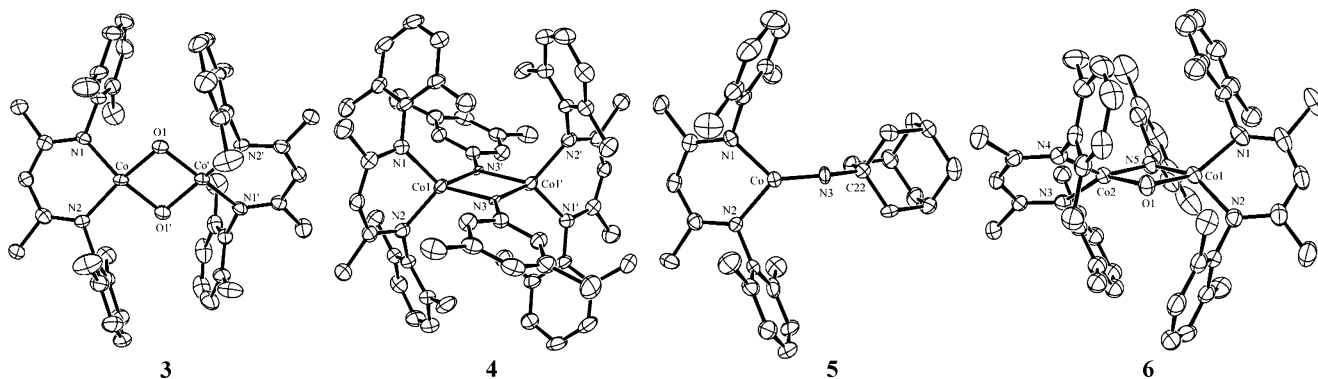


Figure 1. X-ray structures of 3–6.

which is at the short end of the range 1.64–1.70 Å observed in sparse examples of Fe,^{12a,18} Co,^{12b} and Ni^{11a,19} terminal imides. Although in the solid state the imido substituent is somewhat bent (Co–N3–C22 = 161.5(3)°), diamagnetic **5** exhibits C_{2v} -symmetric ¹H and ¹³C NMR spectra down to –70 °C (toluene-*d*₈). DFT calculations support the presence of a low-spin d⁶ Co(III) center in **5**, stabilized by $1\sigma,2\pi$ -donation from the imido ligand which leads to considerable multiple bond character in this 16-electron, three-coordinate complex.

To explore the generality of **2** as a precursor to oxo and imido species via reductive cleavage of double bonds to O and N, we exposed **2** to 0.5 equiv of O=NAr (Ar = 3,5-Me₂C₆H₃) in ether which results in the formation of the binuclear {[Me₂NN]Co}₂(μ-O)(μ-NAr) (**6**) in 33% isolated yield (Scheme 1). This 4-electron reduction of a nitrosobenzene stands in contrast to the reaction of the related CpCo(C₂H₄)₂ with O=NPh which leads to [CpCo]₂(μ-η²:η¹-PhNO)₂.²⁰ The X-ray structure of **6** (Figure 1) is intermediate between the structures observed for the square-planar bis(μ-oxo) **3** and tetrahedral bis(μ-imido) **4** with opposing [Me₂NN]Co fragments that are nearly orthogonal (89.2° twist angle). While the Co–Co separation (2.7420(6) Å) and Co–O distances (1.783(2) and 1.786(2) Å) in **6** are similar to those found in the square-planar bis(μ-oxo) **3**, the Co–N distances (1.821(3) and 1.823(3) Å) lie between those in the tetrahedral bis(μ-imido) **4** and terminal imido **5**. In the solid state, **5** exhibits Curie–Weiss behavior over 50–300 K with an average $\mu_{\text{eff}} = 4.4 \pm 0.4 \mu_{\text{B}}$ with a solution magnetic moment (benzene-*d*₆) of 4.9 μ_{B} at room temperature, the spin-only value predicted for a $S = 2$ system.

Future reports will examine the reactivity of the electronically and coordinatively unsaturated μ-oxo and imido species prepared by reductive cleavage of O=O, N=N, and O=N bonds by [Me₂NN]Co(η⁶-toluene) (**2**), a useful synthon to the highly reactive 12-electron, two-coordinate [Me₂NN]Co fragment.

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Supporting Information Available: Experimental procedures with characterization data and DFT calculation details (PDF) as well as crystallographic details (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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