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Oxidative Group Transfer to Co(I) Affords a Terminal Co(III) Imido Complex

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Atom and group-transfer reactions mediated by transition metal centers represent a prominent and heavily scrutinized area of current research in inorganic chemistry.[1] Not only are such processes finding relevance in the field of catalytic synthesis,[2] but they have also been proposed in many catalytic processes that occur in metalloprotein active sites. First row transition metals that can accept and/or release oxo and nitrene functionalities are particularly interesting.[3] For the first row metals Fe, Co, Ni, and Cu, isolable complexes with a terminal imido and/or oxo functionality bonded to a single metal center, $M{=}E$ or $M{\equiv}E$ ($E = O$, NR), are extremely rare.[4] This apparent incompatibility of later metals (groups 9, 10, and 11) with multiply bonded, strong π-donor ligands was overcome in the third row more than 10 years ago (e.g., $Cp^*Ir{\equiv}NR$ and $Mes_3Ir{\equiv}O$).[5,6]

We recently prepared an anomalous low-spin cobalt(II) complex, $[PhBP_3]CoI$ (**1**), exhibiting a distorted tetrahedral geometry.[7,8] The ground-state electronic configuration proposed for **1** (Figure 1b) presumably arises from a strong axial distortion, geometrically enforced by the $[PhBP_3]$ ligand, coupled with its strong ligand-field-donor strength. These factors suggested to us that it should, in principle, be possible to replace the iodide ligand by a divalent, strongly π-donating ligand. This would conceptually afford an 18-electron, closed-shell configuration similar to that of cobaltocenium (Figure 1c). We therefore sought to install a terminal imido functionality on the "$[PhBP_3]Co$" unit and herein report a strategy that proved viable.

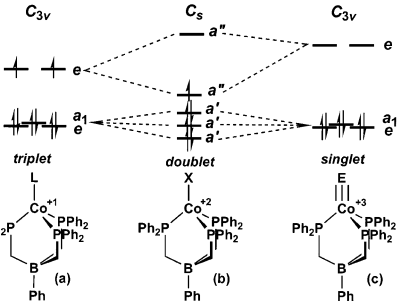
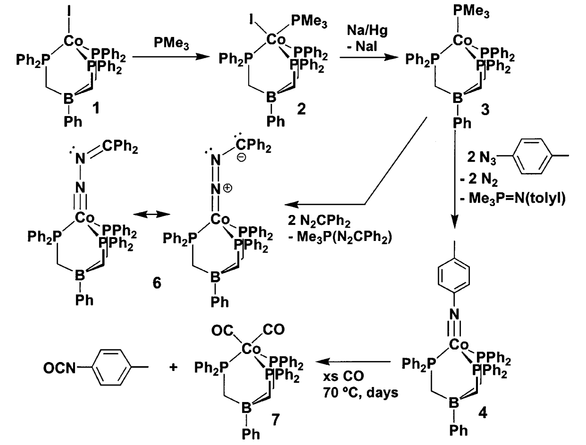


Figure 1. Qualitative splitting diagram assuming approximate C_{3v} or C_s symmetry for the frontier orbitals of (a) $[PhBP_3]Co{-}L$; (b) Jahn−Teller distorted low-spin $[PhBP_3]Co{-}X$; (c) $[PhBP_3]Co{\equiv}E$. The relative orbital energies are not accurately known.

Scheme 1



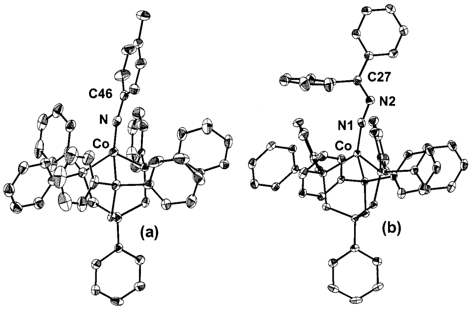


Figure 2. Displacement ellipsoid (50%) representations of (a) complex **4**, and (b) complex **6**. Bond lengths (Å) and angles (deg) for **4**: Co−N, 1.658(2); Co−N−C46, 169.51(2); P1−Co−N, 115.32(6); P2−Co−N, 131.89(6); P3−Co−N, 125.64(6). For **6**: Co−N1, 1.667(2); N1−N2, 1.280(2); N2−C27, 1.311(2); Co−N1−N2, 163.08(2); C27−N2−N1, 123.11(2).

While several synthetic strategies were considered, the most straightforward concerns a two-electron "NR" group-transfer reaction to a suitable cobalt(I) derivative. Accordingly, the key cobalt(I) precursor was prepared in two steps (Scheme 1). The addition of PMe_3 to a green solution of **1** in benzene resulted in the quantitative formation of red $[PhBP_3]Co(I)(PMe_3)$ (**2**). Complex **2**, which was characterized as a low-spin (SQUID, EPR), approximately trigonal bipyramidal (X-ray) complex, then underwent smooth reduction by sodium amalgam in THF solution to afford the pseudotetrahedral cobalt(I) complex $[PhBP_3]Co(PMe_3)$ (**3**). Complex **3** is bright green in the crystalline state; its magnetic and EPR data establish a triplet ground state, consistent with the qualitative splitting scheme depicted in Figure 1a.

Delivery of a nitrene (or imido) functionality to the cobalt(I) center was accomplished readily by addition of (*p*-tolyl)azide to **3** in benzene solution at 25 °C. Steady effervescence of nitrogen was observed during the first several minutes of the reaction. This was accompanied by a solution color change from brown to deep red. The PMe_3 consumes 1 equiv of added azide to form $Me_3P{=}N$(*p*-tolyl). A high isolated yield (97%) therefore requires 2 equiv of azide. The diamagnetic, crystalline red product, $[PhBP_3]Co{\equiv}N$-*p*-tolyl (**4**), proved amenable to an X-ray diffraction study. Its solid-state structure,[9] shown in Figure 2a, reveals a pseudo-tetrahedral complex in which the six phenyl rings of the $[PhBP_3]$ donor arms flank the terminal imido ligand of the cobalt center. The imido ligand is bent slightly (Co−N−C46 = 169.51(2)°), and the very short Co−N bond distance of 1.658(2) Å suggests strong multiple bond character in the Co−N linkage. Complex **4** can be heated for

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days in toluene solution at 100 °C with only modest decomposition. Moreover, the parent ion ($M + H = 850$) can be observed by electrospray MS. We also prepared an ^{15}N-labeled phenyl complex, $[PhBP_3]Co(^{15}NPh)$ (**5a**), and its nonlabeled derivative, **5b**, by an analogous route. Difference IR spectra for **5a** and **5b** revealed a band associated with coupled modes of the *Co−N*Ph and the Co*N−Ph* linkages at 1340 cm^{-1}. We have been unable to resolve the ^{15}N NMR signal for **5a**.

The solid-state structure of **4**, its thermal stability, and its modest reactivity (vide infra) are consistent with formulating the Co−N interaction as a strong triple bond. This is plausible in view of simple symmetry considerations and isolobal concepts.[10] A preliminary DFT study on the geometry-optimized electronic structure of **4** corroborated this suggestion and provided an orbital splitting diagram consistent with the qualitative frontier orbital diagram sketched in Figure 1c.[11] The DFT study suggested the orbital of predominantly d_{z^2} parentage actually lies lower in energy than the xy and $x^2 - y^2$ orbitals of the filled lower set. Two empty orbitals of xz and yz parentage, strongly destabilized by a pair of orthogonal π-bonds from the imido ligand, lie at higher energy.[12,13]

In a related reaction, we canvassed the ability of **3** to intercept a diphenylcarbene unit from Ph_2CN_2. Rather than undergoing carbene transfer and concomitant expulsion of N_2, we found that 2 equiv of Ph_2CN_2 reacted with **3** to generate the phosphazine $Me_3P(N_2CPh_2)$ and the thermally stable diazoalkane adduct complex, $[PhBP_3]Co(N_2CPh_2)$ (**6**). Terminal diazoalkane adducts of group 9 metals are very rare;[14a,b] the single cobalt diazoalkane derivative previously reported exhibits side-on η^2-coordination.[14c] The X-ray structure of diamagnetic **6** was therefore of interest (Figure 2b).[15] Most prominent is that complex **6** features an η^1-ligated diazoalkane ligand.[16] The Co−N bond length (1.667(2) Å) is nearly as short as the Co−N distance observed in **4**. This again suggests strong multiple bond character at the Co−N linkage in **6** and perhaps explains the reluctance of this system to expel N_2 under mild conditions. The relatively short N1−N2 bond distance of 1.280(2) Å indicates there is still multiple bond character between these two atoms. The two resonance contributors shown in Scheme 1 for **6** are emphasized.[17]

A cursory survey of the reactivity of **4** indicates that it is fairly resistant to nitrene transfer chemistry. We did find that the imido functionality can be transferred to carbon monoxide to produce the isocyanate (O═C═N-*p*-tolyl), albeit sluggishly (14 equiv of CO, 70 °C, 12 days).[18] The isolated cobalt(I) byproduct (90%) was the diamagnetic dicarbonyl species $[PhBP_3]Co(CO)_2$ (**7**) (ν(CO) = 2008, 1932; KBr/THF).

The successive transformations **3** → **4** and **4** → **7** comprise a system in which (i) a late first-row complex acts as an acceptor in a high yielding, oxidative, two-electron-group-transfer process (**3** → **4**). The resulting species can then (ii) undergo a reductive two-electron group-transfer process to deliver the accepted group to a substrate (**4** → **7**). The method by which **4** is prepared suggests that direct, two-electron group-transfer processes to cobalt, and perhaps other later first-row metals, are possible. Maintaining approximate 3-fold symmetry is a promising design strategy for further developments in this area of synthesis.

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Supporting Information Available: Experimental procedures (PDF), characterization data, and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) $\mathbf{4}\cdot C_6H_6$ ($C_{55}H_{51}BCoNP_3$), MW = 888.62, red plate, collection temperature = 96(2) K, monoclinic, space group $P2_1/c$, $a = 14.1174(11)$ Å, $b = 14.3252(11)$ Å, $c = 22.3306(18)$ Å, $\alpha = 90°$, $\beta = 96.202(1)°$, $\gamma = 90°$, $V = 4489.6(6)$ Å^3, $Z = 4$, $R_1 = 0.0415$ [$I > 2\sigma(I)$], GOF = 1.670.

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(11) These studies will be elaborated in a forthcoming full paper. Briefly, a geometry optimization was carried out with the program JAGUAR (B3LYP/LACVP**) using the complete crystal coordinates of complex **4**. Convergence was achieved, and the theoretical structure obtained for **4** was in fair agreement with that determined experimentally (Figure 2a).

(12) To correlate the frontier orbitals of $[PhBP_3]Co-Y$ fragments ($Y = PMe_3$, I, or NR) to those of an octahedron, a redefinition of axes is required. Using a notation in which the z-axis of an octahedral ML_6 molecule proceeds through the center of one triangular face of an octahedron, the orbital parentages transform to the following: t_{2g} set, z^2; $\{(^2/_3)^{1/2}(x^2 - y^2) - (^1/_3)^{1/2}yz\}$; $\{(^2/_3)^{1/2}xy - (^1/_3)^{1/2}xz\}$; e_g set, $\{(^1/_3)^{1/2}x^2 - y^2 + (^2/_3)^{1/2}yz\}$; $\{(^1/_2)^{1/2}xy + (^2/_3)^{1/2}xz\}$. Under this notation, the ground-state electronic configuration predicted for complex **4** is $(z^2)^2$ $(\{(^2/_3)^{1/2}(x^2 - y^2) - (^1/_3)^{1/2}yz\})^2$ $(\{(^2/_3)^{1/2}xy - (^1/_3)^{1/2}xz\})^2$ $(\{(^1/_3)^{1/2}x^2 - y^2 + (^2/_3)^{1/2}yz\})^0$ $(\{(^1/_2)^{1/2}xy + (^2/_3)^{1/2}xz\})^0$.

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(15) **6** ($C_{58}H_{51}BCoN_2P_3$), MW = 938.66, red plate, collection temperature = 98(2) K, monoclinic, space group $P2_1/n$, $a = 13.1284(8)$ Å, $b = 16.5975(11)$ Å, $c = 21.8205(14)$ Å, $\alpha = 90°$, $\beta = 97.168(1)°$, $\gamma = 90°$, $V = 4717.5(5)$ Å^3, $Z = 4$, $R_1 = 0.0466$ [$I > 2\sigma(I)$], GOF = 1.572.

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(18) Free isocyanate was observed (30% by ^1H NMR integration; GC/MS, 133 *m/z*). An additional product(s) was also observed by ^1H NMR (~45%), which presumably arises from thermal isocyanate degradation during the course of the reaction.

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