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Terminal Cobalt(III) Imido Complexes Supported by Tris(Carbene) Ligands: Imido Insertion into the Cobalt−Carbene Bond

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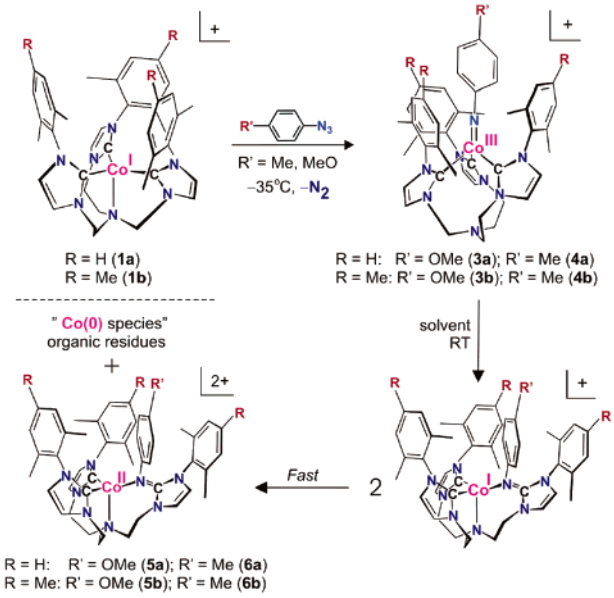
Transition metal imido species have attracted much attention due to their postulated roles in catalysis and their potential in N-atom transfer chemistry.[1,2] Late-transition metal imido complexes, however, are rare, which is likely due to mismatched reactivity of the hard imido ligand and the soft electron-rich metal center.[3−7] For about 10 years, Bergman's iridium derivatives of the general formula [(*Cp**)Ir≡NR] (R = aryl, alkyl, silyl) represented the only structurally characterized late-metal complexes bearing a terminal imido functionality.[3] More recently, the work of Hillhouse and Mindiola on [(*dtbpe*)Ni(N(2,6-$(CHMe_2)_2C_6H_3$))] (*dtbpe* = 1,2-bis-(di-*tert*-butylphosphino)ethane) revived this field of research and demonstrated that late first-row metal imido complexes are accessible by employing electron-rich bulky ancillary ligands.[4] Soon after, Peters et al. prepared the first mononuclear Co(III) and Fe(III) imido complexes via oxidative nitrene transfer to a Co(I) and Fe(I) tris-(phosphine) species.[5,6] Following similar strategies, Theopold et al. and Warren et al. synthesized transient and stable Co(III) imido complexes supported by tris(pyrazolyl)borate and β-diketiminate ligands.[8,9]

In our quest to develop tripodal N-heterocyclic carbene complexes for small molecule activation, we recently synthesized the Co(I) tris(carbene) complex [(TIMEN^{xyl})Co]Cl (**1a**, TIMEN = tris-[2-(3-arylimidazol-2-ylidene)ethyl]amine, xyl = 2,6-dimethylphenyl)[10] that reacts with a variety of small molecules. For example, **1a** reacts with dioxygen to form a Co(III) peroxo species, which is able to transfer a single oxygen atom to electrophilic organic substrates.[10] Herein we report the reaction of **1a** and its mesitylene analogue, [(TIMEN^{mes})Co]Cl (**1b**), with aryl azides, yielding monomeric Co(III) imido complexes. The cobalt−imido fragment in these complexes is electrophilic, and as a result, the imido group readily inserts into the cobalt−carbene bond. To the best of our knowledge, this intramolecular imido insertion reaction has not been observed before[11] and thus reveals a new type of reactivity of this interesting and valuable class of compounds.

In an initial attempt to prepare a Co(III) imido species, we treated **1a** with trimethylsilyl azide. The reaction proceeds smoothly but yields the one-electron oxidized azido species [(TIMEN^{xyl})Co(N_3)]-Cl (**2**, 92% yield). However, reaction of **1a** and **1b** with aryl azides at −35 °C produced the desired deep-green Co(III) imido complexes [(TIMEN^{R})Co(NAr$^{R'}$)]Cl (**3a**−**4b**, Scheme 1) that could be isolated at low temperature in near quantitative yields. Complex **2** was fully characterized, including paramagnetic ^{1}H NMR, IR, UV−vis spectroscopy, SQUID measurements, CHN analysis, and X-ray crystallography.[12] Complexes **3a**−**4b** are diamagnetic (d^6 low-spin, $S = 0$), and the ^{1}H spectra suggest a C_3-symmetry of these molecules in solution. In the solid-state structure of **3b(BPh$_4$)**,[12] the TIMEN^{mes} ligand is coordinated in a tridentate fashion, rendering the complex in a pseudotetrahedral geometry of three carbenoid carbons and the imido nitrogen atom (Figure 1, left).

Scheme 1



The Co−N_{imido} distance of 1.675(2) Å compares well with that of 1.624(4) and 1.658(2) Å in the only other two reported terminal Co(III) imido species.[6,9] This short distance, together with an almost linear Co−N_{imido}−C_{Ar} angle of 168.6(2)°, is indicative of strong multiple bond character within the Co−NAr entity. The N_{imido}−C_{aryl} distance of 1.386(4) Å is significantly smaller than that of an N−C single bond (sum of the N and C covalent radii is 1.52 Å),[13] suggesting a substantial degree of electron delocalization within

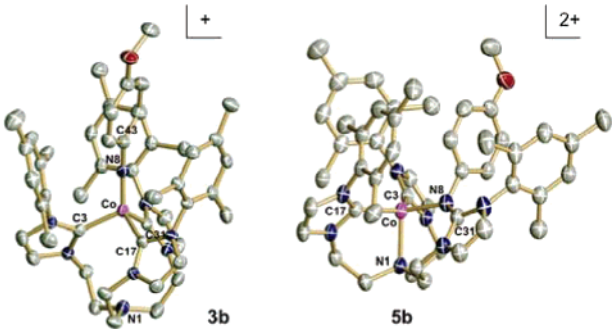


Figure 1. Solid-state molecular structures of **3b(BPh$_4$)** (left) and **5b(BPh$_4$)$_2$·1.5Et$_2$O** (right). Hydrogen atoms, counteranions, and solvent molecules are omitted for clarity, thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (deg): **3b**: Co−C3 1.940(3), Co−C17 1.938(3), Co−C31 1.962(3), Co−N8 1.675(2), N8−C43 1.386(4), Co−N8−C43 168.6(2), Co−N1 4.01. **5b**: Co−C3 2.043(2), Co−C17 2.019(2), Co−N1 2.169(2), Co−N8 1.9973(19), N8−C31 1.330(3).

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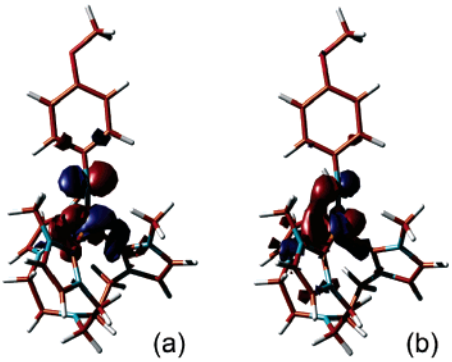

Figure 2. Representative frontier orbitals of model complex **3bm**. (a) One of the two π-antibonding orbitals, LUMO+1, with $d(xz)/d(yz)$ parentage and (b) HOMO-2 orbital showing interaction between carbene carbon (C3) and imido nitrogen (N8).

the aryl imido ligand. Also notable is the short distance between the imido nitrogen (N8) and one of the coordinated carbene carbon (C3) ligands: the N8−C3 distance of 2.982 Å is considerably smaller than the sum of their van der Waals radii (3.25 Å).[13]

To gain insight into the electronic structure of complexes **3a**−**4b**, DFT calculations (ADF 2003.1, ZORA/TZP, BP86) were carried out on the model compound **3bm**, in which the TIMEN mesitylene substituents were replaced by methyl groups.[12] The calculation results in a core geometry that is in good agreement with the experimentally determined structure of **3b(BPh$_4$)** (Figure S5 and Table S1). In the orbital splitting diagram (Figure S7), the Co(III) ion adopts a $d_{(xy)}^2 d_{(x^2-y^2)}^2 d_{(z^2)}^2 d_{xz}^0 d_{yz}^0$ ground-state electron configuration.[12] Accordingly, the electronic structure of this cationic cobalt(III) imido complex appears to be similar to that of the neutral tris(phosphine) cobalt imido complex synthesized by Peters et al.[6] As expected, MOs of d_{xz} and d_{yz} parentage are greatly destabilized by strong π-bonding interaction with the imido π-lone pairs and thus lie at highest energies (Figure 2a). The six d electrons occupy MOs up to the d_{z^2} orbital, which is σ-antibonding with respect to the Co−NR bond; the π^* orbitals d_{xz} and d_{yz} remain unoccupied (LUMOs). Although the metal−imido group is often formulated as a triple bond, comprising two degenerate π- and one σ-type orbital interactions,[2] the bonding within the cobalt imido unit reported here is best described as a formal double bond.[14] Interestingly, the DFT study also suggests that there is a considerable amount of electron density donated from one of the σ-orbitals of the carbenoid carbon into the π-orbital of the imido nitrogen (Figure 2b). This finding correlates well with the short distance between the C3 and N8 atom observed in the crystal structure and the tendency of the imido group to insert into the Co−C bond in solution.

Complexes **3a**−**4b** are stable in solid state and in solution at −35 °C. In solution at room temperature, however, the imido group readily inserts into one of the cobalt−carbene bonds as established by ^{1}H NMR spectroscopy and X-ray crystallography. We propose that the immediate product of the insertion reaction is a cobalt(I) imine species, which further disproportionates to form cobalt(II) imine complexes $[(\text{TIMEN}^{\text{aryl}})^*\text{Co}]^{2+}$ (**5a**−**6b**), metallic cobalt(0) species, and unidentified organic side products (Scheme 1). The molecular structure of divalent **5b(BPh$_4$)$_2$·1.5Et$_2$O** and **6a(BPh$_4$)$_2$·Et$_2$O** were determined and show isostructural geometries (**5b**, Figure 1 right; **6a**, Figure S13).[12] The modified TIMEN* ligand coordinates to the Co ion through two of its remaining carbenoid carbons, the anchoring nitrogen and the newly formed imine N atom. The disproportion rate is likely faster than that of the imido insertion, thereby preventing the isolation of the cobalt(I) imine complexes. However, monitoring this reaction by UV−vis spectroscopy confirmed that the reaction follows first-order kinetics and the rate-limiting step is indeed the imido insertion (Figures S8−S11).[12] The rates of these reactions are independent of the solvent and were determined to be 1.6×10^{-4} (**3a**), 8.7×10^{-5} (**3b**), 3.4×10^{-4} (**4a**), and 3.0×10^{-4} s^{-1} (**4b**), respectively (at 20 °C). In general, the insertion is faster for less electron-rich species, suggesting that the reaction proceeds via an electrophilic attack of the imido group on the Co−C bond.

As evidenced by these unusual intramolecular imido insertion reactions,[11] the highly electrophilic imido complexes **3a**−**4b** are distinctively different from other terminal cobalt(III) imido species. The slightly nucleophilic tris(phosphine) cobalt imido complex reacts slowly, for instance, with CO to form an isocyanate,[6] and the transient tris(pyrazolyl)borate cobalt imido species undergoes intramolecular C−H activation to form a cobalt amide complex.[8] It is noteworthy that reactions of **3a**−**4b** with an excess of nucleophiles, such as styrene and tetramethylimidazol-2-ylidene, do not result in intermolecular imido transfer, proving the intramolecular insertion reaction to be favored (faster). Our results support the perspective of using well-defined late-metal imido complexes as N-group transfer agents for nucleophilic organic substrates, such as alkenes, in the absence of intramolecular reactive sites. Work is currently underway to control the intramolecular insertion rates while maintaining the electrophilicity of these imido species.

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Supporting Information Available: Experimental and spectroscopic details of new compounds, ORTEPs, and complete listings of structural parameters for **2b(BPh$_4$)·CH$_3$CN**, **3b(BPh$_4$)**, **5b(BPh$_4$)$_2$·1.5Et$_2$O**, and **6a(BPh$_4$)$_2$·Et$_2$O**. This material is available free of charge via the Internet at http://pubs.acs.org.

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