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TECHNICAL REPORT NO. 3

The First Transition Metal Isonitrite:
Synthesis and Characterization of $K[Co(2,6-Me_2C_6H_3NC)_4]$

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<p>Addition of 4 equiv of 2,6-Me₂C₆H₃NC to K[Co(C₂H₄)₄] in THF results in displacement of the ethylene and formation of the homoleptic isonitrilate [Co(2,6-Me₂C₆H₃NC)₄]²⁻ (2⁻), isolated as K₂, [K(DME)]₂, and [K(18-crown-6)]₂. IR and ¹H NMR spectra are consistent with formulation of 2⁻ as a complex of terminal isonitrile ligands, and chemical characterization of 2⁻ was provided by addition of Ph₃SnCl in THF to give [Co(2,6-Me₂C₆H₃NC)₄SnPh₃] (4).</p>			
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Isonitriles, like carbon monoxide, interact synergistically with transition metal centers and can balance σ donation to the metal from a carbon based orbital with π back donation into an antibonding orbital of the isonitrile ligand,¹ and there is an extensive chemistry of transition metal isonitrile complexes². It is, however, generally believed, largely on the basis of spectroscopic³ and electrochemical⁴ studies, that isonitriles are better σ donors and poorer π acceptors than CO, consistent with the observation that typical homoleptic isonitrile complexes of many metals are in higher oxidation states than the typical carbonyl complexes of the same metals. In the case of cobalt, for example, a range of stable homoleptic isonitrile complexes of Co(I) have been known for years,⁵ and there is at least one reliable early report of a homoleptic complex of Co(II),⁶ but the first homoleptic Co(0) isonitrile complexes, isoelectronic with $[\text{Co}_2(\text{CO})_8]$, were not reported until 1977,⁷ and there are no reports of isonitrile analogues of $[\text{Co}(\text{CO})_4]^-$ nor indeed of any other transition metal isonitrilates.⁸

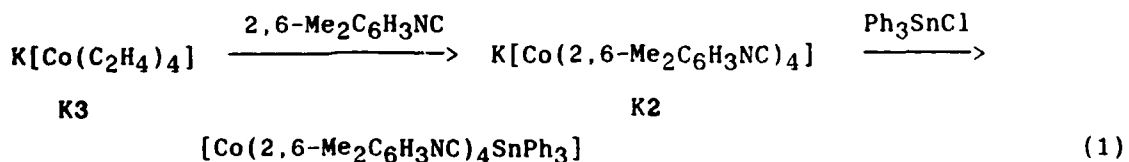
The mild description of Co(0) isonitrile complexes as "air-sensitive even in the solid state"^{7c} and the accessibility of Co carbonyls in oxidation states as low as -3,⁹ suggested that cobalt isonitrilates should be synthetically accessible. The lack of reactivity of $[\text{Co}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_8]$ (1) towards sodium amalgam^{7b,c} and of $[\text{Co}_2(\text{t-BuNC})_8]$ towards potassium amalgam^{7a,d} indicated, however, that reduction of a zerovalent isonitrile complex was unlikely to provide a successful approach to Co isonitrilates, and ligand substitution within a preformed complex of Co in a negative oxidation state provides the most obvious alternative strategy. The remarkable ethylene complex of Co(-1) reported by Jonas¹⁰ seemed to be an ideal substrate for such an experiment, and we now wish to report the synthesis and characterization of $\text{K}[\text{Co}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4]$, (K2), an unprecedented transition metal isonitrilate, by ethylene displacement from $\text{K}[\text{Co}(\text{C}_2\text{H}_4)_4]$ ¹⁰ (K3):

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In a typical preparation 4 molar equiv. of 2,6-Me₂C₆H₃NC¹¹ (1.35 g, 10.27 mmol) in THF (30 mL) were added to a grey sample of solid K[Co(C₂H₄)₄] (0.54 g, 2.57 mmol) at room temperature. Effervescence indicated immediate reaction and within 5 minutes a deep orange-red solution had formed. IR spectra indicated complete consumption of the free isonitrile ($\nu_{\text{CN}} = 2116 \text{ cm}^{-1}$ in THF), and formation of a complex characterized by an intense, broad absorption centered at 1815 cm^{-1} . This suggested that all of the ethylenes had been displaced to form the potassium salt of the tetra-isonitrilate (Eq. 1), and this was isolated by concentration under reduced pressure to ca. 5 mL and addition of pentane (20 mL) to the stirred solution to precipitate K[Co(2,6-Me₂C₆H₃NC)₄] (K2)¹² (1.17 g, 1.85 mmol \approx 73%) as an orange powder. In this form the material is extremely air sensitive, and the powder turns black in seconds following exposure to air, but recrystallization from 1,2-dimethoxyethane (DME, 5 mL) by addition of diethyl ether (50 mL) gave a 61% yield (based on K3) of dark crimson parallel-pipedes of a mono-DME solvate [K(DME)][Co(2,6-Me₂C₆H₃NC)₄]¹³ which, although they still decomposed in air in minutes, were significantly easier to handle than the unsolvated powder.

Formulation of K2 as an isonitrilate containing terminal isonitrile ligands, although awaiting structural confirmation, is strongly supported by IR spectra of K2 in THF, which are dominated by broad absorptions centered at 1890 (sh) and 1815 (vs) cm^{-1} . These bands are ca. 200 cm^{-1} below the frequency of the terminal $\nu_{\text{C}\equiv\text{N}}$ stretch in 1,7^c but over 150 cm^{-1} above the bridging $\nu_{\text{C}=\text{N}}$ stretch in 1,7^c consistent with assignment to a stretching absorption of a

terminal C≡N bond which has been dramatically weakened by back-donation from the electron-rich metal center in 2⁻. The broadening probably reflects ion pairing effects analogous to those often observed for carbonylmetalates,¹⁴ and this is supported by the reduction in the width at half height of the absorptions from 180 cm⁻¹ to 120 cm⁻¹ (without a significant shift in position) when one equiv. of 18-crown-6 (18-C-6) was added to a THF solution of K2 to form [K(18-C-6)]2.¹⁵ The low frequencies of the ν_{C≡N} absorptions in all these salts are consistent with marked bending of the isonitrile ligands similar to that observed for the radial ligands of [Fe{CN(t-Bu)}₅]¹⁶ - it has been suggested that the radial ligands are responsible for the unusually low 1830 cm⁻¹ bands of this complex, and that such bending reflects extensive back bonding from the electron-rich metal.¹⁶ The single chemical environment observed for the isonitrile ligands is consistent with the proposed formulation.

Addition of Ph₃SnCl provided chemical characterization of K2,¹⁷ and established that derivatives of 2⁻ can be prepared by reaction with electrophiles. When a solution of Ph₃SnCl (0.62 g, 1.61 mmol) in THF (30 mL) was added dropwise to a solution of K2 (1.0 g, 1.61 mmol) in THF (35 mL) at -78°C a transient green color changed to bright yellow as the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure and the product extracted into diethyl ether (200 mL). After filtration the ether was removed under reduced pressure, and the yellow glass solidified by scraping under pentane. The solvent was again removed under reduced pressure to give 1.20 g, 1.28 mmol (≅ 80%) of crude [Co(2,6-Me₂C₆H₃NC)₄SnPh₃] (4). Recrystallization from ether (0.8 g in 8 mL) by addition of pentane (240 mL) and cooling to -30°C gave analytically pure 4¹⁸ (0.55 g, 0.59 mmol) in 69% yield (2 crops).

We have attempted to circumvent the need to prepare the intermediate ethylene complex K3 by a direct synthesis of K2 in which 1 is reduced with K/Hg or potassium naphthalenide, but such experiments have been unsuccessful. By

analogy with the preparation of K3¹⁰ we have also examined the reduction of cobaltocene with potassium in the presence of 2,6-Me₂C₆H₃NC, but have been unable to obtain tractable products from this reaction and see no IR evidence for formation of K2 in THF.

The accessibility of stable, crystalline salts of [Co(2,6-Me₂C₆H₃NC)₄]⁻ indicates that the ability of isonitriles to stabilize metals in negative oxidation states has probably been underestimated, and that isonitrilates may have a chemistry as rich as that of metal carbonylates. Substitution of highly reduced precursors with labile alkene ligands offers a high yield and convenient route (and so far the only route) to such complexes, and we are currently exploring the extension of this approach to the synthesis of other cobalt isonitrilates and to isonitrilates of other transition metals.

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- (13) IR(Nujol, ν_{CN}): 2005 (vw), 1880 (sh), 1815 (vs) cm^{-1} . ^1H NMR spectra in CD_3CN are identical to those of K2, except for the presence of 1.0 ± 0.1 molecules of DME for every 4 isonitrile ligands. Anal. Calcd for $\text{C}_{40}\text{H}_{46}\text{CoKN}_4\text{O}_2$: C, 67.40; H, 6.50. Found (Dornis u. Kolbe, Mulheim a.d. Ruhr): C, 67.28; H, 6.60.
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- (18) IR (Nujol mull, ν_{CN}): 2110 (w), 2035 (sh), 1992 (s, br) cm^{-1} . ^1H NMR ($\text{CD}_3\text{OCD}_2\text{CD}_2\text{OCD}_3$) δ 7.9 to 6.7 (m, 27H, $\text{C}_6\text{H}_3+\text{C}_6\text{H}_5$), 2.12 (s, 24H, CH_3).
Anal. Calcd for $\text{C}_{54}\text{H}_{51}\text{CoN}_4\text{Sn}$: C, 69.47; H, 5.51; N, 6.00. Found (Dornis u. Kolbe, Mulheim a.d. Ruhr): C, 69.32; H, 5.46; N, 5.91.

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