of the hydrogen molecule has been spectacularly enhanced by coordination to the metal.

The interconversion of **2a** and **2b** was probed by spin saturation transfer experiments at 190 K. Saturation of the methyl resonance of **2b** causes an intensity decrease in the methyl resonance due to **2a**. From these observations, an approximate rate constant of 2.5 s^{-1} was calculated for the conversion of **2b** to **2a**.[27] Thus the observed product ratio is clearly a reflection of an equilibrium between **2a** and **2b**, not a kinetic selectivity in the protonation. From the observed product ratio and the spin saturation transfer data, a semiquantitative free energy diagram for the isomers of **2** can be constructed (see Scheme I).

These observations are in marked contrast to the recent report by Gladysz and Fernández[18] that protonation of (η-C_5H_5)Re(PPh_3)(NO)H affords only cationic dihydride complexes, as both cis and trans isomers (with the trans:cis ratio of 60:40 at room temperature). These complexes presumably adopt a distorted capped square pyramid geometry, with the cyclopentadienyl group capping. In this coordination geometry, the terms cis and trans are only approximate descriptors. In the rhenium system described here the replacement of a σ-donor PPh_3 ligand with an effective π-acceptor such as CO presumably renders the metal center much less electron rich, reducing the tendency to oxidative addition. The dihydrogen complex **2a** is thus favored over the dihydride **2b**. An ambiguity remains as to the stereochemistry of the dihydride **2b**. Complex **2b** exhibits only one hydride resonance in the ^1H NMR spectrum. This is consistent with a trans structure or with a highly fluxional cis geometry. The latter possibility is considered less likely since the related cis dihydride [(η-C_5H_5)Re(PPh_3)(NO)H_2]BF_4 exhibits two hydride resonances in the ^1H NMR, which coalesce only at high temperature ($\Delta G^{\ddagger}_{295\,K}$ = 13 kcal mol^{-1}).[18]

Complex **2a** is the first well-characterized example of dihydrogen coordination to a metal center with a nitrosyl coligand. The extraordinary activation of dihydrogen toward heterolysis upon coordination in **1** and **2a** is understandable, since the metal centers involved are strong Lewis acids. Although H_2 is bound only weakly by these acidic metal centers, dihydrogen coordination is still thermodynamically favored over oxidative addition, in contrast to the more basic PPh_3-containing complexes of Re reported by Gladysz, where oxidative addition is favored.[18] We are continuing to investigate the chemistry of H_2 coordination to Lewis acid metal centers, with particular emphasis on catalysis of isotopic exchange reactions between hydrogen and basic substrates such as water.

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[27] Proton T_1 values for **2** were determined by using a 180–τ–90 pulse sequence. At 190 K, T_1 values for the hydride resonances in **2a** and **2b** are 5 and 500 ms, respectively. The methyl resonances for both species give a T_1 value of 760 ms. Saturation of the methyl resonance of **2b** causes a decrease in the intensity of the methyl resonance due to **2a** of ca. 15%. The rate constant was calculated as previously outlined for a two-site exchange process.[28]

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

Garry F. Warnock and N. John Cooper*

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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Summary: Addition of 4 equiv of 2,6-$Me_2C_6H_3NC$ to K[Co($C_2H_4)_4$] in THF results in ethylene displacement and formation of the homoleptic isonitrilate [Co(2,6-$Me_2C_6H_3NC)_4]^-$ (**2**$^-$), isolated as K**2**, [K(DME)]**2**, and [K(18-crown-6)]**2**, and formulated as a complex of Co(1–) with terminal isonitrile ligands. Addition of Ph_3SnCl to **2**$^-$ in THF gave [Co(2,6-$Me_2C_6H_3NC)_4SnPh_3$] (**4**).

Isonitriles, like carbon monoxide, interact synergistically with transition-metal centers, balancing 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 complexes.[2] It is, however, generally believed, largely on the basis of spectroscopic[3] and electrochemical[4] 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 [$Co_2(CO)_8$], were not reported until 1977,[7] and there are no reports of isonitrile analogues of [$Co(CO)_4]^-$ 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.

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[8] We propose that homoleptic isonitrile complexes of metals in negative oxidation states be termed "isonitrilates" by analogy with metal carbonylates.

[9] Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686.

The lack of reactivity of $[Co_2(2,6\text{-}Me_2C_6H_3NC)_8]$ (**1**) toward sodium amalgam[7b,c] and of $[Co_2(t\text{-}BuNC)_8]$ toward 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 provided the most obvious alternative strategy. The remarkable ethylene complex of Co(1−) reported by Jonas[10] seemed to be an ideal substrate for such an experiment, and we now wish to report the synthesis and characterization of $K[Co(2,6\text{-}Me_2C_6H_3NC)_4]$ (K**2**), an unprecedented transition-metal isonitrilate, by ethylene displacement from $K[Co(C_2H_4)_4]$[10] (K**3**):

$$\underset{\textbf{K3}}{K[Co(C_2H_4)_4]} \xrightarrow{2,6\text{-}Me_2C_6H_3NC} \underset{\textbf{K2}}{K[Co(2,6\text{-}Me_2C_6H_3NC)_4]} \xrightarrow{Ph_3SnCl} \underset{\textbf{4}}{[Co(2,6\text{-}Me_2C_6H_3NC)_4SnPh_3]} \quad (1)$$

In a typical preparation 4 molar equiv of $2,6\text{-}Me_2C_6H_3NC$[11] (1.35 g, 10.27 mmol) in THF (30 mL) were added to a gray sample of solid $K[Co(C_2H_4)_4]$ (0.54 g, 2.57 mmol) at room temperature. Effervescence indicated immediate reaction and within 5 min a deep orange-red solution had formed. IR spectra indicated complete consumption of the free isonitrile (ν_{CN} = 2116 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 tetrakis 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 $K[Co(2,6\text{-}Me_2C_6H_3NC)_4]$ (K**2**)[12] (1.17 g, 1.85 mmol = 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 K**3**) of dark crimson parallelepipeds of a mono-DME solvate $[K(DME)][Co(2,6\text{-}Me_2C_6H_3NC)_4]$[13] which, although they still decomposed in air in minutes, were significantly easier to handle than the unsolvated powder.

Formulation of K**2** as an isonitrilate containing terminal isonitrile ligands, although awaiting structural confirmation, is strongly supported by IR spectra of K**2** 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 $\nu_{C\equiv N}$ stretch in **1**[7c] but over 150 cm^{-1} above the bridging $\nu_{C\equiv N}$ stretch in **1**,[7c] 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 to 120 cm^{-1} (without a significant shift in position) when 1 equiv of 18-crown-6 (18-C-6) was added to a THF solution of K**2** to form [K(18-C-6)]**2**.[15] The low frequencies of the $\nu_{C\equiv N}$ absorptions in all these salts are consistent with marked bending of the isonitrile ligands similar to that observed for the radial ligands of $[Fe\{CN(t\text{-}Bu)\}_5]$[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 Ph_3SnCl provided chemical characterization of K**2**[17] and established that derivatives of **2**$^-$ can be prepared by reaction with electrophiles. When a solution of Ph_3SnCl (0.62 g, 1.61 mmol) in THF (30 mL) was added dropwise to a solution of K**2** (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 $[Co(2,6\text{-}Me_2C_6H_3NC)_4SnPh_3]$ (**4**). Recrystallization from ether (0.8 g in 8 mL) by addition of pentane (24 mL) and cooling to −30 °C gave analytically pure **4**[18] (0.55 g, 0.59 mmol) in 69% yield (two crops).

We have unsuccessfully attempted to circumvent the need to prepare the intermediate ethylene complex K**3** by a direct synthesis of K**2** in which **1** is reduced with K/Hg. We have also examined the reduction of cobaltocene with potassium in the presence of $2,6\text{-}Me_2C_6H_3NC$ (reduction to K**2** would be analogous to the preparation of K**3**[10]) but have been unable to obtain tractable products from this reaction and see no IR evidence for the formation of K**2** in THF.

The accessibility of stable, crystalline salts of $[Co(2,6\text{-}Me_2C_6H_3NC)_4]^-$ 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 to such complexes, and we are currently exploring the extension of this approach to the synthesis of other cobalt isonitrilates and of isonitrilates of other transition metals.

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(13) IR (Nujol, ν_{CN}): 2005 (vw), 1880 (sh), 1815 (vs) cm^{-1}. ^{1}H NMR spectra in CD_3CN are identical with those of K**2**, except for the presence of 1.0 ± 0.1 molecules of DME for every 4 isonitrile ligands. Anal. Calcd for $C_{40}H_{46}CoKN_4O_2$: C, 67.40; H, 6.50. Found (Dornis u. Kolbe, Mulheim a.d. Ruhr): C, 67.28; H, 6.60.

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(15) Analytically pure dark crimson crystals of [K(18-C-6)]**2** could be obtained in 80% yield (from K**2**) by recrystallization from THF by addition of diethyl ether, and ^{1}H NMR spectra in CD_3CN confirmed the presence of 1.0 ± 0.1 molecules of 18-C-6 for every 4 isonitrile ligands. IR (Nujol, ν_{CN}): 2005 (w), 1890 (sh), 1815 (vs) cm^{-1}. Anal. Calcd for $C_{48}H_{60}CoKN_4O_6$: C, 64.99; H, 6.82; N, 6.32. Found (Dornis u. Kolbe, Mulheim a.d. Ruhr): C, 64.78; H, 6.65; N, 6.18.

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