C-H Activation

Intramolecular C–H Activation by an Open-Shell Cobalt(III) Imido Complex[**]

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Stable terminal imido complexes of the late transition metals (Group 9 and beyond) are rare,[1] presumably owing to a lack of empty d orbitals available for π donation from the NR^{2-} ligand. Such complexes are of interest as intermediates in catalytic NR-group transfer reactions. Our particular interest in the chemistry of cobalt imido complexes of the type $[Tp^{R,R'}Co{=}NR]$ ($Tp^{R,R'}$ = hydrotris(3-R,5-R′-pyrazolyl)borate) stems from their isoelectronic relationship to the elusive $[Tp^{tBu,Me}Co{=}O]$. We have postulated the formation of $[Tp^{tBu,Me}Co{=}O]$ as a reactive intermediate in the activation of O_2 and N_2O by various $\{Tp^{tBu,Me}Co\}$ complexes.[2] Alas, the oxo species has eluded direct observation, and to our knowledge no terminal cobalt oxo complex has ever been isolated. Herein we describe the synthesis and reactivity of stable cobalt imido analogues.

Addition of one equivalent of adamantyl azide (AdN_3) to a THF solution of $[Tp^{tBu,Me}Co(N_2)]$ at room temperature resulted in the rapid evolution of N_2 accompanied by a color change from brown to dark green. Evaporation of the solvent followed by recrystallization from pentane afforded $[Tp^{tBu,Me}Co{=}NAd]$ (**1**) as green plates in 78 % yield. A similar reaction of $[Tp^{tBu,Me}Co(N_2)]$ with *tert*-butyl azide ($tBuN_3$) yielded a mixture of $[Tp^{tBu,Me}Co{=}NtBu]$ (**2**) (40 %) and $[Tp^{tBu,Me}CoN_3]$. We attribute the formation of the azide side product to the greater stability of the *tert*-butyl radical. Both imido complexes have been structurally characterized by X-ray diffraction; the representative molecular structure of **1** is shown in Figure 1.[3]

Compound **1** is a four-coordinate molecule adopting pseudo-tetrahedral coordination of cobalt by four nitrogen ligands. Of note are the short Co(1)-N(7) bond of 1.655(2) Å and the Co(1)-N(7)-C(25) angle of 178.3(2), both of which are consistent with multiple bonding between cobalt and nitrogen center N(7). The parameters of the coordination by the Tp ligand ($Co{-}N_{av}$, 2.046(7) Å; $N\text{-}Co\text{-}N_{av}$, 89(1)°) are not unusual; indeed, they are a testament to the rigidity of the Tp ligand and underscore the deviation of the geometry of **1** from tetrahedral coordination.

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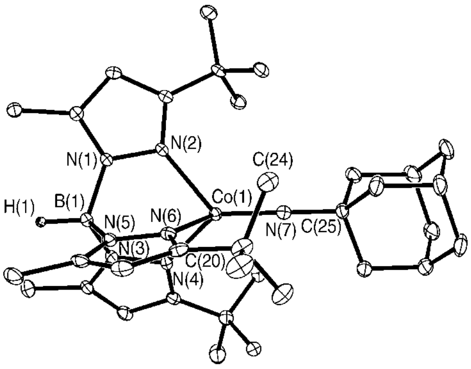

Figure 1. The molecular structure of **1** (thermal ellipsoids set at 30 % probability). Selected interatomic distances [Å] and angles [°]: Co(1)-N(7) 1.655(2), Co(1)-N(2) 2.051(2), Co(1)-N(4) 2.038(2), Co(1)-N(6) 2.049(2); Co(1)-N(7)-C(25) 178.3(2), N(2)-Co(1)-N(4) 89.54(8), N(2)-Co(1)-N(6), 88.10(8), N(4)-Co(1)-N(6) 90.09(9).

Compound **1** is thermally stable at room temperature both in solution and in the solid state. However, it decomposes upon exposure to air. At first glance its ^{1}H NMR spectrum seemed consistent with a closed-shell species (all resonances between $\delta = 0$ and 10 ppm), but closer inspection revealed some unusual chemical shifts, line broadening (full width at half maximum (fwhm) $\leq$ 14 Hz) and a significant temperature dependence. Noteworthy is that the imido complex also gave a ^{13}C NMR spectrum with sharp resonances in the range $\delta = 13$–201 ppm, albeit with some apparent isotropic shifts. The paramagnetic nature of **1** was established by a measurement of its magnetic moment in the solid state. The value of $\mu_{\mathrm{eff}} = 2.8(2)\ \mu_B$ is consistent with the presence of two unpaired electrons. Two additional observations support this notion. First, the ^{15}N NMR spectrum of a 1:1 mixture of **1** and $[Tp^{tBu,Me}Co{=}^{15}NAd]$ (**1**-^{15}N) did not reveal a detectable signal; this is probably due to the strong interaction between the observed nucleus and the cobalt atom housing the unpaired electrons. However, both the ^{1}H and ^{13}C NMR spectra of this mixture revealed some unusually large ^{15}N/^{14}N isotope effects on the chemical shifts of **1**.[4] For example, $\Delta\delta$ ranged from 16 to 73 ppb in the ^{1}H NMR and from 28 to 410 ppb in the ^{13}C NMR spectrum. We have already observed large deuterium isotope effects on the chemical shifts of paramagnetic organometallic compounds (an effect we have termed paramagnetic isotope effect on chemical shift (PIECS));[5] the present observations—while unprecedented for ^{15}N—are of a similar nature.

The preparation of **1**-^{15}N was also meant to facilitate the identification of a cobalt–nitrogen stretching frequency ($\nu_{\mathrm{Co=N}}$). Unfortunately, this proved unsuccessful; difference spectra of pure **1** and **1**/**1**-^{15}N did not reveal any assignable features.[6]

The high-spin configuration of the d^6 ion in this cobalt(III) complex distinguishes it from the few other known cobalt imido complexes, all of which are diamagnetic.[1d–f] Considering the typical d-orbital splitting of a [TpCoX] fragment under C_{3v} symmetry, we suggest a $1e^4a^12e^1$ (d^6, $S = 1$) electronic configuration for **1**.[7] We wondered whether the difference in the electronic structure would affect the reactivity of **1**. The coupling of imido ligands with CO to form isocyanates is a common reaction of metal imido complexes.[1,8] Monitoring the reaction of **1** with excess CO (1 atm) by ^{1}H NMR showed the reaction to be complete after 20 h at room temperature, with AdNCO and $[Tp^{tBu,Me}Co(CO)]$ being formed exclusively. $[Tp^{tBu,Me}Co(CO)]$ in turn reacted with AdN$_3$ to regenerate **1**, but this reaction was slow and several byproducts were detected. Protonation of **1** resulted in cleavage of the Co–N bond. Thus addition of water to **1** yielded $[Tp^{tBu,Me}CoOH]$[2a] and AdNH$_2$. Similarly, reaction of **1** with one equivalent of [lutedinium]BARF (BARF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) gave $[Tp^{tBu,Me}Co(NC_5Me_2H_3)]$BARF and AdNH$_2$. The mechanism of these reactions, which involve a reduction of Co$^{\mathrm{III}}$ to Co$^{\mathrm{II}}$ has not yet been elucidated in detail. One possible pathway involves homolytic cleavage of the Co–N bond of an intermediate of the type $[Tp^{tBu,Me}Co{-}N(H)Ad]$BARF.

Most interesting is the thermal decomposition of **1**, as it revealed a pattern related to that of the postulated reactive intermediates "$[Tp^{tBu,Me}Co{=}NSiMe_3]$" and "$[Tpt^{Bu,Me}Co{=}O]$".[9,2] This reaction was discovered upon heating **1** to 40 °C for 10 days in the presence of ethylene (1 atm); however, the ethylene merely served to reversibly trap the reaction product as an ethylene complex, and the reaction product **3** can also be prepared in the absence of ethylene. The olefin is not functionalized and can be pumped off completely to leave **3**. The molecular structure of **3** was determined by X-ray crystallography and the result is shown in Figure 2.[3]

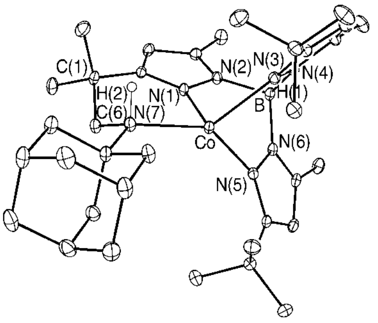

Figure 2. The molecular structure of **3** (thermal ellipsoids set at 30 % probability). Selected interatomic distances [Å] and angles [°]: Co-N(7) 2.1675(14), Co-N(1) 2.0284(13), Co-N(3) 2.1068(13), Co-N(5) 2.0771(14), C(6)-N(7) 1.501(2), N(7)-C(25) 1.5517(2); N(1)-Co-N(3) 90.99(5), N(1)-Co-N(5) 92.69(5), N(1)-Co-N(7) 89.12(5), N(3)-Co-N(5) 86.46(5), N(3)-Co-N(7) 133.41(5), N(5)-Co-N(7) 140.08(5), Co-N(7)-C(6) 107.61(10), Co-N(7)-C(25) 128.08(10) C(6)-N(7)-C(25) 112.20(12).

Compound **3**, an isomer of **1**, is a four-coordinate TpCo$^{\mathrm{I}}$ complex featuring binding of a tethered secondary amine nitrogen atom to cobalt. The amine is formally produced by insertion of the NAd moiety of **1** into a C–H bond of one of the *tert*-butyl groups of the Tp ligand. While the structural parameters of the Tp coordination hardly change (Co–N$_{\mathrm{av}}$, 2.07 Å; N-Co-N$_{\mathrm{av}}$, 90.0°), the Co-N(7) bond (2.1675(15) Å) is unusually long for cobalt complexes of secondary amines, which reflects the extreme steric congestion of **3**.[10] Like other

16-electron complexes of the type [TpCo^{I}(L)], **3** is paramagnetic. Its coordinated amine is readily replaced by other donors; thus various derivatives containing cobalt in the oxidation states +I and +II were readily prepared.

Open-shell cobalt(III) imido complex **1** is a stable representative of a broader class of multiply bonded terminal [TpCo=X] species (for example, X = NR); its existence suggests that other isoelectronic embodiments (X = O, S, PR, CR$_2$) may also be accessible and possess some—albeit fleeting—stability. Nevertheless, the facile transformation of **1** into **3** by a C−H activation demonstrates the inherent reactivity of compounds of this nature.

Experimental Section

1: 177 mg AdN$_3$ (1.0 mmol) was added in one portion to a stirred solution of [Tp^{tBu,Me}Co(N$_2$)] (510 mg, 1.0 mmol) in THF (20 mL). Evolution of a gas (N$_2$) and a color change from brown to green was observed. After stirring for 60 min, the solvent was removed under reduced pressure and the resulting dark green residue was dissolved in a minimal amount of pentane and cooled to −35 °C for 24 h. The resulting green crystals were collected by filtration, washed with cold pentane, and dried under vacuum to yield 523 mg (78 % yield) of **1**. ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 7.57$ (s, 3H), 6.51 (s, 3H), 3.49 (s, 9H), 2.505(d, 3H $J_{HH} = 12$ Hz), 2.185 (d, 3H $J_{HH} = 12$ Hz), 0.79 (s, 6H), 0.63 ppm (s, 27H); IR (KBr): $\tilde{\nu} = 2956$ (s), 2906 (s), 2513 (w, B-H), 1540 (s), 1358 (s), 1214 (s), 1063 (s), 777 (s), 646 (w), 534 cm^{-1} (w); UV/Vis (pentane): $\lambda_{max}(\varepsilon) = 373$ nm (772), 848 nm (292); m.p. decomposition above 85 °C; μ_{eff} (295 K) = 2.8(2) μ_B; elemental analysis (%) calcd for C$_{34}$H$_{55}$N$_7$BCo·1/2 C$_5$H$_{12}$: C 65.65, H 9.23, N 14.68; found: C 65.14, H 9.18, N 14.66.

[HB{κ^2-3-CMe$_2$CH$_2$N(H)Ad,5-Me-pyrazolyl}(^{tBu,Me}pz)$_2$Co] (**3**): An NMR tube filled with **1** (25 mg, 0.04 mmol) and dry C$_6$D$_6$ (0.8 mL) was charged with dry ethylene (1 atm). The NMR tube was flame-sealed and kept in an oil bath at 40 °C; formation of [HB(3-CMe$_2$CH$_2$N(H)Ad,5-Me-pyrazolyl)(^{tBu,Me}pz)$_2$Co(C$_2$H$_4$)] was monitored by ^{1}H NMR spectroscopy. After 10 days the volatiles were evaporated and the solid was recrystallized from pentane at −35 °C to produce 15 mg (60 % yield) of lime green crystals of **3**. ^{1}H NMR (360 MHz, C$_6$D$_6$): $\delta = 51.54$ (s), 3.85 (br), 2.82 (s), 2.80 (s), −1.20 (br shoulder), −2.18 (br), −3.51 (s), −9.95 ppm (s); IR (KBr, exclusion of N$_2$): $\tilde{\nu} = 2956$ (s), 2912 (s), 2843 (s), 2503 (s, B-H), 1537 (s), 1422 (s), 1359 (s), 1190 (s), 1060 (m), 883 (w), 772 (s), 647 cm^{-1} (w); m.p. decomp above 85 °C; HRMS (EI): M^+/e = 631.3915 (obs) 631.3944 (calcd); μ_{eff} (295 K) = 4.6(2) μ_B.

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[3] Crystal data for **1**: orthorhombic, *Pccn*, $a = 15.5337(9)$, $b = 43.126(2)$, $c = 11.0273(6)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7387.2(7)$ Å^3, $\rho_{calcd} = 1.201$ g cm^{-3}, $\theta = 1.39$–28.28°, Mo$_{K\alpha}$; $\lambda = 0.71073$ Å, $T = 150(2)$ K, 43875 reflections, 8738 independent, R(int) = 0.076, *SADABS* absorption correction, $\mu = 0.499$ mm^{-1}, max and min transmission: 0.980 and 0.842, solved by direct methods and refined by full-matrix least-squares on F^2, hydrogen atoms were found from the F-map and refined with isotropic thermal parameters, 608 parameters, $R = 0.0611$, $wR = 0.1309$, largest difference peak and hole: 0.970 and −0.593 e Å^{-3}. A highly disordered molecule of pentane centered on a two-fold axis was resolved with Squeeze [PLATON: A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13], void space = 752.3 Å^3, 158 e/cell assigned as four pentane molecules per cell (calcd: 168e/cell). Crystal data for **3**: orthorhombic, *Pbca*, $a = 17.499(3)$, $b = 18.992(3)$, $c = 23.944(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7957(2)$ Å^3, $\rho_{calcd} = 1.185$ g cm^{-3}, $\theta = 1.70$–28.27°, Mo$_{K\alpha}$, $\lambda = 71073$ Å, $T = 120(2)$ K, 77362 reflections, 9453 independent, *SADABS* semiempirical absorption correction from equivalents, $\mu = 0.468$ mm^{-1}, max and min transmission: 0.9547 and 0.8350, solved by direct methods and refined by full-matrix least-squares on F^2, 459 parameters, $R = 0.0433$, $wR = 0.1247$, largest difference peak and hole: 0.712 and −0.510 e Å^{-3}. CDCC-253897 (**1**) and CDCC-253898 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] A search of the Cambridge Structural Database (F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380–388) using the program Conquest (I. J. Bruno, J. C. Cole, P. R. Eddington, M. Kessler, C. F. Mcrae, P. McGabe, J. Pearson, R. Taylor, *Acta Crystallogr. Sect. B* **2002**, *58*, 389–397) yielded 11 structures containing secondary amines coordinated to Co, showing a mean Co−N separation of 2.019 Å.