Reactivity of a Co(I) [N$_2$P$_2$] complex with azides: evidence for a transient Co(III) imido species†

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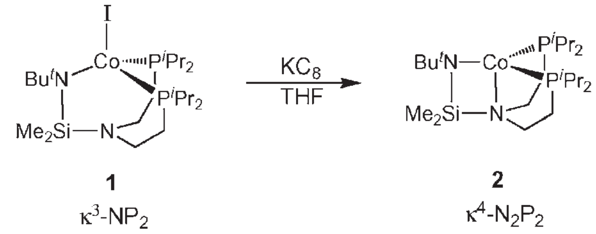
The synthesis of a monomeric Co(I) complex supported by a multidentate monoanionic [N$_2$P$_2$] ligand is described; interaction with aryl azides at low temperature generates a species whose reactivity is consistent with imido ("Co=NR") character.

Development of ligand scaffolds capable of engendering new and unusual reactivity at metal centers has led to numerous advances in reaction chemistry and has been a major focus of our group for some time.[1] Recently we reported the synthesis and reduction chemistry of a number of new transition metal complexes supported by the monoanionic multidentate [N$_2$P$_2$] ligand, where [N$_2$P$_2$] = [^{t}BuNSiMe$_2$N(CH$_2$CH$_2$P^{i}Pr$_2$)$_2$].[2] One area of research that has garnered much attention is the synthesis and isolation of complexes containing metal–ligand multiple bonds due to their proposed existence in many catalytic cycles. In addition to their role in hydroamination[3] and C–H bond activation,[4] imido species act as isoelectronic analogues to oxo functionalities, which are well known to be participants in biologically active catalytic systems.[5] Typically, Co(III) imido species are low-spin;[6–9] however, spin-crossover behavior that leads to intramolecular C–H activation has been observed.[9] Here we propose the involvement of a transient Co(III) imido species in reactions that result in H-atom abstraction as well as nitrene group transfer.

Treatment of Li[N$_2$P$_2$] with CoI$_2$ yields [N$_2$P$_2$]CoI (**1**) in 83% yield as dark green blocks following crystallization from toluene.[10] An X-ray diffraction study showed the geometry of **1** to be a distorted tetrahedral with the ligand coordinated κ^3-NP$_2$ (ESI†).[11] Reduction of **1** with KC$_8$ under an atmosphere of N$_2$ in THF resulted in a color change from dark green to deep blue. The resulting compound [N$_2$P$_2$]Co (**2**) was isolated in 84% yield as large blue needles following crystallization from Et$_2$O. The structure of **2** was obtained from an X-ray diffraction study, and no N$_2$ coordination was observed. Instead, the coordination mode of the [N$_2$P$_2$] ligand changes from κ^3-NP$_2$ in **1** to κ^4-N$_2$P$_2$ in **2** (Scheme 1).[11] We believe that coordination of the basal nitrogen in **2** acts as a trap to stabilize the low-valent Co(I) center. The solution magnetic susceptibility of **2** was found to be 3.0 μ_B, in agreement with an S = 1 ground state.

In attempts to generate the imido species, the reaction of **2** with arylazides (phenylazide **3**, *p*-tolylazide **4**) was examined.

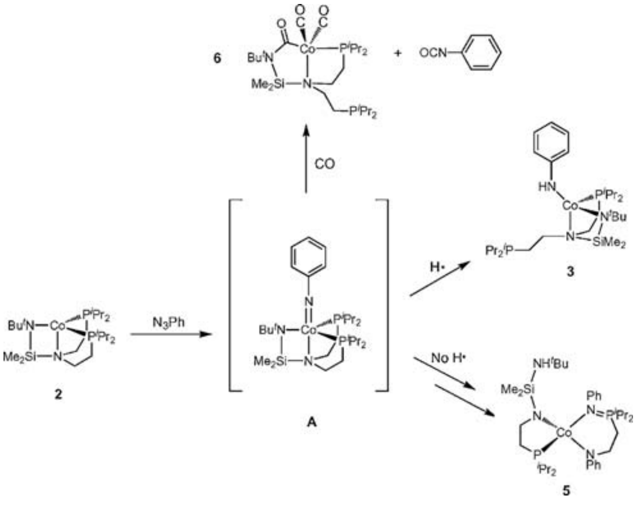


Scheme 1 Reduction of Co(II) to Co(I).

When phenylazide was added to a solution of **2** in pentane at −116 °C (Et$_2$O/N$_2$(l)), a green precipitate (**A**) formed immediately (Scheme 2). When allowed to warm, the green suspension quickly transformed to a dark red solution.

The same dark red solution could be obtained immediately if arylazide was added to **2** at −70 °C or above. After filtration, concentration, and cooling, red-orange crystals of [N$_2$P$_2$]-CoNHPh (**3**) were collected in 57% yield.

To elucidate the composition of paramagnetic **3**, an X-ray diffraction study was performed (ESI†).[11] The [N$_2$P$_2$] ligand is bound κ^3-N$_2$P with one neutral phosphine moiety uncoordinated due to steric congestion around the metal center. The geometry about the cobalt is best described as distorted tetrahedral with angles of 77.03(16)° (N1-Co1-N2), 118.23(13)° (N1-Co1-P1), 131.49(17)° (N1-Co1-N3), and 109.78(16)° (N2-Co1-N3). The Co1-N3 bond distance was found to be 1.906(4) Å, and the N–H hydrogen was located



Scheme 2 Formation and reactivity of the Co(III) imido "[N$_2$P$_2$]Co=NPh" (**A**).

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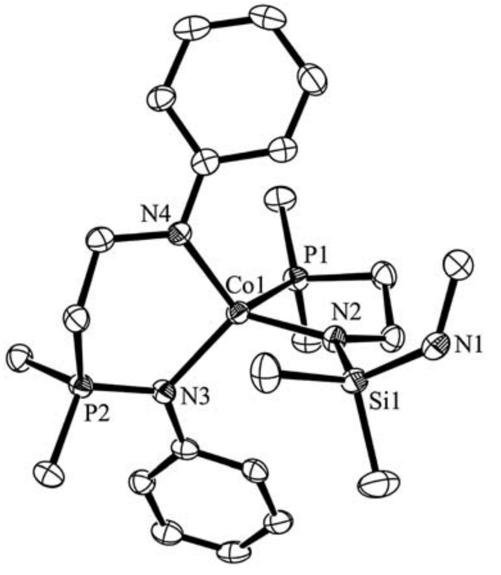

Fig. 1 Thermal ellipsoid (50%) plot of **5**. Hydrogen atoms, *iso*-propyl methyl, and *tert*-butyl methyl groups have been omitted for clarity.

in the Fourier map; however, a fixed position was used in the structural refinement. The magnetic susceptibility of **3** was determined to be 3.8 μ_B, in agreement with an $S = 3/2$ ground state. Complex **3** was independently synthesized through the reaction of **1** with LiNHPh to further confirm the identity of **3**.

In addition to red-orange crystals of **3**, a small quantity of a bright green crystalline material was isolated following the reaction of **2** with phenylazide. The identity of this side-product was elucidated with the aid of an X-ray diffraction study, and an ORTEP diagram is shown in Fig. 1.[11]

The $[N_2P_2]$ ligand has undergone a number of transformations, the first being the oxidation of one neutral phosphine donor to a phosphinimine.[7] Next, the C–N bond linking the basal nitrogen to the phosphinimine moiety has been cleaved and rendered anionic, and the original anionic nitrogen has been protonated, forming the Co(II) species $[\mathrm{PhN{=}P^{i}Pr_2(CH_2)_2NPh}][^{t}\mathrm{BuNHSiMe_2N(CH_2)_2P^{i}Pr_2}]\mathrm{Co}$ (**5**). The isolated yield of **5** was found to be solvent dependent with the highest isolated yield of **5** (15%) obtained with toluene or benzene as the solvent. A summary of the yields of **3** and **5** in different solvents in provided in Table 1. Analysis of the crude reaction mixture revealed the presence of starting material **2** and products **3** and **5**, in addition to a small quantity of another unidentified product(s). The paramagnetic nature of this product and its small quantity has made identification elusive to-date. The solution magnetic susceptibility of **5** was found to be 4.1 μ_B, in agreement with a high-spin Co(II) center.

Hydrogen atom abstraction by transient metal imido species has previously been observed.[12,13] A common test for identifying hydrogen atom abstraction is conversion of 1,2-diphenylhydrazine to azobenzene.[12] To support the formation of **3** *via* hydrogen atom abstraction by a transient Co(III) imido species, the reaction of **2** with an arylazide (phenylazide **3**, *p*-tolylazide **4**) in the presence of 0.5 equivalents of 1,2-diphenylhydrazine was examined: quantitative conversion of 1,2-diphenylhydrazine to azobenzene was observed by ^{1}H NMR and **5** was not observed in the crude reaction mixture.

Table 1 Isolated yields of **3** and **5**[a]

Solvent	Yield of **3**(%)	Yield of **5**(%)
Pentane	57	<1
Toluene	23	15
Benzene	20	15
THF	34	7.3

[a] All reactions were performed at −40 °C and allowed to warm to room temperature and stirred for 3 h. The yields reported are isolated yields from crystallization.

The reaction of **2** and phenylazide was also performed in C_6D_6 and **3** was analyzed for deuterium incorporation. The IR spectrum of **3** did not reveal any new N–D stretch in the expected region; only the N–H stretch at 3320 cm^{-1} was observed. The high resolution EIMS, however, did reveal incorporation of deuterium into the ^{t}Bu group of the $[N_2P_2]$ ligand. Similar results have been observed previously with a related transient Co oxo species supported by the Tp′ (Tp′ = hydridotris(3-*tert*-butyl-5-methylpyrazolylborate) ligand.[14] Our data suggests that two competing reactions are operative in the formation of **3** and **5**. The solvent dependent isolated yields and the deuterium labelling experiments suggest that the formation of **3** involves an imido assisted hydrogen atom abstraction from solvent by the ^{t}Bu group of the ligand. Adding 0.5 equivalents of phenylazide to **2** led to crude reaction mixtures of **2** and **3**, with no **5** observed. Increasing the amount of azide added to two equivalents led to messy reaction mixtures that would not yield crystalline products. The yields of **3** and **5** do not follow an obvious trend but are likely the result of a combination of the polarity of the solvent and the BDE of available C–H bonds in solution (Scheme 2).

Under certain conditions (toluene and sufficient amounts of N_3Ph), intramolecular nitrene group transfer is more competitive with hydrogen abstraction, which leads to a higher isolated yield of **5**. When the reaction of **2** and phenylazide is performed in the presence of 1,2-diphenylhydrazine in toluene; however, compound **5** is not observed, further supporting the premise that **5** forms in the absence of good hydrogen-atom donors.

To further probe whether a transient imido species was being formed, the reaction of **A** with excess CO was explored to determine whether nitrene group transfer would occur.[6,9,15] To a flask containing complex **A** at −116 °C was added an atmosphere of CO; the flask was sealed, and the cold bath was removed. As the flask warmed, the reaction mixture changed color from green to yellow. The volatile materials were vacuum-transferred and analyzed by GCMS; phenyl isocyanate was observed exclusively in 30% yield.[16]

The remaining yellow solid was extracted with toluene, and following concentration and cooling at −40 °C yellow crystals of the diamagnetic complex $[^{t}\mathrm{BuN(C{=}O)SiMe_2N((CH_2)_2P^{i}Pr_2)_2}]\mathrm{Co(CO)_2}$ (**6**) were isolated in 80% yield. The IR spectrum of **6** showed three C–O bands at 1952, 1893, and 1583 cm^{-1}. An X-ray diffraction study confirms the connectivity of **6** and helps explain the low frequency of the stretch at 1583 cm^{-1} (ESI†).[11] The latter absorption is the result of a CO insertion into the amide-metal bond.[17] To our knowledge this is the first crystallographically characterized example of this transformation with

Co. The structure of **6** is best described as trigonal bipyramidal with one neutral phosphine uncoordinated due to electron saturation at the metal center (18 e$^-$ species).

While direct confirmation of complex **A** as a Co(III) imido is hampered by its instability in suspension above −70 °C, our experimental results infer the presence of a transient "[N_2P_2]Co═NAr" imido species. The observed H-atom abstraction to obtain **3** and the proposed nitrene group transfer observed in **5** and **6** support this conclusion. Reaction of **A** with a variety of substrates such as alkenes, alkynes, isocyanides, and isocyanates did not lead to additional nitrene group transfer products. Future work will focus on modest ligand modifications with the intent of encouraging group transfer reactions over H-atom abstraction.

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11 Crystal data for **1**: $C_{22}H_{51}CoIN_2P_2Si$. f_w = 619.51, monoclinic, $P2_1/c$, a = 9.356(2), b = 34.812(8), c = 9.299(2) Å, $\alpha = \gamma = 90^\circ$, β = 105.015(4)°, V = 2925.4(11) Å^3, Z = 4, ρ_{cacld} = 1.407, θ = 2.3–23.3, MoK$_\alpha$; λ = 0.71073 Å, T = 168(2) K, 5914 reflections, 4254 independent, R(int) = 0.0457, *SADABS* absorption correction, μ = 1.804, max and min transmission: 1.00 and 0.83, solved by direct methods and refined by full-matrix least-squares on F^2, hydrogen atoms were placed using constrained conditions, 261 parameters, R(observed) = 0.0396, wR(observed) = 0.0881, largest difference peak and hole: 0.639 and −0.451 eÅ^{-3}. CCDC 677811 (**1**). Crystal data for **2** $C_{22}H_{51}CoN_2P_2Si$. f_w = 492.61, orthorhombic, *Pnma*, a = 14.742(4), b = 11.265(3), c = 17.148(5) Å, $\alpha = \gamma = \beta = 90^\circ$, V = 2847.6(13) Å^3, Z = 4, ρ_{cacld} = 1.149, θ = 3.3–25.3, MoK$_\alpha$; λ = 0.71073 Å, T = 244(2) K, 2931 reflections, 1747 independent, R(int) = 0.0423, *SADABS* absorption correction, μ = 0.768, max and min transmission: 1.00 and 0.89, solved by direct methods and refined by full-matrix least-squares on F^2, hydrogen atoms were placed using constrained conditions, 141 parameters, R(observed) = 0.0528, wR(observed) = 0.1429, largest difference peak and hole: 0.408 and −0.300 eÅ^{-3}. CCDC 677814 (**2**). Crystal data for **3**: $C_{28}H_{57}CoN_3P_2Si$. f_w = 584.73, monoclinic, $P2_1/n$, a = 13.154(5), b = 15.801(6), c = 16.304(6) Å, $\alpha = \gamma = 90^\circ$, β = 102.657(5)°, V = 3307(2) Å^3, Z = 4, ρ_{cacld} = 1.175, θ = 3.4–25.1, MoK$_\alpha$; λ = 0.71073 Å, T = 151(2) K, 4423 reflections, 2642 independent, R(int) = 0.0745, *SADABS* absorption correction, μ = 0.672, max and min transmission: 1.00 and 0.73, solved by direct methods and refined by full-matrix least-squares on F^2, hydrogen atoms were placed using constrained conditions, 321 parameters, R(observed) = 0.0531, wR(observed) = 0.1122, largest difference peak and hole: 0.457 and −0.328 eÅ^{-3}. CCDC 677812 (**3**). Crystal data for **5**: $C_{34}H_{62}CoN_4P_2Si$, f_w = 675.84, monoclinic, $P2_1/n$, a = 11.044(3), b = 14.324(4), c = 23.454(6) Å, $\alpha = \gamma = 90^\circ$, β = 93.105(4)°, V = 3704.7(16) Å^3, Z = 4, ρ_{cacld} = 1.212, θ = 2.2-24.2, MoK$_\alpha$; λ = 0.71073 Å, T = 167(2) K, 20702 reflections, 7547 independent, R(int) = 0.0455, *SADABS* absorption correction, μ = 0.610, max and min transmission: 1.00 and 0.89, solved by direct methods and refined by full-matrix least-squares on F^2, hydrogen atoms were placed using constrained conditions, 379 parameters, R(observed) = 0.0436, wR(observed) = 0.1056, largest difference peak and hole: 0.410 and −0.303 eÅ^{-3}. CCDC 677813 (**5**). Crystal data for **6**: $C_{25}H_{51}CoN_3O_3P_2Si$, f_w = 576.64, monoclinic, $P2_1$, a = 8.3023(11), b = 12.279(17), c = 15.354(2) Å, $\alpha = \gamma = 90^\circ$, β = 93.718(2)°, V = 1562.1(4) Å^3, Z = 2, ρ_{cacld} = 1.226, θ = 2.6–23.5, MoK$_\alpha$; λ = 0.71073 Å, T = 160(2) K, 8958 reflections, 5638 independent, R(int) = 0.0336, *SADABS* absorption correction, μ = 0.716, max and min transmission: 1.00 and 0.83, solved by direct methods and refined by full-matrix least-squares on F^2, hydrogen atoms were placed using constrained conditions, 307 parameters, R(observed) = 0.0417, wR(observed) = 0.0889, largest difference peak and hole: 0.474 and −0.284 eÅ^{-3}. CCDC 677815 (**6**).

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