

Three-Coordinate Cobalt(IV) and Cobalt(V) Imido Complexes with N-Heterocyclic Carbene Ligation: Synthesis, Structure, and Their Distinct Reactivity in C–H Bond Amination

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S Supporting Information

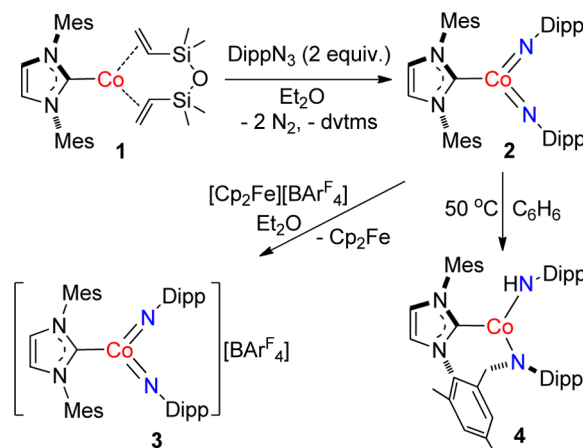
ABSTRACT: The reaction of the cobalt(0) alkene complex [(IMes)Co(η^2 : η^2 -dvtms)] (**1**) (IMes = 1,3-bis(1',3',5'-trimethylphenyl)imidazol-2-ylidene, dvtms = divinyltetramethyldisiloxane) with 2 equiv of DippN₃ (Dipp = 2,6-diisopropylphenyl) afforded the cobalt(IV) imido complex [(IMes)Co(NDipp)₂] (**2**), which could be oxidized by [Cp₂Fe][BAR^F₄] (Ar^F = 3,5-di(trifluoromethyl)phenyl) to give the cobalt(V) imido species [(IMes)Co(NDipp)₂][BAR^F₄] (**3**). The molecular structures of all these complexes were established by single-crystal X-ray diffraction studies. Characterization data and theoretical calculations suggest ground spin states of $S = 1/2$ and $S = 0$ for the cobalt(IV) and cobalt(V) species, respectively. When heated, the cobalt(IV) imido species was converted to a cobalt(II) diamido complex via an intramolecular C–H bond amination reaction, but the cobalt(V) species was stable under similar conditions. The different outcomes suggest that a high oxidation state does not guarantee C–H bond activation reactivity of late-transition-metal imido species.

Terminal imido complexes of late transition metals have attracted great interest because of their unique reactivity of C–H bond amination and olefin aziridination.¹ The metal center's oxidation state is perceived to be a key factor affecting the reactivity of the imido moiety. Thus, with the success in the preparation and reactivity studies of di- and trivalent late-transition-metal imido species, endeavors in this area have now shifted to high-valent complexes that are rare.² To date, several iron(IV)³ and iron(V)⁴ imido species are known. For the cobalt and nickel triads, M(III) has remained the highest oxidation state observed in isolable terminal imido complexes. Prominent examples of the type include Cp*Ir^{III}(NR),⁵ (triphosphine)-M^{III}(NR) (M = Co, Rh),⁶ (tris-NHC)Co^{III}(NR),⁷ (tris(pyrzoly)borato)Co^{III}(NAd),⁸ (β -diketiminato)M^{III}(NAd) (M = Co, Ni),⁹ (guanidinato)Co^{III}(NAd),¹⁰ (dipyrrin)-Co^{III}(NR),¹¹ and [(bisphosphine)Ni^{III}(NAr)]⁺.¹² In addition to these, we report herein the first synthesis and structural characterization of cobalt(IV) and cobalt(V) terminal imido complexes of the form [(IMes)Co(NDipp)₂]^{0,+} along with the distinct reactivity of the two species in C–H bond amination.

The cobalt(IV) imido complex [(IMes)Co(NDipp)₂] (**2**) (IMes = 1,3-bis(1',3',5'-trimethylphenyl)imidazol-2-ylidene, dvtms = divinyltetramethyldisiloxane) was obtained using our

recently reported synthetic protocol for its iron(IV) analogue [(IMes)Fe(NDipp)₂].^{3d} Treatment of the three-coordinate cobalt(0) precursor [(IMes)Co(η^2 : η^2 -dvtms)] (**1**), which was prepared from the one-pot reaction of CoCl₂ with IMes, dvtms, and KC₈ (2 equiv),¹³ with 2 equiv of DippN₃ in diethyl ether led to a quick change in color from green to brown accompanied by effervescence of dinitrogen. Brown crystals of **2** were isolated from the resulting mixture in 55% yield after recrystallization (Scheme 1).

Scheme 1. Synthetic Routes for the Three-Coordinate Cobalt Complexes



The ¹H NMR spectrum of **2** features paramagnetically shifted signals in the range +81 to +1 ppm, and its solution magnetic moment (2.2(1) μ_B in C₆D₆ at room temperature)¹⁴ corroborates an $S = 1/2$ ground state. Its X-band EPR spectrum in tetrahydrofuran (THF) measured at 103 K displays an eight-line signal centered at $g_{av} \approx 1.98$ with a characteristic hyperfine feature due to the ⁵⁹Co nuclei ($I = 7/2$) (Figure S1 in the Supporting Information (SI)). No obvious nitrogen hyperfine coupling is observed, which might be due to unresolved ¹⁴N ($I = 1$) splitting.¹² X-ray crystal structure analysis established the molecular structure of **2** as a trigonal-planar cobalt diimido complex (Figure 1) that is isostructural to [(IMes)Fe(NDipp)₂].^{3d} The molecule displays C_{2v} symmetry with a

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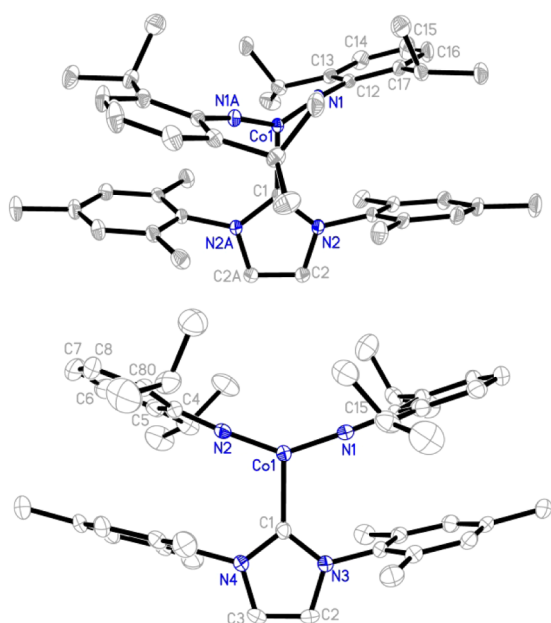


Figure 1. Molecular structures of (top) [(IMes)Co(NDipp)₂] (**2**) and (bottom) the cation in [(IMes)Co(NDipp)₂][BARF₄] (**3**) with 30% probability ellipsoids and partial atom numbering schemes. Selected distances (Å) and angles (deg) for **2**: Co(1)–C(1) 1.879(5), Co(1)–N(1) 1.665(3), N(1)–C(12) 1.357(4), C(1)–Co(1)–N(1) 106.50(12), N(1)–Co(1)–N(1A) 147.0(2), C(12)–N(1)–Co(1) 173.0(3), C(1)–N(2)–C(3) 128.7(3). For **3**: Co(1)–C(1) 1.941(4), Co(1)–N(1) 1.640(3), Co(1)–N(2) 1.642(3), N(1)–C(15) 1.354(5), N(2)–C(4) 1.348(5), C(1)–Co(1)–N(1) 109.17(16), C(1)–Co(1)–N(2) 109.70(16), N(1)–Co(1)–N(2) 141.10(16), C(15)–N(1)–Co(1) 173.7(3), C(4)–N(2)–Co(1) 174.7(3), C(1)–N(3)–C(27) 127.2(3), C(1)–N(4)–C(36) 127.0(3).

slightly bent Co–N(imido)–C(aryl) moiety (173.0(3)°) and short Co–N(imido) bonds (1.665(3) Å). The Co–N(imido) distance is on the long end of the range 1.61–1.68 Å observed in reported cobalt imido complexes.^{6–11} The N(imido)–C(aryl) bond distance (1.357(4) Å) is between those of typical N=C double bonds (1.28 Å) and N–C single bonds (1.45 Å), close to that in Hillhouse's nickel(III) species [(bisphosphine)Ni(NC₆H₃-3,5-Mes₂)⁺] (1.359(5) Å),¹² and longer than that of Betley's iron complex (dipyrrin)Fe(NC₆H₄-*p*-Bu^t)Cl (1.331(2) Å).¹⁵ The short N(imido)–C(aryl) bonds hint at a substantial degree of electron delocalization in the [NDipp] moieties that, on the other hand, weakens the N 2p lone pair → Co 3d orbital π donation and leads to the relatively long Co–N separation.

Cyclic voltammetry studies of **2** in THF revealed a reversible oxidation process with $E_{1/2} = -0.16$ V vs SCE (Figure 2). Accordingly, the cobalt(V) imido complex [(IMes)Co(NDipp)₂][BARF₄] (**3**) was prepared in 88% isolated yield by one-electron oxidation of **2** using [Cp₂Fe][BARF₄] (Ar^F = 3,5-di(trifluoromethyl)phenyl) in diethyl ether (Scheme 1).¹³ Complex **3** is diamagnetic. Its ¹H and ¹³C NMR spectra indicate C_{2v} symmetry for the cation [(IMes)Co(NDipp)₂]⁺ in solution. The characteristic ¹³C NMR signal for C(carbene) was observed at 176.8 ppm. The solid-state structure of the cation in **3** is shown in Figure 1. While its cobalt center displays a trigonal-planar geometry like that of **2**, the Co–N(imido) (1.642(3) Å average) and N(imido)–C(aryl) (1.351(5) Å average) distances are slightly shorter than the corresponding ones in **2** and the Co–C(carbene) distance is longer (1.941(4) Å vs 1.879(5) Å in **2**). The elongation of the Co–C bond might be due to the

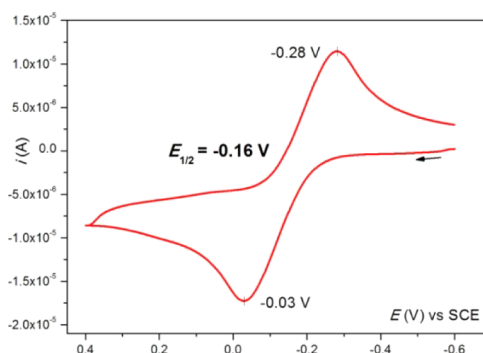


Figure 2. Cyclic voltammogram (100 mV/s) of [(IMes)Co(NDipp)₂] (**2**) in THF.

strengthened trans effect of the imido ligands in **3** as one-electron oxidation of **2** to form **3** removes an electron from the antibonding orbital (vide infra). Moreover, the five-membered imidazole ring of the N-heterocyclic carbene (NHC) ligand in the cation is found to be nearly coplanar with the CoCN₂ coordination plane, in sharp contrast to the large dihedral angle of 46° observed in **2**.

Complexes **2** and **3** are among the rare examples of isolable high-valent cobalt complexes. Cobalt(IV) complexes are known for tetrakis(1-norbornyl)cobalt,¹⁶ five- and six-coordinate complexes with tetradentate macrocyclic ligands,¹⁷ tris-(dithiocarbamate)cobalt complexes,¹⁸ tetraamide macrocycle-supported cobalt species,¹⁹ a tetranuclear cobalt oxide cluster,²⁰ and tetrakis(ketimide)cobalt.²¹ Recently, Meyer reported the spectroscopic characterization of an intermediate cobalt(IV) nitride species supported by an NC₂O tripodal ligand.²² The only reported cobalt(V) complexes are Theopold's tetrakis(1-norbornyl)cobalt cation²³ and Brookhart's dihydridodisilyl complexes Cp^{*}Co(H)₂(SiHPh₂)(SiRPh₂) (R = H, Et).²⁴ Compared with these complexes, the presence of the imido ligands in **2** and **3** and their low coordination number signify their uniqueness.

In order to probe the electronic structures of **2** and **3**, density functional theory calculations (B3LYP/TZVP, SVP, ORCA)^{13,25,26} on [(IMes)Co(NDipp)₂]ⁿ ($n = 0$ with $S = 1/2$, $n = 1+$ with $S = 0$) were performed. Geometry optimization produced structures in which the key bond distances and angles accorded well with those observed in the crystal structures (Table S1 in the SI).²⁷ For the neutral species, in-plane and out-of-plane π interactions as well as σ interactions between the cobalt 3d and nitrogen 2p orbitals (UNOs 191, 190, 185, and 181 in Figure S2) are found. The singly occupied orbital (UNO 192, shown in Figure 3) is antibonding in character and contains predominantly ligand-based orbitals with a ca. 28% contribution from cobalt 3d orbitals, in agreement with the observed small EPR g value in **2**. The sum of these interactions leads to a net Mayer bond order of 1.39 for the Co–N bonds. As the nature of the frontier molecular orbitals (FMOs), with almost equal contributions from both the cobalt and imido ligand orbitals, makes the assignment of the spectroscopic oxidation state for the cobalt center difficult,²⁸ resonance structures of the form [(IMes)Co^{IV}(NDipp²⁻)₂] ↔ [(IMes)Co^{III}(NDipp^{•-})(NDipp²⁻)] might explain the electronic structures of the neutral species.

In contrast to the neutral species, the FMOs of the cationic species have much less pronounced covalent character between the metal and imido ligand orbitals (Figure S3). In the closed-

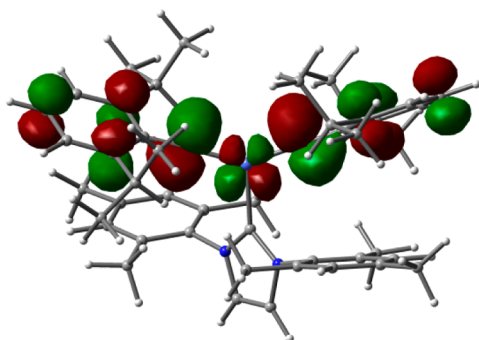


Figure 3. Singly occupied orbital of $[(\text{IMes})\text{Co}(\text{NDipp})_2]$ ($S = 1/2$), depicted using isodensity at 0.03 au. Major orbital composition: 28% Co 3d, 34% N 2p, and 28% C 2p.

shell species, the highest nine filled FMOs are essentially ligand-based with cobalt 3d contributions of less than 23%. The HOMO–LUMO gap is 2.66 eV. Two low-energy filled MOs (MOs 180 and 182) are metal-based with cobalt 3d characters of 69% and 75%, respectively. These orbital compositions argue for a $(3d_{xz})^2(3d_z)^2(3d_{yz})^0(3d_{xy})^0(3d_{x^2-y^2})^0$ configuration for the cobalt center in the cation. Removal of the electron in the antibonding singly occupied orbital of $(\text{IMes})\text{Co}(\text{NDipp})_2$ renders a higher bond order of 1.47 for the Co–N bonds in $[(\text{IMes})\text{Co}(\text{NDipp})_2]^{1+}$, which is consistent with the experimental observation of shorter Co–N bonds in **3** than in **2**.

The attainment of the cobalt(IV) and cobalt(V) imido complexes provided an opportunity to examine the effect of the metal's oxidation state on the C–H bond amination reactivity of cobalt imido species. While both **2** and **3** are stable in solution and the solid state at room temperature, heating a benzene solution of **2** at 50 °C led to the formation of cobalt(II) amido complex **4** (Scheme 1). Figure 4 depicts its molecular structure.²⁹

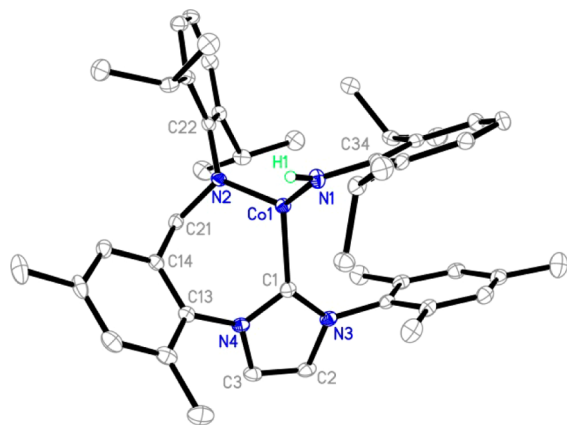
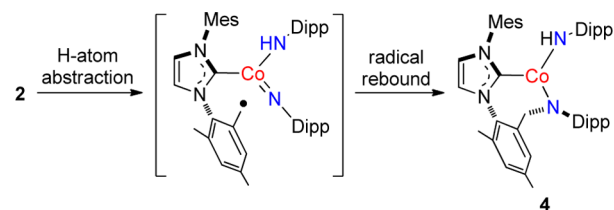


Figure 4. Molecular structure of **4** with 30% probability ellipsoids and the partial atom numbering scheme. Selected distances (Å) and angles (deg): Co(1)–C(1) 2.034(3), Co(1)–N(1) 1.885(2), Co(1)–N(2) 1.883(2), N(1)–C(34) 1.379(3), C(1)–Co(1)–N(1) 123.1(1), C(1)–Co(1)–N(2) 100.8(1), N(1)–Co(1)–N(2) 131.2(1).

The formation of the cobalt(II) complex can be rationalized by the sequential processes of H-atom abstraction of a benzylic C–H bond by one imido moiety followed by benzyl radical rebound with the other imido moiety (Scheme 2).^{8,11,30} In contrast, no reaction took place when a THF solution of the cobalt(V) imido complex was heated to 60 °C. The distinction indicates that a metal center's high oxidation state does not guarantee the C–H

Scheme 2. Possible Route for the Formation of **4**



bond activation reactivity of a late-transition-metal imido species.^{15,31} The C–H bond amination reactivity of the open-shell species **2** resonates with Theopold and Betley's observation that open-shell cobalt(III) imido species are able to undergo C–H bond activation^{8,11} and suggests that the spin state could affect these reactions, probably indirectly via changes in driving force, as noted by Mayer on the effect of spin state and spin density on H-atom transfer reactivity.³² Theoretical studies aiming to disclose the difference between **2** and **3** in the C–H bond amination reaction are ongoing.

In summary, we have shown that the reaction of a three-coordinate cobalt(0) alkene compound with a bulky organic azide can produce a three-coordinate cobalt(IV) imido complex that can further be converted to a cobalt(V) imido complex by one-electron oxidation. A preliminary reactivity study has shown that the cobalt(IV) imido complex can undergo intramolecular C–H amination to form a cobalt(II) diamido complex, whereas the cobalt(V) imido species does not undergo a similar transformation. The difference suggests that a high oxidation state does not guarantee the C–H bond activation reactivity of late-transition-metal imido species.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data (CIF) for complexes **1–4**, experimental procedures, characterization data, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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difference suggests that the formation of a stacked structure in the solid state might be caused by crystal-packing forces.

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