

Three-Coordinate Co(I) Provides Access to Unsaturated Dihydrido-Co(III) and Seven-Coordinate Co(V)

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Pincer ligands underpin a broad range of chemistry of the transition metals, especially the later metals with 6–8 d electrons. Applications abound, in part because such a *mer*-tridentate supporting ligand leaves 2–3 coordination sites available for substrate binding and can provide steric bulk which can rationally control product stereoselectivity.¹ For the d⁸ configuration, the fundamental unit (pincer)M is a postulated but undetected transient in both rhodium and iridium chemistry of some particularly challenging substrate transformations.² A pincer ligand pioneered by Fryzuk ($\{R_2PCH_2SiMe_2\}_2N^-$, “RPNP”) is predisposed to *mer*-stereochemistry on a metal,³ a ligand arrangement pervasive in three-coordinate, 14-electron, d⁸ species. Frequently, the metal coordination sphere in these complexes is completed by a weak intramolecular interaction (e.g., agostic C–H);⁴ consequently, genuine three-coordinate d⁸ complexes are rare, and those involving pincer ligands are currently unknown. Two recent reports have succeeded in isolating bona fide three-coordinate d⁸ complexes, both utilizing monoanionic, bidentate β -diketiminate ligands with bulky aryl groups.^{5,6}

We are interested in expanding the rich late transition element PNP chemistry already developed primarily for R = Ph to the 3d elements with the bulkier pincer, where R is ‘Bu. This would allow us to explore odd-electron organometallic chemistry and one-electron redox changes, and to achieve the “naked” (pincer)M species. Herein we report the successful isolation of the T-shaped, three-coordinate PNPCo complex and its propensity to undergo oxidation.

In a manner analogous to its phenyl derivative,^{3b} ^tBuPNPCoCl is readily obtainable in excellent yield.⁷ Subsequent treatment with excess magnesium powder led, overnight, to a new green paramagnetic product. Spectroscopic studies revealed solution C_{2v} symmetry, with three resonances in the ¹H NMR spectrum that were significantly shifted from the diamagnetic region; in concordance, no ³¹P{¹H} resonance was observed.⁷ A triplet ground state was established by a solution magnetic moment measurement (at 25 °C) of 3.2 μ_B , fully consistent with a high-spin (i.e., triplet) d⁸ electron configuration and analogous to the three-coordinate (β -diketiminate)Ni^{II}Cl.⁵ An X-ray diffraction study confirmed the anticipated three-coordinate ^tBuPNPCo^I structure (Figure 1), with no agostic or other weak donor (e.g., THF, toluene solvent). The geometry around cobalt is planar and closely approximates T-shaped. Complex **1** is therefore the skeletal (pincer)M complex previously postulated in a range of Rh and Ir chemistry.² The high-spin nature of **1** prevents any agostic interaction, with the energy needed to induce spin-pairing (to generate a low-lying vacant orbital) presumably not recouped by weak donors. This effect is further exemplified by the observation of reversible binding of N₂ to **1**, generating diamagnetic PNPCo(N₂) (Figure 1). This process is calculated to be essentially thermoneutral ($\Delta G^\circ_{298} = 0 \pm 3$ kcal mol⁻¹),⁷ in contrast to the calculated binding of N₂ to the related 4d complex (PCP)Rh ($\Delta G^\circ_{298} = -15.8$ kcal mol⁻¹; PCP = κ^3 -[2,6-(ⁱPr₂PCH₂)₂C₆H₃]⁻).^{2a}

The 1+ Co oxidation state, the low coordination number and the electron-rich environment present in **1** suggest that it should

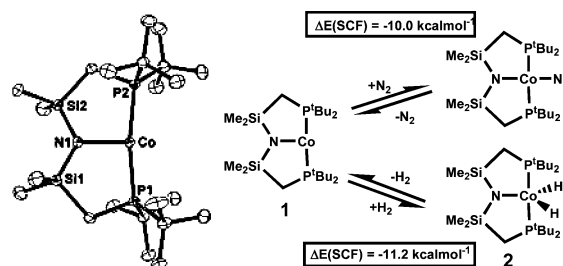


Figure 1. (Left) ORTEP drawing (50% probability ellipsoids) of complex **1**. Selected angles (deg): P1–Co–P2 = 170.56(2), N1–Co–P1 = 94.65(5), and N1–Co–P2 = 94.75(5). (Right) Equilibria involving **1** and N₂ (top) and H₂ (bottom) along with electronic energies for the forward reactions.

be amenable to oxidative addition of H₂, analogous to the heavier Rh and Ir congeners. Exposure of **1** to a large excess of dihydrogen (ca. 4 atm) resulted in only partial conversion of **1** to a single new diamagnetic product that displayed solution C_{2v} symmetry, a broad intensity two-hydride resonance at high field (–32.2 ppm t, J_{H–P} = 51 Hz), and a very broad ³¹P{¹H} resonance at 89.9 ppm. This allows for the formulation as the dihydride complex, PNPCo(H)₂ (**2**). Vacuum removal of the dihydrogen atmosphere yielded **1** quantitatively, while recharging with H₂ reproduced the incomplete conversion to **2** (Figure 1). Cooling a sample of **1** under 4 atm of H₂ to 205 K effects complete consumption of **1**, and only NMR resonances attributable to **2**, with no new fine couplings, are observed. DFT calculations using the full ligand set for a number of hydride-containing products derived from **1** and H₂ were performed to investigate possible thermodynamically favorable products.⁷ This revealed a number of energetically comparable species, most of which can be ruled out on the basis of spectroscopic data. The formation of a heterolytic H₂ activation product, namely the amine cobalt complex (P₂NH)CoH₃, is precluded by the failure to observe a N–H resonance and the observation of only one hydride environment, even at 205 K. The lack of paramagnetic resonances consistent with divalent cobalt precludes an intermolecular homolytic cleavage of H₂ to give PNPCoH (observed in the related reaction of dihydrogen with TpCo^IN₂).⁸ It is noteworthy that singlet PNPCo(η²-H₂) is not a stationary state, converging to dihydride **2**. The calculations support the thermoneutral conversion of **1** to **2** and find a trigonal bipyramidal optimized geometry for **2**, with a singlet ground state and a nonbonding H–H distance (1.62 Å), supporting a Co(III) oxidation state.

Dihydride **2** is electronically and coordinatively unsaturated but exhibits no inclination to bind two electron donors (e.g., PhCN). It does, however, undergo rapid dehydrogenation with ethene, producing **1** and ethane quantitatively. Hydrogenation of ethene is rapid (22 °C), a rare occurrence for cobalt complexes,⁹ but the steric bulk inherent in **2** limits its efficacy, with no hydrogenation of 1-hexene or cyclohexene observed at 22 °C. At elevated temperatures (60 °C) hydrogenation occurs, albeit slowly.⁷ Compound **1** shows no tendency to bind ethene, even at –60 °C.

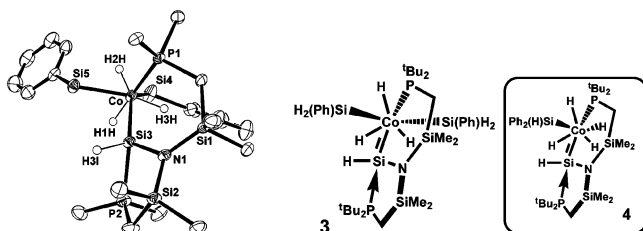


Figure 2. (Left) ORTEP view (50% probability ellipsoids) of **3** with the ^tBu carbons and most hydrogens omitted for clarity. (Center) Schematic of **3** at a similar angle. (Inset) Structure of complex **4**.

To further probe the oxidation chemistry of **1**, its reactivity with a primary silane, PhSiH₃, was explored. Complex **1** reacts rapidly with 4 equiv of PhSiH₃ at 25 °C, with loss of 1 equiv of Ph₂SiH₂ and H₂ (by ¹H and ²⁹Si NMR) to form a single pale yellow diamagnetic product. An X-ray diffraction study of this complex revealed the addition of 3 equiv of PhSiH₃ to the cobalt center of

1, yielding {κ²-^tBu₂PCH₂Me₂SiNSiMe₂CH₂^tBu₂P(H)Si=}Co(H)₃-(SiH₂Ph)₂ (**3**). The structure (Figure 2) consists of a formally Co(V) center ligated by three hydrides, two primary silanes, a phosphine, and a base (R₃P)-stabilized silylene formed by cleaving one Si–Ph bond. The Co–Si bond distance of the silylene (2.1848(8) Å) is shorter than the two pure σ-bonded Co–Si(Ph)H₂ groups (2.2622(9) and 2.2477(8) Å), confirming some multiple bond character. The NMR spectra for **3** are fully consistent with this formulation.⁷

Despite the mild reaction conditions, the reaction shows Si–C bond cleavage (forming Ph₂SiH₂), multiple Si–H additions to Co, silylene formation (followed by Lewis base stabilization of that silicon), and elevation of d⁸ Co(I) to a high oxidation state with corresponding low (for Co) d electron count. The resulting high coordination number (7) leads to rapid fluxionality (the slow hydride exchange regime is not reached at –70 °C), but the fluxionality is selective for hydride migration among inequivalent sites and does not involve site exchange between the two SiH₂Ph ligands, nor is there a low barrier to exchange between any Si–H and a hydride on cobalt. It is also noteworthy that the structure adopted does not exploit steric size and a lower cobalt oxidation state by reductive coupling of H and SiH₂Ph (i.e., an intact silane ligand resulting in a Co^{III}{η²-H–SiH₂Ph}). Furthermore, the Si4–Si5 distance of 3.726 Å is clearly nonbonding, confirming two PhH₂Si[–] ligands.¹⁰ The lack of exchange between Co–H and free H₂ (or D₂), the absence of H₂ evolution from **3** on evacuation, and no reaction with PhCN all support a classical hydride formulation in **3**.

Compound **3** is not the only molecular Co(V) compound,¹¹ but another example, Cp*Co(H)₂(SiH₂Ph)₂, illustrates that hydride and silyl ligands are nearly always what enables achieving such high formal oxidation numbers. While 4d and 5d transition metals always prefer high oxidation states relative to their 3d analogues, Cp*ReH₆,¹² Cp*Ir(H)₂(SiR₃)₂,¹³ and Cp*Ir(H)₄¹⁴ illustrate how often H and SiR₃ are the accompanying ligands even there. Probably this can be explained by these low-electronegativity (i.e., “electropositive”) ligands (and also alkyls, as in WMe₆)¹⁵ making the oxidation state formalism meaningless. This can be attributed to highly covalent M–ligand bonds; thus, GeMe₄ does not contain Ge⁴⁺.

The formation of **3** at 25 °C proceeds via an observable brown intermediate, which was characterized at –78 °C and reveals that silylene formation has occurred even at this low temperature, as determined by the characteristic ³¹P{¹H} spectra and the ¹H NMR spectrum showing no symmetry.⁷ This intermediate compound is also observed on the addition of 1 equiv of PhSiH₃ to **1** at –78 °C, that on warming to 25 °C produces one new diamagnetic product, **4** (along with unreacted **1**). In the ¹H NMR complex, **4** displays an

integral four-hydride resonance, along with three signals observed in the Si–H region (one singlet and one doublet for the silylene proton, ²J_{P–H} = 49 Hz), along with four ²⁹Si resonances. A reasonable structure for **4**, fully consistent with the spectroscopic data, is an analogue of **3** (Figure 2, inset).⁷ In **4** the Co is still oxidation state V, but the phenyl group from the silylene silicon has migrated from Co to Si, forming a Si(H)Ph₂ moiety that is prearranged to eliminate Ph₂SiH₂ on addition of further PhSiH₃; similar facile Si–H/M–R exchanges are well documented.^{16–11} Complex **4** can be cleanly synthesized from **1** by addition (at –78 °C) of 2 equiv of PhSiH₃. The addition of further PhSiH₃ to **4** leads to **3** quantitatively, along with the evolution of stoichiometric Ph₂SiH₂. Formation of the silylene functionality even at –78 °C implies an extremely low barrier to multiple silane activation and insertion into P–Co and N–Co bonds.

Taken together, the formation of **2**, **3**, and **4** reveals that the three-coordinate pincer complex (PNP)Co readily undergoes oxidation (which with dihydride **2** is thermally reversible), consistent with an electron-rich metal center; but due to its high-spin nature only weakly binds “redox-inactive” ligands.

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Supporting Information Available: Full synthetic, spectroscopic, and computational details (PDF); crystallographic details for compounds **1** and **3** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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