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Reducing Power of Three-Coordinate Cobalt(I)

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A characteristic difference in the reactivity of 3d metal complexes versus their 4d and 5d analogues is the tendency to react by one-electron redox changes, while 2 e changes are more common for the heavier analogues. This is certainly true for Rh and Ir, where oxidation states of +1 and +3 are common. The recent synthetic availability[1] of three-coordinate, T-shaped (PNP)Co^{I}, **1**, where PNP is ($^{t}Bu_2PCH_2SiMe_2$)$_2$N, permits evaluation of this idea since, although Co^{II} is abundant (e.g., (PNP)CoCl, from which (PNP)Co is synthesized by Mg reduction), Co^{III} is the foundation for a huge range of Werner chemistry: $Co(NH_3)_6^{3+}$ and the like. The ability to rationally control one-electron changes lies at the heart of radical catalysis (e.g., ATRP),[2] which makes the title subject of some significance. We report here several examples of reactivity of (PNP)Co which are initially surprising, and which put new perspective on how to understand late transition metal redox chemistry in a low-coordination number environment.

The C≡O stretching frequency of some moiety L_nM is a traditional probe of its "π-basicity", which is another manifestation of its reducing power. (PNP)Co binds carbon monoxide rapidly and completely in C_6D_6 to form (PNP)Co(CO),[3] whose crystal structure shows it to be conventional: square planar. The ν_{co} value for (PNP)Co(CO) is 1885 cm^{-1}, while the corresponding value we measure[3] for (PNP)Rh(CO) is 1932 cm^{-1}. It is interesting that cobalt is more reducing (π-basic) than Rh in identical environments. This is surprising in that conventional wisdom has it that π-basicity increases down a periodic group.[4] The same generalization applies to the enthalpy of protonation;[5] it increases down group VI (Cr, Mo, W), while this protonation is formally a 2 e redox change, and what it really reflects is the (heterolytic) bond dissociation energy. However, a survey of IR data shows that the trend of decreasing ν_{co} down group VI is in fact reversed for a later group ($CpM(CO)_2$ for M = Co vs Rh).[6−8] Likewise, the CO stretching frequencies[9−11] are *higher* for Pd than for Ni for any of the four molecules $M(CO)_n$ where $n = 1-4$. The same is true[12] from Cu$^+$ to Ag$^+$ and Au$^+$. It would appear that there is a reversal of 3d versus 4d π-basicity between group VI and group VIII. Does the back-donation implied from the (PNP)Co(CO) stretching frequency translate into easy two-electron oxidation to Co(III)?

Attempt at conventional oxidation revealed surprises.[3] With an aim of reaching Co(III), the addition of equimolar I_2 to (PNP)Co at 25 °C rapidly gives one major product, but it is the divalent complex (PNP)CoI (confirmed by independent synthesis); a second minor product was consistently observed along with unreacted **1**. Changing the reagent ratio to 1:2 (complex **1**:I_2) resulted in the quantitative formation of this other paramagnetic compound that displayed C_s symmetry (by ^1H NMR) in solution. The solution magnetic moment measurement of 4.7 μ_B ($S = {}^3/_2$ ground state), mass spectroscopy, and an X-ray diffraction study (Figure 1) allowed for the unambiguous characterization as the zwitterionic, tetrahedral, four-coordinate, high spin Co(II) complex, [κ^2-($^tBu_2P(I)CH_2SiMe_2NSiMe_2CH_2P^tBu_2$)$CoI_2$], **2**. Thus, I_2 reacts with (PNP)Co (1.5:1 mole ratio) to give first (PNP)CoI, and then not Co(III) but rather to oxidize phosphorus: phosphorus is more reducing than Co(II) in (PNP)CoI and has been oxidized to an iodophosphonium moiety. This is particularly surprising because the PPh_2 analogue (PNP^{Ph})Co is oxidized[13] to isolable (PNP^{Ph})CoX_2; this may originate from the diminished reducing power of P carrying two phenyl substituents and the bulk of iodide. In **2**, the resultant cobalt coordination sphere is occupied by two iodides, one phosphine, and the amide. The $^{31}P\{^1H\}$ resonance for the oxidized (P$^{(V)}$) noncoordinated phosphine is observable as a broadened singlet at +269 ppm; the larger than expected downfield shift arises from the long-range paramagnetic influence of the high spin Co center. Complex **2** is also directly accessible from combination of (PNP)CoI and I_2, a reaction that is reversible on addition of two equivalents of **1** to **2** by Co disproportionation. At no stage is the five-coordinate, trivalent complex (PNP)CoI_2 observed. Complex **1** does react with excess alkyl halides (e.g., iodobenzene and benzyl chloride) but only to give divalent (PNP)CoX.

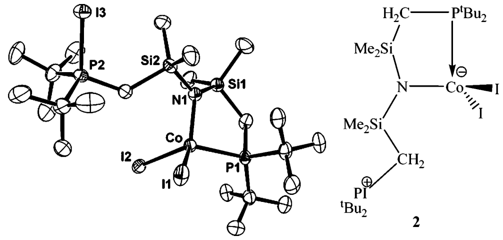
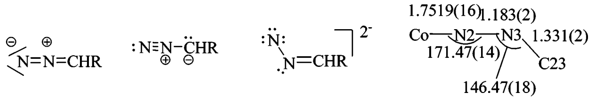


Figure 1. ORTEP view (50% probabilities) of the non-hydrogen atoms of [κ^2- ($^tBu_2P(I)CH_2SiMe_2NSiMe_2CH_2P^tBu_2$)$CoI_2$], showing selected atom labels; unlabeled atoms are carbon. Selected distances (Å) and angles (deg): Co−I1, 2.5973(9); Co−I2, 2.6279(9); Co−N1, 1.957(4); Co−P1, 2.3594(16); N1−Co−P1, 94.34(14); N1−Co−I1, 119.21(13); N1−Co−I2, 109.56(13); P1−Co−I1, 112.32(5); P1−Co−I2, 114.02(5); I1−Co−I2, 107.25(3).

Scheme 1



Fuller understanding of the perhaps surprising higher π-basicity of Co than Rh, in (PNP)M, is provided by the multifunctional diazoalkane reagent (Scheme 1) which is[14] not only a σ-donor (**A** and **B**) but also a π-acid, extending even to a two-electron oxidant (**C**). Extreme back-donation is just a different name for full "oxidative addition", as is also true for dihydrogen versus dihydride structures. Reaction of (PNP)Co with equimolar (Me_3Si)HCN_2 in C_6H_6 at 22 °C is complete in time of mixing, as judged by a color change from green to dark yellow. The sole product **3** is diamagnetic, of local C_{2v} symmetry, and shows an unusual ^1H NMR chemical shift for the diazoalkane-derived unique hydrogen: −3.04 ppm, a value we associate with carbanionic character (structure **B**). A single-crystal structure determination (Figure 2) shows a planar coordination geometry with CoNNC and C(N)(Si) angles which do not clearly fit any single Lewis structure in Scheme 2.

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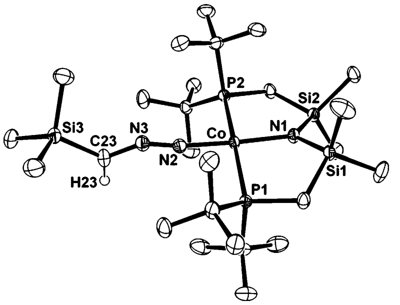
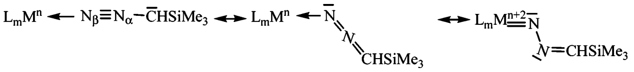


Figure 2. ORTEP view (50% probabilities) of the non-hydrogen atoms of (PNP)Co[NNCH(SiMe$_3$)], showing selected atom labels; unlabeled atoms are carbon. Selected distances (Å) and angles (deg): Co1−N2, 1.7519(16); Co1−P1, 2.262(1); Co1−P2, 2.249(1); Co1−N1, 1.9148(15); N1−Co1−N2, 175.56(17); N1−Co1−P1, 90.121(5); N1−Co1−P2, 89.1(2); N2−Co1−P1, 90.01(6); P1−Co1−P2, 170.90(16).

Scheme 2



Note, first, that Co binds to the more sterically accessible N_β, not at N_α or the unique carbon. Bond lengths and angles in the CoNNCSi substructure of **3** (Scheme 1) show some Co/N multiple bonding, a strong N/N bond, and short N/C bond, so we suggest the molecule shows electron transfer to diazoalkane “oxidant”, but far short of conversion to a Co^{III} imide (**C**). The metric features of the cobalt/diazoalkane unit in **3** (essentially linear at N2 and bent at N3) fail to agree fully with those expected for nonredox binding of neutral ligand (e.g., **A** and **B**), just as they fail to agree fully with full two-electron redox transfer (**C**). In addition, the bond lengths fail to fit either simple model. The Co/N2 distance is short (i.e., multiple vs the Co/PNP amide distance here, 1.9148 Å), but not as short as the authentic Co/N double bond distance reported recently[15] in a (tetrahedral) Co/η^1-N_2CPh_2 example: 1.667 Å. This suggests that, while there is a degree of intramolecular electron transfer from cobalt(I) to the diazoalkane in forming **3**, it falls short of the full two-electron transfer implied by **C**. Multiple bond character in the coordinated cumulene of **3** is indicated by a stretching frequency of 2069 cm^{-1}. Binding at the unique carbon is suggested[16] as essential to the conversion observed for (PCP pincer)Rh[N_2CHPh], forming the carbene complex (PCP pincer)-Rh[═CHPh]; compound **3**, in contrast, is unchanged in benzene after 7 days at 22 °C. It is thus noteworthy that heating of (PNP)-Co[N_2C(H)(SiMe$_3$)] at 60 °C for 4 h in benzene shows complete consumption of the reagent, with a majority of the cobalt transformed to (PNP)Co, along with release of olefin and azine; full “redox” conversion of cobalt to carbene (PNP)Co[═C(H)(SiMe$_3$)] is not detected.

Why does a cobalt center which is so powerfully reducing toward CO not effect a full two-electron reduction of diazoalkane (as in **C**) or I_2? We propose that this is related to the fact that four-coordinate Co^{III} is difficult to access without the benefit of *several* new Co/ligand bonds (d^6 cobalt is most often found with a coordination number six, or five when there is a strong trans effect ligand present). It is the high energy character of four-coordinate and planar Co^{III} which limits the reducing power of (PNP)Co toward two-electron oxidants which will not split, on reduction, to form two new Co/oxidant bonds. With I_2 as oxidant (and thus five-coordinate Co(III) could be envisioned), the reducing center phosphorus diverts the reactivity from metal to P. When the oxidant has a delocalized π-system (e.g., diazoalkane), which offers a single electron reduction alternative, then a spin singlet derived from redox states (PNP)Co^{II} and singly reduced oxidant becomes energetically preferred. Cast in this light, the frequency of single electron redox changes found among the 3d elements may often originate from low coordination numbers for the reduced metal and an inadequate number of new bonds formed, on oxidation, to make the two-electron oxidized form thermodynamically accessible. The observed reactivity with chemical oxidants is not controlled simply by reversible electron transfer redox potentials (i.e., pure outer sphere electron transfer energetics), but also by whether the requisite number of bonds can be formed to the oxidant in the product. Moreover, when a redox reaction involves spin pairing in product versus reactant, the spin pairing energy makes the reaction less favorable thermodynamically.[17−20] While ν(CO) might be a measure of the reducing power of the metal in the absence of new bond formation, oxidative addition also involves new bond formation, so it is subject to bond strength trends, not merely ionization potential values. It is also relevant that the half-filled orbitals of these low-coordinate 3d reagents may make single electron transfer more favorable (radical-like reagent). However, it is clear that we do not completely understand all factors dictating the Co(II/III) redox couple because the Fryzuk group has reported a number of cases where benzyl bromide adds to the PPh$_2$ analogue of (PNP)-Co−Br to give (PNP)Co(Br)$_2$, which are persistent Co(III) compounds. In contrast, (PNP)CoCl is recovered unchanged after treatment with 2 equiv of benzyl bromide for 48 h at 22 °C as well as 2 h at 75 °C in C_6D_6 or C_6D_{12}. This contradicts the expectation that P(alkyl)$_2$ substituent should make the metal more reducing than a PPh$_2$ set.

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Supporting Information Available: Full experimental details and CIF files for two structures are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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