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Isocyano Analogues of $[Co(CO)_4]^n$: A Tetraisocyanide of Cobalt Isolated in Three States of Charge

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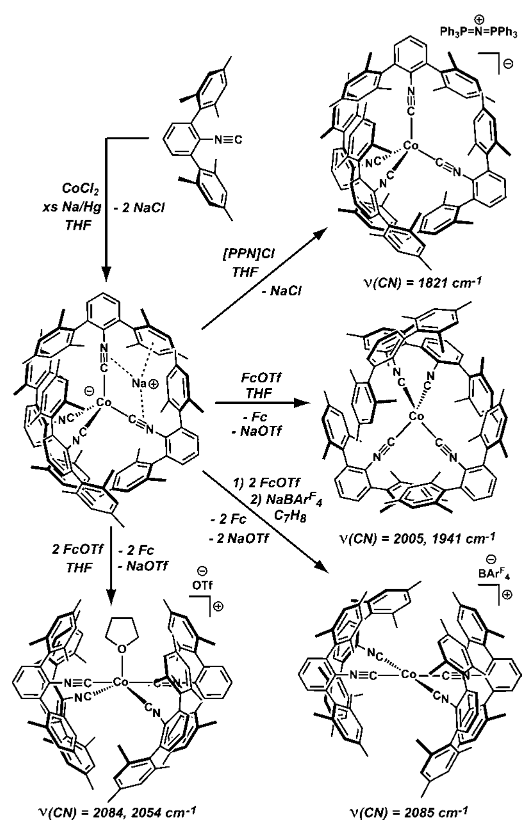
Intense interest in the unsaturated mononuclear cobalt carbonyls (i.e., $Co(CO)_4$ and $[Co(CO)_4^+]$) has stemmed from their presumed role as reactive intermediates in industrial hydroformylation and carbonylation processes.[1−3] Despite such attention, the inherent high reactivity of these species has precluded a definitive description of their geometric and electronic structures in the condensed phase. Based on the isolobal relationship between isocyanides (CNR) and CO,[4] we reasoned that use of encumbering R-groups might provide access to stable unsaturated cobalt isocyanide complexes which formally mimic their carbonyl analogues. Notably, commonly employed isocyanide variants including CN*t*-Bu and CNXyl (Xyl $= 2,6\text{-}Me_2C_6H_3$) have been unsuccessful in this regard.[5−7] Herein we show that the *m*-terphenyl isocyanide[8] $CNAr^{Mes2}$ (Mes $= 2,4,6\text{-}Me_3C_6H_2$) allows for the isolation of a full series of mononuclear $[Co(CNR)_4]^n$ complexes ($n = 1+, 0, 1-$) relevant to the binary carbonyls. Most importantly, the geometric and electronic structure properties of the Co complexes reported here elucidate d^n/valence combinations where aspects of CNR for CO isolobal substitution are valid, and others where the analogy seemingly fails.

Synthetic entry to the $[Co(CNAr^{Mes2})_4]^n$ system is achieved by the addition of sodium amalgam to a $CoCl_2/CNAr^{Mes2}$ mixture in THF (Scheme 1). This protocol provides the dark red tetraisocyanometalate salt $Na[Co(CNAr^{Mes2})_4]$, crystallographically characterized as a contact ion pair with interactions between the Na cation and isocyano C≡N units (Figure S4.1). Similar cation−CN_{iso} interactions were observed in Cooper's salt, $[K(DME)][Co(CNXyl)_4]$ (Xyl $= 2,6\text{-}Me_2C_6H_3$),[7b] which is the only other structurally characterized homoleptic cobalt isocyanometalate.[9] FTIR analysis of $Na[Co(CNAr^{Mes2})_4]$ in C_6D_6 solution revealed three intense ν(CN) stretches (1903, 1821, and 1761 cm^{-1}), thereby confirming that a low-symmetry local environment of the $[Co(CNR)_4]$-core is retained in solution. However, the anion−cation interaction in $Na[Co(CNAr^{Mes2})_4]$ can be readily disrupted upon addition of $[Ph_3PNPPh_3]Cl$ ([PPN]Cl) in THF solution. Structural characterization of the resulting purple-red salt, $[PPN][Co(CNAr^{Mes2})_4]$ (Figure 1a), revealed a unique example of an unperturbed tetraisocyanide anion adopting a relaxed tetrahedral geometry (τ_4 geometry index $= 0.95$).[10] Further support for this notion is provided by solution FTIR analysis, which gave rise to a single broad ν(CN) stretch (1821 cm^{-1}) consistent with a complex possessing local tetrahedral symmetry.

In marked contrast to $[Co(CNXyl)_4]^-$, which readily dimerizes to $Co_2(CNXyl)_8$ when oxidized,[7b] the encumbering Ar^{Mes2} units stabilize a zerovalent cobalt tetraisocyanide monomer. Thus treatment of $Na[Co(CNAr^{Mes2})_4]$ with 1 equiv of ferrocenium triflate (FcOTf) affords the neutral, paramagnetic complex $Co(CNAr^{Mes2})_4$ as determined by X-ray diffraction (Figure 1b). To our knowledge, $Co(CNAr^{Mes2})_4$ is a unique example of an isolable zerovalent Co monomer possessing a homoleptic π-acidic ligand field.[11] Accordingly, Evans method magnetic moment determination for $Co(CNAr^{Mes2})_4$ resulted in a μ_{eff} value of 1.79(±0.10) μ_B, consistent with a d^9 $S = {}^1/_2$ Co center. In addition, solution (C_6D_6) FTIR analysis of $Co(CNAr^{Mes2})_4$ at room temperature revealed ν(CN) stretches at 2005 and 1941 cm^{-1}, which reflect a decrease in electron density at the Co center relative to the salts $Na[Co(CNAr^{Mes2})_4]$ and $[PPN][Co(CNAr^{Mes2})_4]$.

Scheme 1



With respect to the relationship between $Co(CNAr^{Mes2})_4$ and $Co(CO)_4$, it is important to note that uncertainty remains concerning the ground state geometry of the latter. Early calculations by Hoffman and Burdett favored a D_{2d}-symmetric structure (*i.e.*, $b_2^2a_1^2e^4b_1^1$), with a C_{3v} trigonal pyramidal structure (*i.e.*, $1e^42e^4a_1^1$) lying *ca.* 2−3 kcal/mol higher in energy.[12,13] More recent consideration at the DFT level, however, reverses the stability of these minima by comparable energies.[14] In addition, spectroscopic studies on matrix-generated $Co(CO)_4$ have concluded that the relative stabilities of its D_{2d} and C_{3v} isomers are highly dependent on the identity of the matrix.[15,16]

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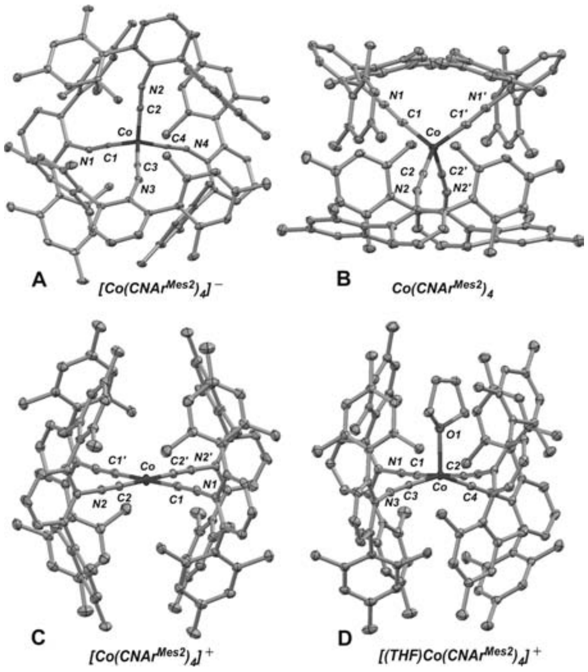

Figure 1. Molecular structures of the cobalt-containing components of $[PPN][Co(CNAr^{Mes2})_4]$ (A), $Co(CNAr^{Mes2})_4$ at 100 K (B), $[Co(CNAr^{Mes2})_4]$-BAr^F_4 (C), and $[(THF)Co(CNAr^{Mes2})_4]OTf$ (D).

Table 1. Variable Temperature Crystallographic Parameters for $Co(CNAr^{Mes2})_4$

Temp K	$\angle$C1−Co−C1′ (deg)	$\angle$C2−Co−C2′ (deg)	$\angle$C1−Co−C2/ $\angle$C1−Co−C2′ (deg)[a]
100	100.2(2)	107.8(2)	112.29(18)/ 112.14(18)
173	101.5(2)	105.5(2)	113.06(14)/112.00(14)
273	102.4(2)	103.8(2)	113.22(15)/ 112.32(15)

[a] Reflects crystallographic 2-fold symmetry.

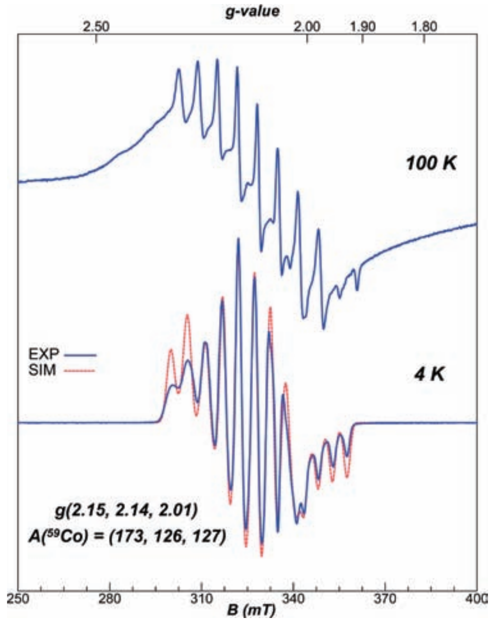

Figure 2. X-Band EPR spectra for toluene glass samples of $Co(CNAr^{Mes2})_4$ at 100 K (top) and 4 K (bottom). *A* values in MHz.

Whereas the presence of two ν(CN) stretches in the room temperature FTIR spectrum of $Co(CNAr^{Mes2})_4$ is consistent with both C_{3v} and D_{2d} symmetric environments, its X-ray structure clearly indicates that a C_{3v} geometry is not adopted. Most plausibly, the encumbering Ar^{Mes2} groups destabilize a C_{3v} geometry in favor of a lower symmetry ground state. However, closer inspection of the X-ray structure of $Co(CNAr^{Mes2})_4$ determined at 100 K reveals that the Co center possesses rigorous C_{2v} point symmetry. As shown in Figure 1b, the C1−Co−C1′ and C2−Co−C2′ angles which bisect the molecular 2-fold rotation axis are 100.3(2)° and 107.7(2)°, respectively, while the four remaining angles are split into two statistically identical sets by crystallographic symmetry (*i.e.*, 112.29(18)° and 112.14(18)°). Remarkably however, the molecular structure of $Co(CNAr^{Mes2})_4$ exhibits a subtle temperature dependence which can be probed crystallographically. Thus redetermination of the X-ray structure at 273 K revealed that the C1−Co−C1′ and C2−Co−C2′ angles expand and contract, respectively, while much less variation in the remaining angles is observed (Table 1). Thus, at higher temperatures $Co(CNAr^{Mes2})_4$ seemingly approaches a more symmetric, D_{2d} geometry. Notably, a third structure determination at 173 K revealed C1−Co−C1′ and C2−Co−C2′ angles intermediate between those of the 100 and 273 K structures (Table 1), thereby providing further evidence for a structural progression to higher symmetry with increasing temperature.

Importantly, Ozin has argued on the basis of variable-temperature EPR studies that the D_{2d} form of $Co(CO)_4$ can further distort to lower symmetry with decreasing temperature.[16a] In addition, it has been suggested that temperature regimes exist where multiple low symmetry (i.e., D_{2d} and C_{2v}) isomers of $Co(CO)_4$ are in equilibrium.[16] Therefore it is particularly noteworthy that a temperature dependence is also manifest in the EPR signatures of $Co(CNAr^{Mes2})_4$. Accordingly, the EPR spectrum of $Co(CNAr^{Mes2})_4$ recorded at 100 K in toluene glass features a complicated pattern that is not readily simulated as a single $S = {}^1/_2$ species (Figure 2 top). However, EPR acquisition at 4 K revealed a well-resolved signal best fit with distinct *g*-values of 2.15, 2.14, and 2.01 (Figure 2 bottom).[17] Whereas a rhombic pattern at 4 K is indicated from the simulation, the two low-field *g*-values of similar magnitude reflect a system that is clearly near axial. Accordingly, such behavior is consistent with a C_{2v}-symmetric system that is only slightly distorted from D_{2d} symmetry.

We suggest the unusual structural and spectroscopic features of $Co(CNAr^{Mes2})_4$ arise to achieve efficient delocalization of its unpaired spin via π back-donation. Thus nominally D_{2d}-symmetric $Co(CNAr^{Mes2})_4$ likely undergoes a C_{2v} distortion to maximize overlap of the $CNAr^{Mes2}$ π^* system with the singly occupied Co d-orbital (*i.e.*, $d_{x^2-y^2}$ in D_{2d} symmetry). Accordingly, this mild distortion would become an important mechanism for static stabilization at low temperatures where thermal access to low-energy vibrations is inhibited. Indeed, DFT vibrational frequency analysis on the simple $Co(CNMe)_4$ molecule in D_{2d} symmetry mimicking that of $Co(CNAr^{Mes2})_4$ revealed a b_2 vibration at 453 cm^{-1} representing a C−Co−C bending mode consistent with such a C_{2v} distortion (Figure 3). Furthermore, single-point energy calculations on the model $Co(CNAr^{Ph2})_4$ in the coordinates of both the 273 and 100 K structures indicate the latter to be more stable on average by *ca.* 1.0 kcal/mol. Importantly, the magnitude of this thermodynamic preference is consistent over several density functionals[18] and corresponds roughly to the energy expected to excite such a C−Co−C bending mode. Whereas C−Co−C bending as a means of augmenting π delocalization may be more important for the CNR function relative to CO due to its decreased π-acidity,[19] we propose that the structural perturbations of $Co(CNAr^{Mes2})_4$ may potentially also illustrate the reported behavior of D_{2d}-symmetric $Co(CO)_4$.[16,20]

In addition to the zero-valent state, the tetra-$CNAr^{Mes2}$ framework stabilizes monovalent Co centers. Treatment of Na[Co-

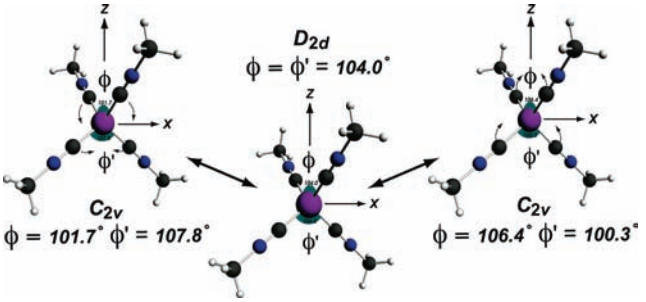

Figure 3. DFT calculated geometry displacement for the origin (D_{2d}) and end points (C_{2v}) of a b_2 C−Co−C bending mode for D_{2d}-symmetric $\mathrm{Co(CNMe)_4}$.

$(\mathrm{CNAr^{Mes2}})_4$] with 2 equiv of FcOTf, followed by the addition of $\mathrm{Na[BAr^F_4]}$ ($\mathrm{Ar^F = 3,5\text{-}(CF_3)_2C_6H_3}$), provides the diamagnetic salt $\mathrm{[Co(CNAr^{Mes2})_4]BAr^F_4}$ as a purple crystalline solid (ν(CN) = 2085 $\mathrm{cm^{-1}}$). Remarkably, crystallographic characterization of $\mathrm{[Co(CNAr^{Mes2})_4]BAr^F_4}$ revealed a square planar coordination geometry for Co (Figure 1c), which readily rationalizes the observed diamagnetism. These findings are notable, since spectroscopic and theoretical studies on gas phase-generated $\mathrm{[Co(CO)_4]^+}$ have strongly favored a "saw-horse", C_{2v}-symmetric structure and an $S = 1$ ground state.[14,21] Thus, while it is tempting to suggest that $\mathrm{[Co(CNAr^{Mes2})_4]^+}$ models the carbonyl derivative $\mathrm{[Co(CO)_4]^+}$, the enhanced σ-donor ability of isocyanides relative to CO,[4,19] coupled with the increased charge of the complex, produces a sufficiently strong ligand field as to favor a D_{4h} over a C_{2v} geometry. Indeed, DFT calculations on the model $\mathrm{[Co(CNXyl)_4]^+}$ indicate that its D_{4h} isomer is energetically preferred to its "saw-horse" C_{2v} isomer by *ca*. 14 kcal/mol. Nevertheless, $\mathrm{[Co(CNAr^{Mes2})_4]BAr^F_4}$ represents a rare square planar monovalent Co complex with a homoleptic ligand set.[22,23]

Most interestingly, pyramidalization concomitant with a spin-state change of the $\mathrm{[Co(CNAr^{Mes2})_4]^+}$ core occurs on coordination of Lewis bases. Thus, addition of 2 equiv of FcOTf to $\mathrm{Na[Co(CNAr^{Mes2})_4]}$ in THF results in the paramagnetic THF adduct, $\mathrm{[(THF)Co(CNAr^{Mes2})_4]OTf}$. Structural characterization of $\mathrm{[(THF)Co(CNAr^{Mes2})_4]OTf}$ revealed a Co center best described as trigonal bipyramidal with an equatorial THF ligand (Figure 1d). However, only moderate pyramidalization is effected by the weak Lewis base THF, as evinced by the C3−Co−C4 angle of 150.29(16)°. Evans method magnetic moment determination resulted in a μ_{eff} value of 2.96(±0.15) μ_{B} for $\mathrm{[(THF)Co(CNAr^{Mes2})_4]OTf}$, consistent with an $S = 1$ ground state. Furthermore, the paramagnetism exhibited by $\mathrm{[(THF)Co(CNAr^{Mes2})_4]OTf}$ is not a consequence of its preparation. Thus, addition of 1.0 equiv of THF to a $\mathrm{C_6D_6}$ solution of $\mathrm{[Co(CNAr^{Mes2})_4]BAr^F_4}$ yields $\mathrm{Ar^{Mes2}}$ ^{1}H NMR shifts identical to those of $\mathrm{[(THF)Co(CNAr^{Mes2})_4]OTf}$, thereby indicating anion independence for ligation-induced spin-state changes. To our knowledge, coordinatively induced $S = 0$ to $S = 1$ spin-state changes are extremely rare, whereas the reverse are quite common.[24] Accordingly, this coordinatively induced spin-state variation may be reasonably expected to significantly affect the reactivity of $\mathrm{[Co(CNAr^{Mes2})_4]^+}$ with certain substrate molecules.

As a final note, both $\mathrm{[(THF)Co(CNAr^{Mes2})_4]OTf}$ and $\mathrm{[Co(CNAr^{Mes2})_4]BAr^F_4}$ react upon mixing with $\mathrm{Na[Co(CNAr^{Mes2})_4]}$ to generate $\mathrm{Co(CNAr^{Mes2})_4}$. These comproportionation reactions are significant in that a seemingly large structural reorganization of the $\mathrm{[Co(CNR)_4]}$ fragment is accommodated along the pathway from the mono- to zero-valent state. Furthermore, they establish fully reversible one-electron modulation of the 1+, 0, and 1− charge states for the $\mathrm{[Co(CNR)_4]}$ fragment. This latter characteristic is expected to feature prominently in the multielectron reactivity of the system. Accordingly, reactivity studies of these $\mathrm{[Co(CNAr^{Mes2})_4]^n}$ complexes and more detailed analysis of their spectroscopic and electrochemical properties are underway.

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

References

(1) For seminal reports and reviews, see: (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 4023–4027. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (c) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal.* **1995**, *104*, 17–85. (d) Hebrard, F.; Kalck, P. *Chem. Rev.* **2009**, *109*, 4272–4282.

(2) For studies establishing $\mathrm{Co(CO)_4}$ as a component in hydroformylation, see: (a) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494–2495. (b) Nalesnlk, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222–223. (c) Klingler, R. J.; Rathke, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 4112–4785.

(3) For studies identifying $\mathrm{[Co(CO)_4]^+}$, see: (a) Winters, R. E.; Kiser, R. W. *J. Phys. Chem.* **1965**, *69*, 1618–1622. (b) Bidinosti, D. R.; McIntyre, N. S. *J. Chem. Soc., Chem. Commun.* **1967**, 1–2. (c) Goebel, S.; Haynes, C. L.; Khan, F. A.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 6994–7002. (d) Zhou, M.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 7773–7784.

(4) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Transition Metals*; Wiley: New York, 1969.

(5) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1978**, *17*, 3111–3114.

(6) Carroll, W. E.; Green, M.; Galas, A. M. R.; Murray, M.; Turney, T. W.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 80–86.

(7) (a) Warnock, G. F.; Copper, N. J. *Organometallics* **1989**, *8*, 1826–1827. (b) Leach, P. A.; Geib, S. J.; Corella, J. A., II; Warnock, G. F.; Cooper, N. J. *J. Am. Chem. Soc.* **1994**, *116*, 8566–8574.

(8) Fox, B. J.; Sun, Q. Y.; DiPasquale, A. G.; Fox, A. R.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2008**, *47*, 9010–9020.

(9) Weber, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1515–1517.

(10) Idealized tetrahedral and trigonal pyramidal geometries give rise to τ_4 values of 1.0 and 0.85, respectively. Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964.

(11) For homoleptic zero-valent Co complexes featuring phosphine or phosphite ligands, see: (a) Rakowski, M. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 739–743. (b) Klein, H.-F. *Angew. Chem., Int. Ed.* **1980**, *19*, 362–375. (c) Muetterties, E. L; Bleeke, J. R.; Yang, Z.-Y.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 2940–2942.

(12) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076.

(13) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599–1613.

(14) (a) Ryeng, H.; Gropen, O.; Swang, O. *J. Phys. Chem. A* **1997**, *101*, 8956–8958. (b) Huo, C.-F.; Li, Y.-W.; Wu, G.-S.; Beller, M.; Jiao, H. *J. Phys. Chem. A* **2002**, *106*, 12161–12169.

(15) Crichton, O.; Poliakoff, M.; Rest, A. J.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1321–1324.

(16) (a) Hanlan, L. A.; Huber, H.; Kundig, E. P.; McCarvey, B. R.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7054–7068. (b) Sweany, R. L. *Inorg. Chem.* **1980**, *19*, 3512–3516.

(17) A clear transition between these two distinct spectra is observed at 75 K. See the Supporting Information.

(18) Single-point energies were assessed with the BP86, PW91, BYLP, and OLYP density functionals (ADF2007.01). In all cases, the 100 K (C_{2v}) isomer was more stable. See the Supporting Information for details.

(19) Cotton, F. A.; Zingales, F. *J. Am. Chem. Soc.* **1961**, *83*, 351–355.

(20) DFT vibrational frequency analysis of $\mathrm{Co(CO)_4}$ in D_{2d} symmetry reveals a b_2 C−Co−C bending mode located at 515 $\mathrm{cm^{-1}}$ which is analogous to that observed for $\mathrm{Co(CNMe)_4}$. See the Supporting Information for details.

(21) Ricks, A. M.; Bakker, J. M.; Douberly, G. E.; Duncan, M. A. *J. Phys. Chem. A* **2009**, *113*, 4701–4708.

(22) For rare examples of square-planar tetraphosphine Co(I) complexes, see: (a) Vaska, L.; Chen, L. S.; Miller, W. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671–6673. (b) Miskowski, V. M.; Robbins, J. L.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 2477–2483.

(23) For rare examples of heteroleptic square-planar Co(I) complexes, see: (a) Fout, A. R.; Basuli, F.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3291–3295. (b) Ingleson, M. J.; Pink, M.; Fan, H.; Caulton, K. G. *Inorg. Chem.* **2007**, *46*, 10321–10334.

(24) Poli, R. *Chem. Rev.* **1996**, *96*, 2135–2204.

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