A Co_2N_2 Diamond-Core Resting State of Cobalt(I): A Three-Coordinate Co^I Synthon Invoking an Unusual Pincer-Type Rearrangement**

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Coordinatively unsaturated transition-metal complexes are expected to be inherently reactive and offer an opportunity to study novel transformations such as homogeneous catalysis[1] and the activation of inert substrates such as N_2.[2] However, generating low-coordinate environments in these systems can often result in degradation or rearrangement of the ancillary ligand. Only in a few cases can reorganization of the ancillary ligand be reversible, thus generating resting states that are capable of behaving as "masked" low-coordinate fragments. For example, Cummins and co-workers reported a reversible β-hydride elimination pathway leading to a masked three-coordinate Mo^{III} fragment capable of reductively cleaving atmospheric nitrogen.[3] A similar reversible β-hydride elimination has also been documented for the complex [Fe-$(PMe_3)_5$], which has been shown to equilibrate with the corresponding iron(II) isomer [Fe(H)(η^2-CH_2PMe_2)($PMe_3)_3$] and free trimethylphosphine.[4] In other amphivalent systems, Fink and co-workers[5] discovered that a dinuclear Pd^0 complex containing bridging bidentate phosphine ligands can equilibrate with its mononuclear scaffold. We report herein an unprecedented ligand rearrangement of a pincer-type framework PNP (PNP = [N{2-P($CHMe_2)_2$-4-MeC_6H_3}$_2$]$^-$).[6,7] Reorganization of the PNP pincer ligand from a terminal chelating mode to a bridging mode allows for isolation of [{(μ_2-PNP)Co}$_2$], a complex bearing a Co_2N_2 diamond-core resting state. [{(μ_2-PNP)Co}$_2$] behaves as a three-coordinate Co^I synthon when treated with substrates

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details and crystallographic data) is available on the WWW under
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such as N_2 and CO. We also report a rare example of a dianionic dinitrogen[8] salt of cobalt(−I), a product likely resulting from overreduction of the "[(PNP)Co]" core under atmospheric nitrogen.

The square-planar complex [(PNP)CoCl] (**1**)[7,9] is a precursor prepared readily from [Li(PNP)][6] and $CoCl_2$ in THF, and displays an irreversible one-electron reduction wave at −2.41 V under N_2.[7] Chemical reduction of **1** with an excess of $NaC_{10}H_8$ in an N_2 atmosphere effected an immediate color change from dark green to black. Upon work up and crystallization from Et_2O at −35°C, dark crystals of the dianionic cobalt–dinitrogen complex [{Na$_2$(thf)$_3$}$_2${(PNP)Co(N$_2$)}$_2$] (**2**) were obtained.[7] However, solid samples of **2** were marred with about 5–10% content of another cobalt species (assayed by ^{31}P and ^{15}N NMR spectroscopy, see below). Complex **2** is diamagnetic and displays an intense absorption in the IR spectrum at $\tilde{\nu}_{NN} = 1784$ cm^{-1}, a value higher in energy than that measured for the isotopomer prepared from [15]N_2 (1732 cm^{-1}). The ^{15}N NMR spectrum of **2** exhibits two broad signals at $\delta = 319$ and 293 ppm, for which no J_{NN} coupling was resolved even upon cooling, an attribute possibly arising from coupling to the [59]Co nucleus ($I = 7/2$, 100% abundance). Complex **2** is exceedingly reactive, and solid samples or solutions of **2** become oxidized over several hours with transformation (albeit not cleanly) into [{(PNP)Co}$_2$(μ_2-N$_2$)][7] (**3**), the same by-product observed in the original synthesis of **2** from **1**. Characterization data for **3** include a weak absorption in the IR spectrum at $\tilde{\nu}_{NN} = 2024$ cm^{-1}, a value blue-shifted from that measured for the [15]N_2 isotopomer (1957 cm^{-1}). In contrast to **2**, the [15]N_2 unit in complex **3** exhibits only one broad ^{15}N NMR resonance at $\delta = 306$ ppm. Complex **3** can be prepared in greater yield from the one-electron reduction of **1** with tBuLi in an N_2 atmosphere or alternatively by addition of two equivalents of **1** to **2**. The latter reaction suggests that **2** is a powerful one-electron reductant and that an unsaturated "[(PNP)Co]" intermediate might play a role in the course of these reactions (Scheme 1). Furthermore, the [15]N_2 isotopomer of **3** slowly exchanges with [14]N_2, as evidenced by a blue shift of the $\tilde{\nu}_{NN}$ stretching frequency in the IR spectrum as well as by the decay of the ^{15}N NMR resonance.
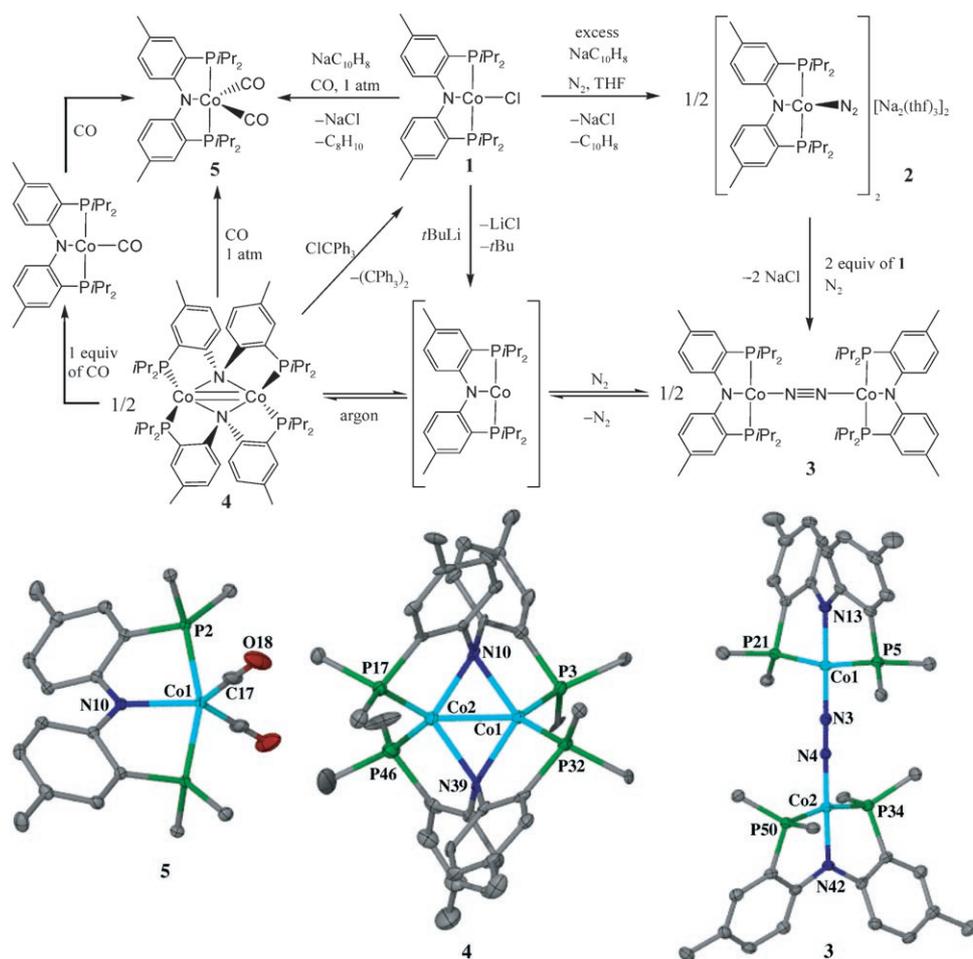
Scheme 1. Synthesis of complexes **2–5** and the intermediate [(PNP)Co(CO)]. Molecular structures are depicted with thermal ellipsoids set at 50% probability with H atoms, isopropyl methyl groups, and solvent molecules omitted for clarity.

Single-crystal solid-state structures for compounds **2** and **3** reveal that each system is composed of two cobalt centers (Figure 1 (**2**) and Scheme 1 (**3**)).[7] The molecular structure of **2** exhibits a Na$_2$Co$_2$N$_4$ core divided into two topologically linear Co−N−N units which are related by an inversion center (Figure 1). One of the Na$^+$ centers bridges another {(PNP)CoN$_2$} unit through the adjacent β-N atom to close the Na$_2$Co$_2$N$_4$ ring in **2**. If one ignores the Na$^+$ ions, each Co atom is confined in a highly distorted tetrahedral geometry with the metal atom deviating from the PNP mean plane by about 0.832°. The molecular structure of **2** unarguably depicts a dianionic {(PNP)Co(N$_2$)}$^{2-}$ unit, but the poor quality of the X-ray data prevents us from discussing any specific metrical parameters (Figure 1).[7]

We were able to reproduce the structural features in **2** by using high-level density functional calculations at the B3LYP/6-31G** level of theory.[10] To ascertain more information on the nature of the Co−N bond in **2**, we computed the bond order directly from the molecular structure,[11] and obtained a bond order of 0.898 for the Co−N linkage and a bond order of 2.322 for the N−N linkage. As a result, we tentatively assign a single bond for the Co−N linkage and a triple bond for the N−N linkage.[7] More importantly, when we computed the
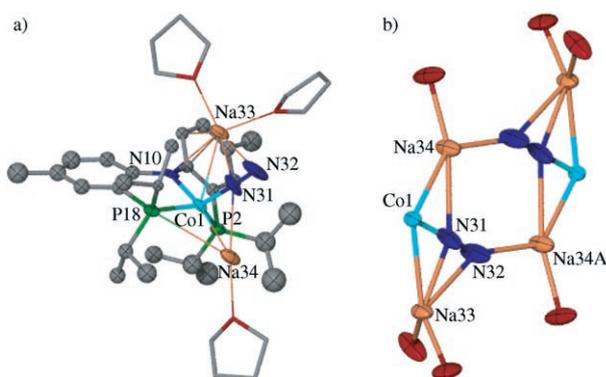
Figure 1. Molecular structure of **2**. The [{Na₂(thf)₃}{(PNP)CoN₂}] unit (a) and [{Na₂(thf)₃CoN₂}₂] core (b) are shown with thermal ellipsoids set at 50% probability. All H atoms in (a) are excluded for clarity, and the disordered thf ligands are depicted with sticks. Only the O atoms (red) of the thf ligands are displayed in (b).

molecular structure of the monomer $[(PNP)Co(N_2)]^{2-}$, the energy of the system fell into a minimum for the analogous geometry observed in the $\{(PNP)Co(N_2)\}^{2-}$ unit of the crystal structure of **2**. As expected for a Co⁻¹ species, the five filled orbitals highest in energy (HOMO through HOMO−4) are all metal-based, and the LUMO is *only* ligand-based and comprises the aryl$_{PNP}$ π* orbital (Figure 2).[7] For all these reasons, complex **2** is best described as a dianionic d¹⁰ cobalt–dinitrogen complex. Compound **2** represents a rare example of a dinitrogen-ligated[8] cobalt(−I) dianion.

In contrast to **2**, the crystal structure of **3** displays a more common Co−N₂−Co linkage (Scheme 1),[8,12] with both cobalt atoms residing in a square-planar geometry in which the two {(mer-PNP)Co} units are essentially orthogonal to each other (ca. 93°). The Co−N$_{PNP}$ bond lengths (1.928(2) and 1.935(2) Å) are much longer than the Co−N$_{NN}$ bond lengths (1.763(2) and 1.768(2) Å), and the N−N bond length is short (1.144(3) Å), hence consistent with the topologically linear resonance structure [(PNP)Co−N=N−Co(PNP)].

Interestingly, in vacuum or in an argon atmosphere, compound **3** expels N₂ to afford a green product.[7] The ¹H and

³¹P NMR spectra both indicate formation of a new diamagnetic material, while the $\tilde{\nu}_{NN}$ stretch originally present in **3** vanishes. The same product can be generated from the one-electron reduction of **1** with *t*BuLi under argon, and when green solutions of the latter material are exposed to N₂, formation of **3** slowly becomes observable (48 h) by NMR and IR spectroscopies. Single-crystal X-ray diffraction analysis of the green material clearly reveals a reorganization of the PNP ligand to give [{(μ₂-PNP)Co}₂] (**4**), in which a dimeric structure with a Co₂N₂ diamond core results from the bridging of the PNP ligand through the amide nitrogen atom. A close Co−Co contact is observed in the Co₂N₂ core in **4**. Unfortunately, the diffraction data originating from single crystals of **4** were weak, hence making the metrical parameters somewhat questionable.[7,13] The gross structural features of **4**, however, are unquestionable and resemble a dinuclear Cuᴵ system recently reported by Harkins and Peters.[14]

The Co₂N₂ diamond core in **4** behaves as a highly reactive three-coordinate Coᴵ synthon as it reversibly binds N₂ (in the solid state and in solution) to afford **3** cleanly (see above). Likewise, the π acid CO reacts smoothly with **4** to generate $[(PNP)Co(CO)_2]$ (**5**), which has been characterized by NMR spectroscopy, elemental analysis (CHN), and single-crystal X-ray diffraction analysis.[7,15] Independent synthesis of **5** can be readily accomplished by reduction of **1** with NaC₁₀H₈ under CO (Scheme 1). In the conversion of **4** into **5**, an intermediate can be observed by the growth and decay of a ³¹P NMR resonance (δ = 69 ppm) and an intense IR absorption ($\tilde{\nu}_{CO}$ = 1901 cm⁻¹). Concomitant with the disappearance of these signals is the appearance of a new ³¹P NMR signal (δ = 94 ppm) and two intense IR absorptions ($\tilde{\nu}_{CO}$ = 1957 and 1893 cm⁻¹) corresponding to **5**. Under depleted CO (2 equiv per **4**), such a putative intermediate can be isolated and characterized. We speculate the identity of this intermediate to be the monocarbonyl complex $[(PNP)Co(CO)]$,[16] based on a combination of solution NMR (¹H, ¹³C, and ³¹P) and IR spectroscopies (Scheme 1).[7] As opposed to π-acid coordination, complex **4** can also be readily oxidized with ClCPh₃ to effect dimer cleavage and ligand reorganization to regenerate **1** along with Gomberg's dimer (Scheme 1). Separation of **1** (67% yield) was achieved by fractional crystallization from cold Et₂O.

In summary, we have prepared a dianionic cobalt(−I)–dinitrogen complex as well as a dinuclear Coᴵ species. For the latter, we have demonstrated the system to be a masked form of a three-coordinate Coᴵ complex. Most notably, the Co₂N₂ diamond core is highly reactive, which is reflected by its reversible binding of N₂ to afford a cobalt(ᴵ)–dinitrogen adduct. Unlike typical Co=Co units reported in the literature,
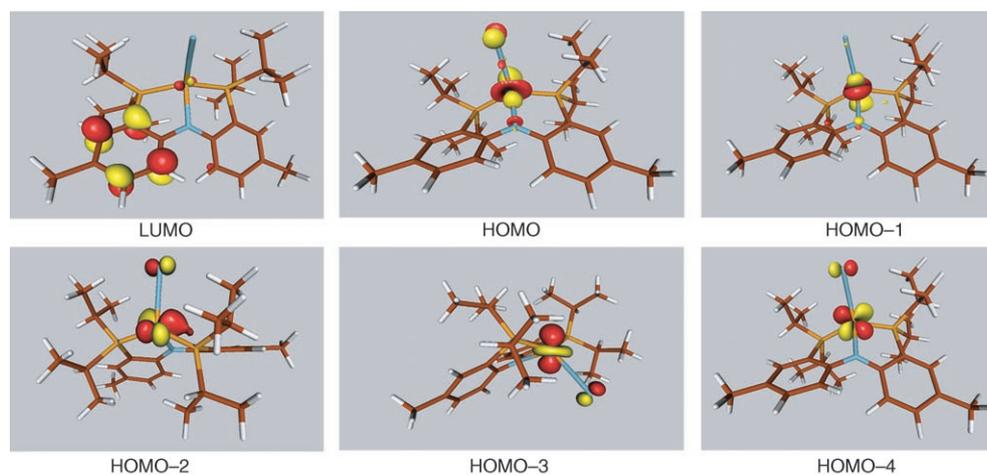
Figure 2. LUMO (π*, ligand-based) and HOMO through HOMO−4 (all cobalt-based) for the full model of the $\{(PNP)Co(N_2)\}^{2-}$ unit of complex **2**.

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the dinuclear complex **4** is a masked form of a low-coordinate Co^I species which in the presence of N$_2$, CO, and ClCPh$_3$ can regenerate the original three-coordinate pincer-type "{(PNP)Co}" framework. We propose that such an unusual ligand rearrangement in complex **4** might be driven by the chelate-enforced nature of the tridentate pincer scaffold, hence preventing the occurrence of metal or ligand disproportionation reactions. The steric crowding imposed by the diisopropyl phosphine substituents might also possibly be a contributing factor to the fragile diamondlike-core resting state in **4**. The mechanism of formation of compounds such as **3**, **5**, and [(PNP)Co(CO)] from compounds possessing cores such as in **4** is currently under scrutiny as ligand reorganization of this kind may play a role in catalytic processes involving pincer-type frameworks.

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[9] Crystallographic details for **1**·C$_7$H$_8$: A dark crystal of approximate dimensions $0.15 \times 0.08 \times 0.06$ mm^3 was selected and mounted on a glass fiber. A total of 3711 reflections ($-13 \leq h \leq 14$, $-12 \leq k \leq 12$, $-18 \leq l \leq 11$) were collected at $T = 126(2)$ K in the range of 2.54 to 26.68° of which 2335 were unique ($R_{int} = 0.0746$); Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. A severely disordered toluene molecule was present in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms not associated with the solvent were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. No attempt was made to locate the hydrogen atoms on the toluene molecule. The residual peak and hole electron densities were 0.488 and -0.382 e A^{-3}. The absorption coefficient was 0.740 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F) = 0.0432$, $wR(F^2) = 0.1036$, and a GOF = 0.707 ($I > 2\sigma(I)$). C$_{33}$H$_{48}$ClCoNP$_2$, monoclinic, space group $P2/n$, $a = 11.530(1)$, $b = 9.685(1)$, $c = 14.377(4)$ Å, $\beta = 90.673(3)°$, $V = 1605.3(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.272$ g cm^{-3}, $F(000) = 654$.

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[12] Crystallographic details for **3**·Et$_2$O: A dark green crystal of approximate dimensions $0.26 \times 0.25 \times 0.16$ mm^3 was selected and mounted on a glass fiber. A total of 13329 reflections ($-17 \leq h \leq 17$, $-21 \leq k \leq 20$, $-21 \leq l \leq 20$) were collected at $T = 120(2)$ K in the range of 2.42 to 24.60° of which 8607 were unique ($R_{int} = 0.0594$); Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. An Et$_2$O molecule was present in the cell. All hydrogen atoms with the exception of those associated with the solvent were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. Hydrogen atoms on the Et$_2$O molecule were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The residual peak and hole electron densities were 0.637 and -0.432 e A^{-3}. The absorption coefficient was 0.721 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F) = 0.0412$, $wR(F^2) = 0.0806$, and a GOF = 0.821 ($I > 2\sigma(I)$). C$_{56}$H$_{90}$Co$_2$N$_4$OP$_4$, triclinic, space group $P\bar{1}$, $a = 13.627(1)$, $b = 16.380(2)$, $c = 16.593(2)$ Å, $\alpha = 60.676(2)$, $\beta = 66.601(2)$, $\gamma = 87.963(2)°$, $V = 2904.4(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.232$ g cm^{-3}, $F(000) = 1152$.

[13] The Co–Co separation in complex **4** is 2.254(1) Å, a value shorter than reported Co^I=Co^I bond lengths. For some Co^I dimers containing short Co=Co bond lengths, see: a) S. Stella, C. Floriani, A. Chiesi-Villa, C. Guastini, *New J. Chem.* **1988**, *12*, 621–631; b) J. J. Schneider, R. Goddard, S. Werner, C. Kruger, *Angew. Chem.* **1991**, *103*, 1145–1147; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1124–1126.

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[15] Crystallographic details for **5**: A green crystal of approximate dimensions $0.30 \times 0.30 \times 0.25$ mm^3 was selected and mounted on a glass fiber. A total of 3957 reflections ($-15 \leq h \leq 15$, $-13 \leq k \leq 9$, $-16 \leq l \leq 18$) were collected at $T = 122(2)$ K in the range of 2.60 to 29.97° of which 3133 were unique ($R_{int} = 0.0514$); Mo$_{K\alpha}$

radiation ($\lambda = 0.71073$ Å). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The molecule lies on a crystallographic twofold axis. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. The residual peak and hole electron densities were 0.555 and -0.332 e Å^{-3}. The absorption coefficient was 0.778 mm^{-1}. The leastsquares refinement converged normally with residuals of $R(F) = 0.0324$, $wR(F^2) = 0.0738$, and a GOF = 0.961 ($I > 2\sigma(I)$). C$_{28}$H$_{40}$CoNO$_2$P$_2$, monoclinic, space group $P2/n$, $a = 11.0228(6)$, $b = 9.3842(6)$, $c = 13.2222(7)$ Å, $\beta = 98.501(2)°$, $V = 1352.7(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.334$ g cm^{-3}, $F(000) = 576$.

[16] Four-coordinate Co^I monocarbonyl complexes are scarce (see reference [8k]).

[17] CCDC-291872–291876 (**1–5**) 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.