

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

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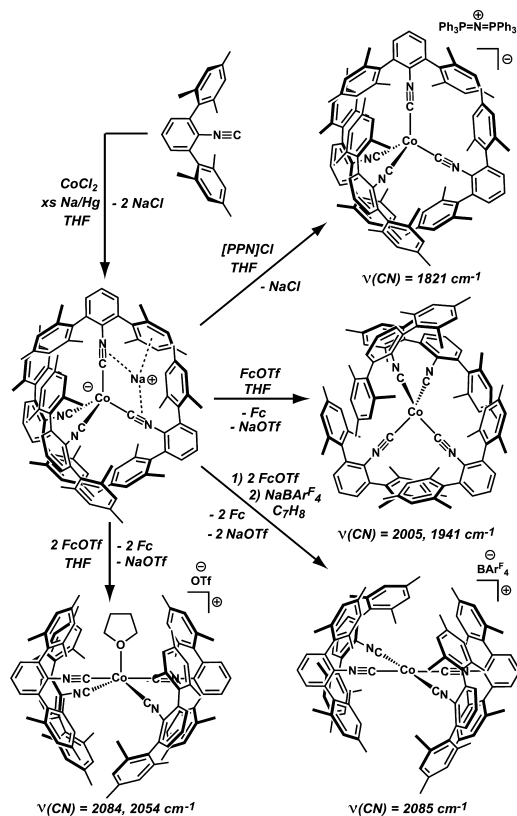
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Intense interest in the unsaturated mononuclear cobalt carbonyls (i.e., $\text{Co}(\text{CO})_4$ and $[\text{Co}(\text{CO})_4]^+$) has stemmed from their presumed role as reactive intermediates in industrial hydroformylation and carbonylation processes.^{1–3} 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 $\text{CN}t\text{-Bu}$ and CNXyl ($\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) have been unsuccessful in this regard.^{5–7} Herein we show that the *m*-terphenyl isocyanide⁸ $\text{CNAr}^{\text{Mes}_2}$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) allows for the isolation of a full series of mononuclear $[\text{Co}(\text{CNR})_4]^n$ 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 $[\text{Co}(\text{CNAr}^{\text{Mes}_2})_4]^n$ system is achieved by the addition of sodium amalgam to a $\text{CoCl}_2/\text{CNAr}^{\text{Mes}_2}$ mixture in THF (Scheme 1). This protocol provides the dark red tetraisocyanometalate salt $\text{Na}[\text{Co}(\text{CNAr}^{\text{Mes}_2})_4]$, crystallographically characterized as a contact ion pair with interactions between the Na cation and isocyano $\text{C}\equiv\text{N}$ units (Figure S4.1). Similar cation– CN_{iso} interactions were observed in Cooper's salt, $[\text{K}(\text{DME})][\text{Co}(\text{CNXyl})_4]$ ($\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$),^{7b} which is the only other structurally characterized homoleptic cobalt isocyanometalate.⁹ FTIR analysis of $\text{Na}[\text{Co}(\text{CNAr}^{\text{Mes}_2})_4]$ in C_6D_6 solution revealed three intense $\nu(\text{CN})$ stretches (1903, 1821, and 1761 cm^{-1}), thereby confirming that a low-symmetry local environment of the $[\text{Co}(\text{CNR})_4]$ -core is retained in solution. However, the anion–cation interaction in $\text{Na}[\text{Co}(\text{CNAr}^{\text{Mes}_2})_4]$ can be readily disrupted upon addition of $[\text{Ph}_3\text{PNPPh}_3]\text{Cl}$ ($[\text{PPN}]\text{Cl}$) in THF solution. Structural characterization of the resulting purple-red salt, $[\text{PPN}][\text{Co}(\text{CNAr}^{\text{Mes}_2})_4]$ (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 $\nu(\text{CN})$ stretch (1821 cm^{-1}) consistent with a complex possessing local tetrahedral symmetry.

In marked contrast to $[\text{Co}(\text{CNXyl})_4]^-$, which readily dimerizes to $\text{Co}_2(\text{CNXyl})_8$ when oxidized,^{7b} the encumbering Ar^{Mes_2} units stabilize a zerovalent cobalt tetraisocyanide monomer. Thus treatment of $\text{Na}[\text{Co}(\text{CNAr}^{\text{Mes}_2})_4]$ with 1 equiv of ferrocenium triflate (FcOTf) affords the neutral, paramagnetic complex $\text{Co}(\text{CNAr}^{\text{Mes}_2})_4$ as determined by X-ray diffraction (Figure 1b). To our knowledge, $\text{Co}(\text{CNAr}^{\text{Mes}_2})_4$ is a unique example of an isolable zerovalent Co monomer possessing a homoleptic π -acidic ligand field.¹¹ Accord-

Scheme 1



ingly, Evans method magnetic moment determination for $\text{Co}(\text{CNAr}^{\text{Mes}_2})_4$ resulted in a μ_{eff} value of $1.79(\pm 0.10)\mu_{\text{B}}$, consistent with a $d^9 S = 1/2$ Co center. In addition, solution (C_6D_6) FTIR analysis of $\text{Co}(\text{CNAr}^{\text{Mes}_2})_4$ at room temperature revealed $\nu(\text{CN})$ stretches at 2005 and 1941 cm^{-1} , which reflect a decrease in electron density at the Co center relative to the salts $\text{Na}[\text{Co}(\text{CNAr}^{\text{Mes}_2})_4]$ and $[\text{PPN}][\text{Co}(\text{CNAr}^{\text{Mes}_2})_4]$.

With respect to the relationship between $\text{Co}(\text{CNAr}^{\text{Mes}_2})_4$ and $\text{Co}(\text{CO})_4$, 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 $\text{Co}(\text{CO})_4$ 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}

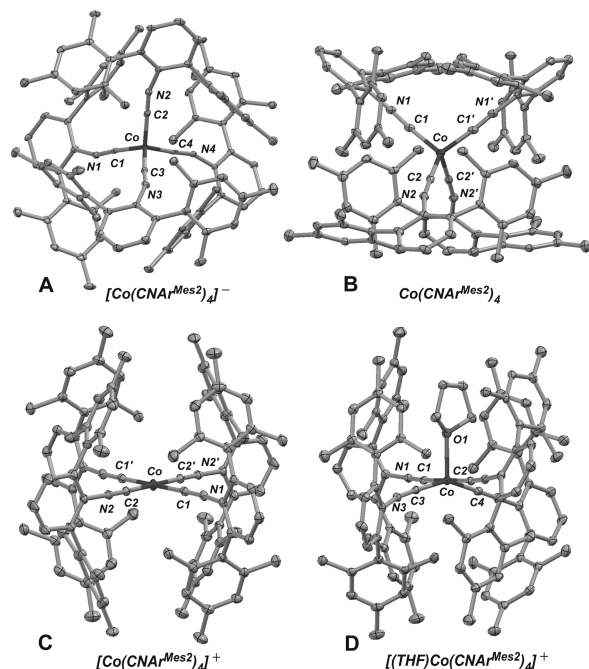


Figure 1. Molecular structures of the cobalt-containing components of [PPN][Co(CNAr^{Mes2})₄] (A), Co(CNAr^{Mes2})₄ at 100 K (B), [Co(CNAr^{Mes2})₄]-BAr^F₄ (C), and [(THF)Co(CNAr^{Mes2})₄]OTf (D).

Whereas the presence of two $\nu(\text{CN})$ 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

Table 1. Variable Temperature Crystallographic Parameters for Co(CNAr^{Mes2})₄

Temp K	$\angle\text{C1-Co-C1'}$ (deg)	$\angle\text{C2-Co-C2'}$ (deg)	$\angle\text{C1-Co-C2}/$ $\angle\text{C1-Co-C2'}$ (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.

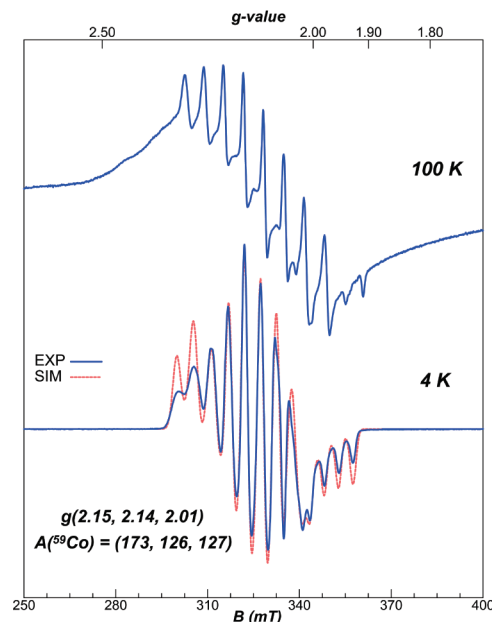


Figure 2. X-Band EPR spectra for toluene glass samples of Co(CNAr^{Mes2})₄ at 100 K (top) and 4 K (bottom). A values in MHz.

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 functionals¹⁸ 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-

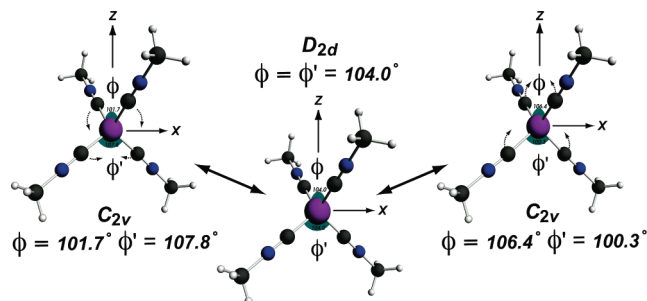


Figure 3. DFT calculated geometry displacement for the origin (D_{2d}) and end points (C_{2v}) of a b_2 C–Co–C bending mode for D_{2d} -symmetric $\text{Co}(\text{CNMe})_4$.

$(\text{CNAr}^{\text{Mes}2})_4$ with 2 equiv of FcOTf , followed by the addition of $\text{Na}[\text{BAR}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$), provides the diamagnetic salt $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{BAR}^{\text{F}}_4$ as a purple crystalline solid ($\nu(\text{CN}) = 2085\text{ cm}^{-1}$). Remarkably, crystallographic characterization of $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{BAR}^{\text{F}}_4$ 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 $[\text{Co}(\text{CO})_4]^+$ 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 $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]^+$ models the carbonyl derivative $[\text{Co}(\text{CO})_4]^+$, 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 $[\text{Co}(\text{CNXyl})_4]^+$ indicate that its D_{4h} isomer is energetically preferred to its “saw-horse” C_{2v} isomer by ca. 14 kcal/mol. Nevertheless, $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{BAR}^{\text{F}}_4$ 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 $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]^+$ core occurs on coordination of Lewis bases. Thus, addition of 2 equiv of FcOTf to $\text{Na}[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]$ in THF results in the paramagnetic THF adduct, $[(\text{THF})\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{OTf}$. Structural characterization of $[(\text{THF})\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{OTf}$ 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 $150.29(16)^\circ$. Evans method magnetic moment determination resulted in a μ_{eff} value of $2.96(\pm 0.15)\mu_{\text{B}}$ for $[(\text{THF})\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{OTf}$, consistent with an $S = 1$ ground state. Furthermore, the paramagnetism exhibited by $[(\text{THF})\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{OTf}$ is not a consequence of its preparation. Thus, addition of 1.0 equiv of THF to a C_6D_6 solution of $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{BAR}^{\text{F}}_4$ yields $\text{Ar}^{\text{Mes}2}\text{-}^1\text{H}$ NMR shifts identical to those of $[(\text{THF})\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{OTf}$, 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 $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]^+$ with certain substrate molecules.

As a final note, both $[(\text{THF})\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{OTf}$ and $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]\text{BAR}^{\text{F}}_4$ react upon mixing with $\text{Na}[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]$ to generate $\text{Co}(\text{CNAr}^{\text{Mes}2})_4$. These comproportionation reactions are significant in that a seemingly large structural reorganization of the $[\text{Co}(\text{CNR})_4]$ 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 $[\text{Co}(\text{CNR})_4]$ fragment. This latter characteristic is expected to feature prominently in the multielectron reactivity of the system. Accordingly, reactivity studies of these $[\text{Co}(\text{CNAr}^{\text{Mes}2})_4]^n$ 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>.

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