efficient carbene complex formation and subsequent CH_2–CH_2 coupling.

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Low-Valent Cyanocobaltate Chemistry. 3. Reactions of $[(\eta^5\text{-}C_5H_5)Co(CN)(CO)]^-$ with Electrophiles, Nucleophiles, and Redox Agents. Synthesis of New (η^5-Cyclopentadienyl)cobalt Cyanide Complexes[1]

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Details of the syntheses and reactivity of (K-crown)[Cp(CN)(CO)] (**1a**) (crown = 18-crown-6 ether), PPN[Cp(CN)(CO)] (**1b**), (K-crown)[$CpCo(CN)PPh_3$] (4), and (K-crown)[$CpCo(CN)_2$] (**10a**) are presented. Compound **1a** is readily formed by reaction of $CpCo(CO)_2$ with cyanide in aprotic media. Reaction of $CpCo(CO)_2$ with excess cyanide under forcing conditions results in the dissociation of cyclopentadienide anion instead of $[CpCo(CN)_2]^{2-}$ formation. Although the $[CpCo(CN)_2]^{2-}$ anion appears to be extremely basic and reactive, an impure form can be isolated by the low-temperature reduction of **10a** in DMF. The electrophiles acetyl chloride, benzyl bromide, and methyl fluorosulfate do not react with **1a** to form isocyanides but unexpectedly produce $CpCo(CO)_2$ and a variety of Co(II) and Co(III) compounds. The pathways that culminate in these products are suggested to originate from an initial one-electron transfer yielding the intermediate [Cp(CN)(CO)]. Treatment of **1a** or **1b** with tosyl chloride yields $[CpCo(CN)_2(\eta^1\text{-}SO_2C_6H_4CH_3)]^-$ and cyanide-bridged cyclopentadienylcobalt(III) polymers, while **1a** or **1b** reacts cleanly with R_3SnCl reagents to form the expected isocyanide complexes. $Hg(CN)_2$ oxidizes **1** to $CpCo(CN)_3^-$. Acyl chlorides lacking α-hydrogens react with **1** to produce novel bis(acyl isocyanide) complexes $CpCo(CNCOR)_2$ in low yields. The spectroscopic characterization of these compounds is presented, and the nature of the cyanide ligand's influence on low-valent metal centers is discussed.

Introduction

We have communicated the crown ether assisted synthesis of the $[CpCo(CN)(CO)]^-$ anion (1; Cp = η^5-C_5H_5) and preliminary observations concerning its reactivity.[1a] Of special interest to us was the opportunity to characterize the properties of cyanide as a ligand in the environment of a relatively electron-rich, low formal oxidation state metal. This could be done by comparing the chemical and physical properties of 1 with those of the well-known compounds $CpCoL_2$ (L = CO, phosphines, or isocyanides). $CpCo(CO)_2$ has been an important molecule in the recent development of transition-metal organometallic chemistry, providing entries into metal clusters,[3] C–C bond formation studies,[4] new organic synthesis methods,[5] and complexes of novel ligands.[6] $CpCo(CO)_2$ is considered to be a relatively electron-rich metal carbonyl,[7] and this can be regarded as a consequence of the $CpML_2$ geometry.[8] The availability of the even more basic $CpCo(PR_3)_2$ complexes has thus provided a test bed for understanding the chemical consequences of extremely electron-rich metal centers.[9] We anticipated that spectroscopic and chemical reactivity comparisons between these compounds and 1 would provide insight into the relative donor and acceptor properties of the cyanide ligand in an environment where we assumed its π-acceptor abilities would be important.

In our preliminary study,[1a] we observed that the CN ligand in 1 is labile; thus reactions of 1, which are dissociative in nature, such as reactions with alkynes, should be little different from the corresponding reactions of $CpCo(CO)_2$, as we observed. On the other hand, reactivity dependent on metal-centered basicity or electron density should provide a significant contrast between 1 and $CpCo(CO)_2$ (2), especially if the σ-donor properties of the CN ligand were dominant. This distinction was observed in the respective reactions of 1 and 2 with HgX_2, X = Cl or CN, and in the resistance of 1 to reduction. This data suggested that the donor strength of CN is the dominant property of this ligand in 1.

If 1 is as electron-rich as it appears from the above results, then analogues of 2 such as $CpCo(CO)PPh_3$ (**3a**) and $CpCo(PMe_3)_2$ (**3b**) should be better models for its chemical behavior. Compounds 3 are characterized by their much greater basicity and nucleophilicity relative to 2. We thus began an investigation of the reactions of 1 with electrophiles. In our previous report, we noted that reactions of 1 with simple alkyl and acyl halides were complex but that in the case of acyl halides lacking α-

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[1] (a) Part 1: Carter, S. J.; Stuhl, L. S. *Organometallics* **1985**, *4*, 197. (b) Part 2: Carter, S. J.; Stuhl, L. S. *Rev. Inorg. Chem.* **1985**, *7*, 341.

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[3] (a) Lee, W. S.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 87. (b) Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Organomet. Chem.* **1975**, *97*, 283.

[4] Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113.

[5] Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

[6] Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

[7] Cook, D. J.; Dawes, J. L.; Kemmitt, R. D. W. *J. Chem. Soc. A* **1967**, 1547.

[8] Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 2554.

[9] (a) Werner, H. *Pure Appl. Chem.* **1982**, *54*, 177. (b) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927.

0276-7333/88/2307-1909$01.50/0

hydrogens, low yields of unusual acyl isocyanide complexes $CpCo(CNCOR)_2$ could be isolated. Herein we report on the reactions of 1 with electrophiles, as well as details of the reactions already communicated. In addition, we present the synthesis of a novel Co^{II} complex, $CpCo(CN)_2^-$, its reaction with an acyl chloride, and its reduction to a species which we believe is $K_2[CpCo(CN)_2]$, a complex which has proven otherwise inaccessible.

Results

Compounds 1 are prepared by the direct reaction of $CpCo(CO)_2$ in acetonitrile with soluble cyanide salts such as (K-crown)CN and PPN(CN). Reaction proceeds slowly but cleanly at ambient temperature, and excellent yields are obtained after a 2-day reaction.

The synthesis of (K-crown)$[CpCo(CN)(PPh_3)]$ (4) from (K-crown)CN and $CpCo(PPh_3)_2$ indicates that the synthetic method employed for the preparation of 1, ligand displacement from $CpCo(CO)_2$, may be generalizable to other $CpCo^IL_2$ systems. A 75% isolated yield of product is obtained in a 2-h reaction in acetonitrile at ambient temperature (reaction 1). Compound 4 is a purple-black

$$CpCoL_2 + CN^- \rightarrow \underset{\substack{\mathbf{1a,b}:\ L = CO \\ \mathbf{4}:\ L = PPh_3}}{[CpCo(L)(CN)]^-} \qquad (1)$$

crystalline solid. As expected for a Co^I complex lacking strong π-acceptor ligands, the spectroscopic properties of 4 are those of a very electron-rich species. The IR cyanide stretch appears at the distinctly low value of 2014 cm^{-1} (compare **1a**, 2066 cm^{-1}), and the ^1H NMR Cp resonance is found at δ 4.09 (compare $CpCo(PPh_3)_2$, δ 4.5,[10] and $CpCo(CO)_2$, δ 4.47[3b]).

Reactions of 1 with nucleophilic ligands were discussed in our preliminary communication.[1a] Equilibria were set up in reacting **1a** with phosphines or phosphites. Diphenylacetylene reacted with **1a** in a very similar manner to its reaction with $CpCo(CO)_2$: the complexes $CpCo(\eta^4\text{-}C_4Ph_4C{=}O)$ and $CpCo(\eta^4\text{-}C_4Ph_4)$ were produced. We present additional results on the redox chemistry of 1 and its reactions with electrophiles herein.

The reaction of compound **1b** with tosyl chloride provides evidence for the accessibility of an oxidative addition pathway. The cobalt(III) compound $PPN[CpCo(CN)_2(\eta^1\text{-}SO_2C_6H_4CH_3)]$ (**5a**) is obtained in 7% isolated yield as a crystalline orange solid (reaction 2). The analogous

$$[CpCo(CN)(CO)]^- + p\text{-}MeC_6H_4SO_2Cl \rightarrow \underset{\mathbf{5}}{[CpCo(CN)_2(\eta^1\text{-}SO_2C_6H_4CH_3)]^-} \qquad (2)$$

(K-crown) salt **5b** is more difficult to isolate and has not been isolated from the corresponding reaction involving **1a**. It has been obtained in impure form from the reaction of tosyl chloride with (K-crown)$[CpCo(CN)(PPh_3)]$ (4).

Reaction of triphenyltin chloride and **1a** produces an isocyanide complex under appropriate conditions (solvent THF, −20 °C). If the reaction is carried out in acetonitrile, or trimethyltin chloride is substituted for Ph_3SnCl, a more complex product mixture results, containing other products such as $CpCo(CO)_2$ and Co^{III} species. As the temperature is raised from −20 °C, the proportion of $CpCo(CO)_2$ to isocyanide complex increases until the former complex is the predominant product. The isocyanide, very unstable in most solvents, is not easily crystallized out after the reaction of **1a** with the triphenyltin reagent. But, if **1b** is used instead, a complex with the formula $CpCo(CO)(CNSnPh_3)\cdot(PPN)Cl$ (**6**) can be readily obtained from THF.

Reaction of pivaloyl chloride or 1-adamantanecarbonyl chloride with **1a** leads to the isolation of the novel complexes $CpCo[C{\equiv}NC({=}O)R]_2$ (**11a**, R = *t*-Bu; **11b** R = 1-adamantyl) (reaction 3). These compounds show strong

$$[CpCo(CN)(CO)]^- + RCOCl \rightarrow \underset{\substack{\mathbf{11a}:\ R = t\text{-}Bu \\ \mathbf{11b}:\ R = 1\text{-adamantyl}}}{CpCo[C{\equiv}NC({=}O)R]_2} \qquad (3)$$

IR absorptions at 2017, 1922 cm^{-1} (**11a**) and 2011, 1913 cm^{-1} (**11b**), which we assign as C≡N stretches. Our independent syntheses of **11b** and $CpCo[C{\equiv}NC({=}O)Ph]_2$[25] from $CpCo(CO)_2$ and free acyl isocyanide and the X-ray structure determination of the last leave no doubt as to their characterization as acyl isocyanides. Chemical ionization was found to be the most useful mass spectrometric technique for the characterization of complexes **11**. Parent ions are observed for both **11a** and **11b**, as are the $(M + 1)^+$ and $(M + C_2H_5)^+$ ions expected in CH_4 CI-MS. As expected, the major fragmentation patthway originates from bond scission between the carbonyl and nitrogen atom of an acyl isocyanide ligand. Compound **11a** gives a much larger protonated molecular ion than does **11b** because of its greater volatility and consequent reduced thermal decomposition.

Simple electrophiles such as benzyl bromide, methyl iodide, protic acids, and acetyl chloride react with 1 to produce complex product mixtures under a variety of conditions. A common component of most of these reactions is $CpCo(CO)_2$, generated in small, varying, quantities. The other components appear to be mainly Co^{II} and Co^{III} complexes (based on the frequencies of their IR CN stretches) which have not been successfully separated and purified. These mixtures appear to originate in part from oxidative processes (vide infra), specifically electron transfer by 1. Consistent with this, 1,2-diphenylethane has been identified as a major organic product in the reaction of benzyl bromide. Methyl fluorosulfate reacts with 1 at −35 °C in THF to produce a red intermediate which on slight warming rapidly decomposes to a brown solution containing $CpCo(CO)_2$. Attempts to isolate tractable products from this mixture were unsuccessful. Reaction of **1a** with acids resulted in decomposition, even at −60 °C.

In the course of examining the redox chemistry of 1, we found that the $[CpCo(CN)_3]^-$ anion, first prepared by Dineen and Pauson[11] as its potassium salt, could be easily obtained as the (K-crown) salt (**7**) by the oxidation of 1 with $Hg(CN)_2$ in warm acetonitrile (reaction 4). This

$$[CpCo(CN)(CO)]^- + Hg(CN)_2 \xrightarrow[\text{MeCN, }\Delta]{} \underset{\mathbf{7}}{[CpCo(CN)_3]^-} \qquad (4)$$

synthesis of anion **7** is preferable to that already in the literature[13] in its simplicity and ease of scaleup. The crown complexed salt is a yellow, crystalline solid with good solubility in acetonitrile.

Oxidation of **3a** by $Hg(CN)_2$ also provides very convenient access to another known $CpCo^{III}$ cyanide, $CpCo(CN)_2(PPh_3)$ (**8**).[10,13] McKinney has previously prepared

$$\underset{\mathbf{3a}}{CpCo(CO)PPh_3} + Hg(CN)_2 \rightarrow \underset{\mathbf{8}}{CpCo(CN)_2(PPh_3)} \qquad (5)$$

8 from $CpCo(PPh_3)_2$ (**9**) by a similar method,[10] with AgCN as the combination oxidant and cyanide source. Our

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(10) McKinney, R. J. *Inorg. Chem.* **1982**, *21*, 2051.

(11) (a) Dineen, J. A.; Pauson, P. L. *J. Organomet. Chem.* **1972**, *43*, 209. (b) Dineen, J. A.; Pauson, P. L. *Ibid.* **1974**, *71*, 77.

method is preferable because **3a** is more easily prepared than **9** on a large scale.

While preliminary work established that alkali metal amalgams were sufficiently powerful to reduce the aforementioned Co^{III} complexes **7** and **8** to the Co^{II} oxidation state, problems were encountered in achieving reasonable pure product yields from **7**. Reduction of **8**, however, in acetonitrile gives a good yield of (K-crown)[$CpCo(CN)_2$] (**10a**). Moreover, 8 can also be reduced in the absence of

$$\underset{\mathbf{8}}{CpCo(CN)_2(PPh_3)} + K/Hg \rightarrow \underset{\mathbf{10}}{[CpCo(CN)_2]^-} \quad (6)$$

crown ether (in THF) to give a virtually quantitative yield of K[$CpCo(CN)_2$] (**10b**); the disadvantage of this salt is that it is only soluble in DMF. Compound **10a** is the first example of a cyclopentadienylcobalt(II) cyanide. The IR ν_{CN} of **10a** appears at 2098 cm^{-1}, intermediate between the corresponding absorptions for **7** (2117 cm^{-1}) and for **1a** (2066 cm^{-1}). We have found this correlation between ν_{CN} and oxidation state to be general, although overlap can occur between the ranges which somewhat limits the utility of this correlation. Cobalt(III) terminal cyanide IR stretches generally occur in the range 2130–2100 cm^{-1}, while Co^{II} cyanide values are found in the region 2105–2060 cm^{-1}, and Co^{I} cyanides fall below 2070 cm^{-1}. A relationship also holds between average cyanide frequencies and the number of cyanide ligands bound to Co^{II} complexes.[16]

Dineen and Pauson have reported on the alkylation of $[CpCo(CN)_3]^-$ and $CpCo(CN)_2(PPh_3)$.[11] We find that the $CpCo^{III}$ cyanide complexes are inert to acylating reagents under reasonably mild conditions. The only reaction we have observed in attempting the acylation of either **7** or **8** has been in the attempted silver-assisted acylation of **8** with acetyl chloride and $AgBF_4$. While acylation of the complex **8** did not occur, a new complex was isolated. Spectral and elemental analysis of the compound established its identity as $CpCoPPh_3(CN)(CNBF_3)$. The infrared spectrum of this complex shows bands at 2126 (ν_{CN}), 2204 (ν_{CN} of $CNBF_3$), 1165 (sh), 1122 (s), and 882 cm^{-1} (BF_3 vibration modes). These data agree well with those published for other metal complexes containing BF_3–cyanide adducts.[12] Methanol dissociates the adduct, re-forming **8**. This is a somewhat surprising alternative to the conventional preparation of metal $CN{\cdot}BF_3$ complexes by treating cyanometallates with BF_3.

Although a rapid reaction ensues whtn 2 equiv of 1-adamantanecarbonyl chloride are added to a solution of **10a** in acetonitrile, workup of the reaction mixture reveals no simple acylation products, with about a 4% yield of the Co^{I} compound $CpCo(CNCOAd)_2$ (Ad = 1-adamantyl) (**11b**). This suggests that the initial Co^{II} product swiftly disproportionates.

The chemical reduction of **10a** at −40 °C in DMF by potassium anthracene radical anion yields a purple-black powder with the following IR spectrum: 2003 (vs), 1950 (vs), 768 (w) cm^{-1}. Cyclic voltammetry of **10a** in DMF shows a partially reversible reduction wave at −1.74 V vs NHE (ambient temperature, glassy carbon electrode, 200 mV/s) indicative of an $E_{rev}C$ process. Both these results lead us to believe that the reduced product is the $CpCo(CN)_2^{2-}$ anion (see Discussion).

Discussion

Synthesis of New Organocyanocobaltates. Monosubstitution of $CpCoL_2$ (L = CO or PPh_3) complexes by cyanide proceeds readily in aprotic solvents, and, in contrast to previous reports[11,13] of reactions conducted in protic solvents, the monosubstitution products are stable and straightforwardly isolated. With $CpCo(CO)_2$, reaction using either (K-crown)CN or (PPN)CN is complete within 2 days at ambient temperature and affords (K-crown)[Cp(CN)(CO)] (**1a**) and (PPN)[Cp(CN)(CO)] (**1b**) in excellent yields. The choice of the cation can be extended to the tetraalkylammonium series including (Bu_4N)CN and (Et_3MeN)CN, but the reaction is not quite as clean, the main byproduct being $[Co(CO)_3(CN)_2]^-$.[14] The tetraalkylammonium complexes are not as easily crystallized but have the possible advantage of considerable solubility in THF.

With $CpCoL_2$ complexes where L is a ligand more labile than CO, substitution by cyanide is more rapid, and a stoichiometric amount of cyanide is required for clean monosubstitution. Thus (K-crown)[$CpCo(CN)PPh_3$] (4) can be prepared in 75% yield from $CpCo(PPh_3)_2$ and (K-crown)CN in 2 h. Unlike **1**, **4** is not thermally stable in the solid state, starting to decompose rapidly at about 45 °C. Thus storage at or below −20 °C is recommended. The moderate electron richness of **1a** described previously[1] is expectedly totally eclipsed by that of **4**. This illustrates the dominance of the cyanide σ-donor effect in these Co^{I} complexes.

Preparation of the fully cyanide-substituted complex (K-crown)$_2$[$CpCo(CN)_2$] (**12**) has proven difficult. The response of $CpCo(CO)_2$ to excess (K-crown)CN under harsh conditions (extended reflux or prolonged photolysis) is the preferential loss of cyclopentadienide anion instead of carbonyl substitution. This results in the formation

$$CpCo(CO)_2 + \geq 2 \text{ equiv of } CN^- \underset{\Delta \text{ or } h\nu}{\not\rightarrow} \underset{\mathbf{12}}{[CpCo(CN)_2]^{2-}} \quad (7)$$

of (K-crown)[$Co(CO)_3(CN)_2$] and decomposition products such as (K-crown)Cp and (K-crown)[$Co(CN)_6$]. $Co(CO)_3(CN)_2^-$ anion was identified by comparison of its IR spectrum with that published for the tetraphenylarsonium salt.[14] Treatment of **1a** with trimethylamine *N*-oxide plus cyanide or with bis(trimethylsilyl)amide anion does not form **3** either. Examination of sequential IR spectra from the reaction of $CpCo(\eta^2\text{-}C_2H_4)_2$ with excess cyanide strongly suggested that complete alkene ligand replacement had occurred but that the likely product **12** had reacted with the acetonitrile solvent, perhaps by proton transfer from the solvent. This possibility has precedent in low-valent cyanometalate systems in aprotic solvents.[15a] The reaction was not examined further.

Because of these difficulties in preparing **12**, an alternative approach was adopted. Following the synthesis of the cobalt(II) compound (K-crown)[$CpCo(CN)_2$] (**10a**) (vide infra), we thought that the best change of preparing **12** lay in a low-temperature reduction of **10a** in DMF. A cyclic voltammogram of **10a** conducted in this solvent at room temperature showed the presence of an electrochemically reversible, but not fully chemically reversible, wave at −1.74 V vs NHE (i_{pa}/i_{pc} = 0.86), suggestive of an $E_{rev}C$ process. The follow-up chemical step could be the reduction or deprotonation of DMF or the supporting electrolyte (Bu_4NBF_4) by the Co^{I} product. When the chemical reduction of **10a** at −40 °C by potassium anthracene radical anion was carried out, a purple-black material was isolated which showed cyanide IR stretching

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(12) (a) Shriver, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 1405. (b) Shriver, D. F.; Posner, J. *Ibid.* **1966**, *88*, 1672.

(13) Coffey, C. E. *J. Inorg. Nucl. Chem.* **1963**, *25*, 179.

(14) Farcas, A.; Lupu, D. *J. Inorg. Nucl. Chem.* **1975**, *37*, 837.

(15) (a) del Rosario, R.; Stuhl, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 1160. (b) Eastes, J. W.; Burgess, W. M. *J. Am. Chem. Soc.* **1942**, *64*, 1187.

bands at 2003 and 1950 cm^{-1} in the infrared. The IR spectrum also displayed a band at 768 cm^{-1} at the expected position for a Cp moiety. The relative weakness of the bound crown ether bands at 1105, 968, and 842 cm^{-1} suggests a distinct lack of crown ether in the solid. The finding that the compound is virtually DMF-insoluble, when considered with the very low frequency of the cyanide stretches, strongly argues that the material is $K_2[CpCo(CN)_2]\cdot(crown)_x$, where x is a fraction substantially less than 2. The partial loss of crown ether experienced in this case is typical of many low-valent cyanometallates.[15a,17] At present, there appears to be no way of further purifying the compound to obtain analytical data because no solvents have been found in which the complex is both soluble and unreactive, a situation reminiscent of zerovalent cyanometalates such as $K_4Ni(CN)_4$.[15]

The precursor (K-crown)$[CpCo(CN)_2]$ (**10a**) was readily prepared by alkali-metal amalgam reduction of the $CpCo^{III}$ cyanides **7** or **8**, the latter being preferred. The magnetic moment (1.86 μ_B) of **10a** in solution is very close to the spin-only value for a single unpaired electron, demonstrating that dimerization is absent. This compound, a blackish purple, crystalline solid, is remarkably stable in the solid state and in solution, showing no tendency to disproportionate or decompose over a period of several months, in contrast to the most well-known Co^{II} cyanide $Co(CN)_5^{3-}$.[16]

Reactions with Electrophiles. Our previous studies have already demonstrated that **1** can behave as either a one- or a two-electron-transfer agent.[1a] It therefore was no surprise that benzyl bromide, methyl fluorosulfate, and acetyl chloride all reacted rapidly with **1a** to generate varying amounts of $CpCo(CO)_2$ and a diverse assortment of incompletely characterizable Co^{II} and Co^{III} complexes.

The formation of organic radicals is expected if the primary reaction pathway for **1** with alkyl halides is single electron transfer. While the ultimate fates of these radicals could be diverse, in favorable cases simple coupling of radicals should be observed. Evidence for the importance of electron-transfer processes in the reactions of **1** with electrophiles is clearest in the reaction with benzyl bromide. 1,2-Diphenylethane can be positively identified in ^1H NMR spectra of solvent extracts obtained from the reaction residues of **1a** with benzyl bromide. These NMR spectra are complicated, reflecting the large variety of organic and organometallic products. The relative proportions of these products depend upon whether a proton scavenger such as collidine is present in the reaction mixture. The overall reaction pattern is similar to that of (K-crown)$_2[(\eta^2\text{-}C_2Ph_2)Ni(CN)_2]$ with benzyl bromide.[17]

We did not initially anticipate the importance of one-electron transfer in the chemistry of **1**, and its significance does *not* follow simply from the σ-donor strength of cyanide and the consequent electron richness of **1**. The similarly electron-rich $CpCoL_2$ complexes studied by Werner and co-workers generally undergo formally two-electron reactions with simple electrophiles.

For example, $CpCo(CO)PMe_3$, in principle a close analogue of **1**, reacts with MeI by methylation at the metal center; the product of this oxidative addition, $[CpCo(PMe_3)(CO)Me]I$, is in equilibrium with the product of further CO insertion, $CpCo(PMe_3)(COMe)I$.[18] The contrast between Werner's compounds and ours is perhaps most striking in the case of protonation of the very electron-rich $CpCo(PR_3)_2$ compounds, which produces stable cationic hydrides $[CpCoH(PR_3)_2]^+$ in high yield (reaction 8).[19] A mechanism involving protonation at the metal should produce a hydride having significant stability. This is inconsistent with the rapid decomposition of **1** by strong acids even at low temperature. There is also no obvious reason why protonation of **1** at the cyanide nitrogen should produce an unstable product, given the stability of other $HN{\equiv}C$ complexes[20] and of $CpCo(CO)(CNR)$ complexes.[21] We can only conclude that, for **1**, single electron transfer type chemistry is favored even when the electrophile is a proton and in spite of the formal basicity of the complex.

$$CpCo(CO)PMe_3 + MeI \rightarrow [CpCo(PMe_3)(CO)Me]I \rightleftharpoons CpCo(PMe_3)(COMe)I \quad (8)$$

$$CpCo(PR_3)_2 + H^+ \rightarrow [CpCoH(PR_3)_2]^+$$

$$Cp(CN)(CO)^- + MeI \text{ or } H^+ \rightarrow \text{decomposition}$$

It is tempting to attribute this difference in behavior between **1** and Werner's compounds to the recognized special ability of cyanide to stabilize complexes in successive oxidation states.[22] That this explanation is overly simplistic follows from two observations. We are unable to isolate or detect as a long-lived species $CpCo(CN)(CO)$, although $CpCo(CN)_2^-$ is quite stable. Secondly, McKinney has prepared several $[CpCo^{II}(PR_3)_2]^+$ cations, including $[CpCo(PEt_3)_2]^+$, by one-electron oxidations of $CpCo(PR_3)_2$.[10] On the basis of these observations, we see no reason to believe that the Co^{II} state is any more accessible in reactions of **1** than it is in reactions of $CpCoL_2$ complexes with one or both L groups being σ-donor phosphines. Hence the fondness for apparent single-electron transfer on the part of **1** is somewhat puzzling. A reviewer has pointed out that simple Coulombic considerations may be important; i.e., because **1** is anionic, no charge separation is required for one-electron transfer, in contrast to the reaction involving neutral $CpCoL_2$. Another possibly significant difference between cyanide and phosphines is the ability of cyanide to serve as a bridging ligand, which may facilitate intermolecular redox or ligand disproportionation reactions by inner-sphere-type mechanisms.

The reaction of **1** with acetyl chloride is similar to the alkylation reactions already described, generating as the primary product a green, paramagnetic material that we have been unable to purify. In pleasant contrast, two acyl halides lacking α-hydrogens were found to produce a product derived from electrophilic attack at cyanide, yielding the novel complexes $CpCo[C{\equiv}NC({=}O)R]_2$ (**11**, R = *t*-Bu; **11b**, R = 1-adamantyl). Few acyl isocyanide metal complexes have been described, and most are of the type $M(CO)_5(CNCOR)$ or $M(\eta^6\text{-arene})(CO)_2(CNCOR)$.[23] The infrared spectra of these compounds show ν_{CN} bonds that are weak or undetectable. Just before our communication[1a] was published, details of another kind of bis(acyl isocyanide) complex, $FeTPP(CNCOR)_2$ (R = *t*-Bu, phenyl; TPP = tetraphenylporphyrin), became available.[24] These

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(16) Carter, S. J.; Foxman, B. M.; Stuhl, L. S. *Inorg. Chem.* **1986**, *25*, 2888.

(17) del Rosario, R.; Stuhl, L. S. *Organometallics* **1986**, *5*, 1260.

(18) Spencer, A.; Werner, H. *J. Organomet. Chem.* **1979**, *171*, 219.

(19) Werner, H.; Hofmann, W. *Chem. Ber.* **1977**, *110*, 3481.

(20) King, R. G. *Inorg. Chem.* **1967**, *6*, 25. Fischer, E. O.; Schneider, R. J. *J. Organomet. Chem.* **1968**, *12*, P27.

(21) Yamamoto, Y.; Mise, T.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2743.

(22) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; pp 113–4.

(23) Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2119. Simonneaux, G.; Le Maux, P.; Jaouen, G.; Dabard, R. *Inorg. Chem.* **1979**, *18*, 3167. Höfle, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *B30*, 982.

(24) Le Plouzennac, M.; Bondon, A.; Simonneaux, G. *Inorg. Chem.* **1984**, *23*, 4398.

porphyrin complexes show only a single band assignable to ν_{CN} in the IR at 2040 (R = Ph) and 2045 cm^{-1} (R = *t*-Bu), which are significantly higher than the double bands observed for **11a** (2017, 1922 cm^{-1}) and **11b** (2011, 1913 cm^{-1}). Of interest also, the carbonyl stretch for FeTPP(CO)$_2$ is similarly located at 2042 cm^{-1} and ν_{CN} for complexes of the type FeTPP (L)(CNCOR) (L = CO or pyridine) drops to 1970–1980 cm^{-1}. The difference in ν_{CN} between the porphyrin–acyl isocyanide complexes and compounds **11** can be ascribed to differences in oxidation state (Fe^{II} is a weaker π donor than is Co^{I}) and geometrical configuration (axial acyl isocyanide ligands in the iron complex vs C–Co–C angles in **11** probably near 90°).[25]

The C≡N stretching frequencies of **11a** and **11b** are considerably lower than those measured for the free acyl isocyanide ligands (2100 cm^{-1}),[26] demonstrating that there is extensive charge transfer from cobalt to the ligand with accompanying electron delocalization. The extensive back-bonding to the acyl isocyanide ligands in **11** is also evident from the significant drop in frequency of ν_{CO} relative to the free ligand (average $\Delta\nu$ = 60 cm^{-1} for **11a**). This is consistent with the conclusion of Simonneaux et al.[27] that the acyl isocyanide ligand possesses π-acceptor properties comparable to those of the carbonyl ligand.

In an effort to find other electrophiles which would provide isocyanide complexes from **1**, we briefly examined tosyl chloride and two organotin halides, R$_3$SnCl (R = Me, Ph). The delicate balance between competing pathways in the interaction of **1** with electrophiles is highlighted by these reactions. The reaction of tosyl chloride with **1b** is as complex as the reactions with alkyl and acyl halides. The isolable product in this case, however, is neither an isocyanide (sulfonyl isocyanide complexes are known[28]) nor a Co^{II} species (although unisolated paramagnetic complexes are probably present) but is instead a Co^{III} η^1-tosyl complex, **5a**. A comparison of the bands arising from the SO$_2$ group in the IR of **5a** (1041 and 1187 cm^{-1}) with those from several known (sulfonato)metal complexes[29] shows that the ligand is monodentate and sulfur bonded. **5a** is formally the product of oxidative addition to CpCo(CN)$^-$ derived from CO loss by **1**, followed by displacement of chloride by additional cyanide. The mechanism of formation must be more complicated, however. Our previous studies showed no evidence for CO lability in **1**,[1a] so simple oxidative addition to CpCo(CN)$^-$ can be ruled out.

The isolated yield of **5a** is low. This is partly due to the difficulty of its isolation, but spectroscopic evidence indicates that it is not the major product of the reaction in any case, accounting for not more than about 30% of the total cobalt content. IR spectroscopy suggests that the chief product in this reaction is a neutral bridging cyanide cyclopentadienylcobalt(III) oligomer or polymer with a combination of bridging (ν_{CN} 2164 cm^{-1}) and terminal (ν_{CN} 2119 cm^{-1}) cyanides and *S*-sulfinato ligands (ν_{SO} 1208, 1091, 1046 cm^{-1}) and, in the case of **4**, triphenylphosphines. Consistent with this, the ^{1}H NMR shows multiple Cp resonances.

In contrast to the above electrophiles, isocyanide formation can be made the dominant process in the reaction of **1** with R$_3$SnCl. Control of reaction conditions is crucial though, illustrating again the delicate balance between competing pathways in the reactions of **1** with electrophiles. Isocyanide formation is favored by low temperatures and by less polar solvents (THF). In acetonitrile, or on raising the reaction temperature in THF, the major products become the mixture of CpCo(CO)$_2$ and oxidized Co complexes characteristic of most of the other electrophilic attacks discussed above. The lability of the product from the Ph$_3$SnCl reaction, **6**, and the even less stable Me$_3$SnCl-derived product have prevented more detailed studies of these tin isocyanide complexes and their formation reactions.

Identification of **6** as an isocyanide rests mainly on its IR spectrum. The cyanide stretching frequency of **6** at 2053 cm^{-1} in the IR and that of the analogous unisolated trimethyltin isocyanide complex at 2063 cm^{-1} are in close agreement with two iron complexes previously reported: Fe(CO)$_2$(CNSnMe$_3$)(η^4-C$_4$H$_6$), ν_{CN} 2070 (s) cm^{-1}; Fe(CO)$_2$(CNSeMe$_3$)(η^4-C$_5$H$_8$), ν_{CN} 2059 (s) cm^{-1}.[30] For both **6** and its trimethyltin analogue, the shared carbonyl stretching frequency of 1904 cm^{-1} and position of the Cp resonance in the proton NMR spectrum at δ 4.58 relative to those of compounds **1** suggest that there has been relatively little effect on the electron distribution in the molecule as a result of isocyanide formation. The analytical data for crystalline **6** indicate the presence of equimolar PPNCl. It is possible that this chloride is actually a part of the complex, interacting with cobalt or tin. The available data do not address this situation. Unfortunately, **6** is unstable in solution, preventing us from pursuing this point. The sensitivity of R$_3$MN≡C complexes (M = Sn, Ge, Si) has been noted before.[31]

CpCo(CO)$_2$ is a basic metal carbonyl.[32] This is exemplified by its reactions with mercuric halides to form Lewis acid–base complexes Cp(OC)$_2$Co·HgX$_2$, containing a Co→Hg dative bond.[33] The negative charge of **1** and the σ-donor strength of its CN ligand should make **1** a substantially stronger Lewis base than CpCo(CO)$_2$. But the dative bond represents only a midpoint in a range of interactions, one extreme limit of which would be complete electron transfer. If the donor component is made a stronger base, this could make the acid-base complex unstable with respect to further electron transfer. This is what is observed for **1**. Reaction of **1** with HgCl$_2$ results in formation of a dark red-brown solution and elemental mercury (reaction 9). The strongest IR absorptions in the

$$\underset{\mathbf{1}}{[\mathrm{CpCo(CN)(CO)}]^-} + \mathrm{HgCl_2} \rightarrow \mathrm{Hg^0} + \mathrm{CpCo(CO)_2} + \mathrm{Co^{III}}\ \text{oligomers} \quad (9)$$

filtered reaction mixture are those of CpCo(CO)$_2$. Bands possibly assignable as ν_{CN} are observed as high as 2164 cm^{-1}, well into the linear-bridging cyanide region. No tractable product could be isolated. Consistent with the observation of metallic mercury as a product, the major reaction process appears to be a two-electron oxidation. The one-electron oxidant AgBF$_4$ also oxidizes **1**, but the reaction mixture is green with IR bands at 2022 and 1952 cm^{-1}. No tractable solid product was obtained. These results are in sharp contrast to the behavior of CpCo(PMe$_3$)$_2$, which in spite of its high basicity does form a complex with HgCl$_2$, albeit a very unstable one.[34] Perhaps

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[25] Carter, S. J.; Foxman, B. M.; Stuhl, L. S. *Organometallics* **1986**, *5*, 1918.

[26] Höfle, G.; Lange, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 262.

[27] Saillard, J. Y.; Le Beuze, A.; Simonneaux, G.; Le Maux, P.; Jaouen, G. *J. Mol. Struct.* (*THEOCHEM*) **1981**, *86*, 149.

[28] Höfler, M.; Löwenich, H. *Chem. Ber.* **1982**, *115*, 2423.

[29] Vitzhum, G.; Lindner, E. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 315.

[30] Behrens, H.; Moll, M.; Popp, W.; Seibold, H. J.; Sepp, E.; Würstl, P. *J. Organomet. Chem.* **1980**, *192*, 389.

[31] Treichel, P. M.; Shaw, D. B. *J. Organomet. Chem.* **1977**, *139*, 21.

[32] Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653. Cf. also ref 9b.

[33] Nowell, I. W.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1972**, 2393.

[34] Dey, K.; Werner, H. *Chem. Ber.* **1979**, *112*, 823.

the cyanide ligand provides a "conductive pathway" to facilitate electron transfer.

Oxidation Reactions. Synthesis of $CpCo^{II\ or\ III}$ Complexes. In contrast to the reaction with $HgCl_2$, the use of an oxidant that can also serve as a ligand donor (as demonstrated by McKinney[10]) permits a clean reaction. The reaction of $Hg(CN)_2$ with 1 provides a convenient, high-yield synthesis of the K·crown salt of $[CpCo(CN)_3]^-$.

Similarly, reaction of $Hg(CN)_2$ with $CpCo(CO)PPh_3$ appears to be the best available synthesis of $CpCo(CN)_2PPh_3$. The two literature syntheses[10,13] of this compound are not as readily scaled up, and in one case[10] the reaction starting material is not as conveniently prepared.

Having observed the low-yield formation of the acyl isocyanide complexes **11** from **1**, we thought that these compounds might be more readily prepared by acylation of a higher oxidation state CpCo cyanide complex followed by reduction. This approach would minimize complications from electron transfer but might fail for lack of sufficient nucleophilicity of cyanide coordinated to such a high oxidation state metal. Attempts to acylate either of the Co^{III} complexes **7** and **8** were unsuccessful. We then examined the reduction of **7** and **8**, in the hope that a Co^{II} cyanide would provide the necessary balance between sufficient nucleophilicity and minimal electron-transfer ability.

McKinney[10] has reported on the synthesis of a variety of 17-electron $[CpCoL_2]^+$ and CpCoLX complexes via oxidation of Co^I precursors but was unable to prepare a $CpCo^{II}$ complex containing cyanide, obtaining **8** instead. We found that alkali-metal amalgams reduce **7** and **8** to a novel Co^{II} complex, **10**. As is true for many metals, cyanide stabilizes the +3 oxidation state of cobalt more than it does the +2 state.[35] Thus it is not surprising that McKinney's oxidative approach was unsuccessful while the reductive route is straightforward. What is perhaps most interesting about the synthesis of **10** from **8** is that PPh_3 is lost in preference to cyanide. This could be the result of steric factors but probably also reflects the strength of the Co–C bond. As with the Co^{II} complexes prepared by McKinney, **10** shows no evidence for dimerization in solution. The reduced steric resistance to dimerization of **10** relative to the $CpCo(PPh_3)X$ complexes is undoubtedly counterbalanced by the Coulombic repulsion associated with the negative charge of **10**.

In contrast to **7** and **8**, **10** reacts rapidly with 2 equiv of 1-adamantanecarbonyl chloride. Unfortunately, there is no evidence for the formation of the expected product $[CpCo(CNCOAd)_2]^+$ (Ad = 1-adamantyl). A very low yield of the Co^I complex **11b** is obtained instead, along with intractable oxidized material. Attempts to improve the yield of **11b** by carrying out the reaction in the presence of reducing agents such as metallic zinc or manganese were unsuccessful. The observation of a Co^I product from this reaction raises the possibility that the Co^{II} acyl isocyanide target molecule or an intermediate in its formation such as CpCo(CN)(CNCOAd) may be unstable with respect to disproportionation to **11b** and a Co^{III} cyanide species. Disproportionation of Co^{II} in the presence of strong π-acceptors is well-known, especially when ligands capable of stabilizing Co^{III} are also present in the reaction. An especially relevant example is the reaction of $Co(CN)_5{}^{3-}$ with CO:[36]

$$2[Co(CN)_5]^{3-} + 2CO \rightarrow [Co(CN)_6]^{3-} + [Co(CN)_3(CO)_2]^{2-} + CN^- \quad (10)$$

Reactions of 1 with Nucleophiles and Reducing Reagents. In contrast to the varied reactivity of **1** toward electrophiles and electron acceptors, **1** is relatively unreactive with nucleophiles and reducing agents. As previously described,[1a] nucleophiles such as phosphines and alkynes, which would be expected to bind to cobalt, do so by displacing cyanide. In the case of PPh_3, under a variety of conditions this process is an equilibrium, with the side of free phosphine and **1** favored under a variety of conditions:

$$[CpCo(CN)(CO)]^- + PPh_3 \rightleftharpoons CpCo(CO)(PPh_3) + CN^- \quad (11)$$

Thus the Co^I–CN interaction is not inherently weak.

With nucleophiles which might be expected to attack metal-coordinated carbon, either at CO or CN, no reaction with **1** is observed. The nucleophiles tested include $BHEt_3{}^-$, PhLi, and Me_3NO. This result is not surprising given the electron-rich nature of the metal center in **1**. Activation of coordinated CO toward nucleophilic attack is well-known to require an electron-deficient metal center.[37] Compound **1** is inert to potassium amalgam and shows no cyclic voltammetric reduction wave out to the solvent limit in 0.1 M Bu_4BF_4/MeCN at a Pt electrode.

Conclusions

This study is the most extensive examination of low-valent cobalt cyanide chemistry conducted to date. Several important conclusions can be drawn from it. One is the interesting, albeit disappointing from the synthesis standpoint, discovery of the nongenerality of cyanide ligand alkylation as applied to low-valent complexes such as these. We had hoped that the low-valent cyanide complexes would provide a convenient entry to a wide range of isocyanide complexes, including unusual ones not accessible by direct substitution methods. This hypothesis proved true to a very limited extent in the syntheses of compounds **11**, but we have since shown that these compounds can be and are better prepared by direct substitution. Where the free isocyanide is apparently inaccessible, as in the case of sulfonyl isocyanides,[28] we were also largely unsuccessful in preparing the coordinated ligand via electrophilic attack on cyanide. It is obvious from the nature of the complex product mixtures obtained, and their sensitivity to reaction conditions, that, for **1**, electrophilic attack on coordinated cyanide is just one of several strongly competitive reaction pathways for electrophiles. Our similar experiences with $[(\eta^2\text{-PhC}{\equiv}\text{CPh})Ni(CN)_2]^{2-}$ imply that this will be a fairly general difficulty with the use of low-valent cyanide complexes as nucleophiles. Whether these problems can be overcome by adjusting the electron richness of the metal center, e.g. through the use of a strongly bound, more electron-withdrawing analogue of Cp, remains an unanswered question.

A second conclusion is one noted in our preliminary communication: the lability of the cyanide ligand in **1**.[1a] There are undoubtedly several factors contributing to this. The much poorer π-acceptance of CN^- vs CO should make the $CpCoCN^-$ fragment higher in energy than the corresponding carbonyl-containing unit. At first glance CN^- and CO appear to have identical steric demands, but it is worth remembering that **1** is probably strongly ion-paired in solution, and the site of binding is almost certainly cyanide.[38] Thus, at least for the fraction of molecules which

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[35] Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic: London, 1972; p 171.

[36] Halpern, J.; Pribanic, M. *J. Am. Chem. Soc.* **1971**, *93*, 96.

[37] Koelle, U. *J. Organomet. Chem.* **1977**, *133*, 53. Blumer, D. J.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71.

[38] Darensbourg, M. Y.; Barros, H. L. C. *Inorg. Chem.* **1979**, *18*, 3286.

are tight ion pairs, the cyanide ligand should be viewed as CN plus counterion. Hence, in terms of steric demands, it is more like an isocyanide RN≡C with a bulky R group. The equilibrium data presented earlier[1a] show that the Co–CN$^-$ bond is not at all weak, but cyanide is vastly less effective than CO in stabilizing a Co^{I} center.

It is surprising that the effect of the cyanide ligand in 1 can be understood entirely in terms of cyanide's σ-donor strength. The π-acceptor ability of cyanide is well-established. We expected that the combination of a univalent metal center and an inherently electron-rich molecular arrangement would result in the π-acceptor ability of cyanide being called into play to take some of the back-bonding burden off of the remaining carbonyl. There is not evidence for this occurring. Instead, the carbonyl remains the electron sink for the molecule (as judged from the IR data), and the cyanide acts to substantially increase the basicity of the molecule relative to already relatively basic $CpCo(CO)_2$. Perhaps there is a mismatch of orbital energies which prevents cyanide from manifesting its π-acceptor ability in carbonyl complexes such as 1, even though cyanide is clearly a significant π-acceptor in complexes such as $K_4Ni(CN)_4$, $K_5Mn(CN)_6$, and (K-crown)$_2$[(η^2-PhC≡CPh)Ni(CN)$_2$].

Experimental Section

General Information. All experimental work was conducted under nitrogen in a Vacuum Atmospheres Dri-Lab glovebox or by Schlenk techniques, unless otherwise stated. Flash chromatography was carried out by using the flash chromatography method developed by Still et al.,[39] with a small regulated nitrogen tank serving as pressure source in the glovebox. Specific chromatographic steps involving this method are marked thus: (FC). Melting points were determined in sealed capillaries under nitrogen. IR spectra were recorded on a Perkin-Elmer 683 spectrometer interfaced to a Perkin-Elmer 3500 data station. Calibration was achieved routinely with polystyrene and monitored periodically by using $K_3[Co(CN)_6]$. The precision of wavenumber measurements averaged ±2 cm^{-1}. Spectra are reported as mineral oil mulls with cation peaks omitted except where stated otherwise. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained by using a Varian EM390 and a locally modified Bruker WH90 FT spectrometer, respectively. Mass spectra were recorded on a Hewlett-Packard Model 5985 mass spectrometer in EI (70-eV) or CI (10-eV) mode (reagent gas: methane).

Cyclic voltammetry was performed by using an IBM cell under argon, an EG&G PAR Model 173 potentiostat/galvanostat and Model 175 Universal Programmer, and Bascom-Turner electronic digital recorder. The working electrode was a glassy carbon disk (IBM Instruments). Potentials were measured versus a silver wire quasi-reference electrode and related to ferrocene which was used as an external standard. Electronic *iR* compensation was not used; instead the apparent peak separation of ferrocene at the scan rate of interest (generally 200 mV/s) was taken as the criterion for Nerstian reversibility. Solutions were 0.1 M in Bu_4NBF_4 supporting electrolyte (Southwestern Analytical) and 1.0×10^{-3} M in compound under study. Formal potentials are reported vs NHE by assuming a value of 0.40 V for the ferrocene/ferrocenium couple.[40]

Magnetic susceptibilities were determined according to the method of Evans.[41] Elemental analyses were carried out by Galbraith Labs, Knoxville, Tennessee or Microlytics Inc., S. Deerfield, MA.

Solvents and Reagents. *n*-Hexane and *n*-heptane were stirred with concentrated H_2SO_4 for 2 days and heated to reflux with CaH_2 for 1 day before distillation. Toluene, diethyl ether, and THF were distilled from sodium/benzophenone. Acetonitrile and dichloromethane were distilled from P_4O_{10} (acetonitrile was predried with anhydrous K_2CO_3). DMF (Burdick & Jackson) was stirred with freshly activated 3-Å molecular sieves, filtered through a fine frit, and passed through a column of neutral super alumina (I) (Woelm). Acetone (reagent grade) was dried by stirring with boric oxide (Alfa, 99.99%) for 24 h (0.7 g/100 mL), followed by reflux for 2 h and distillation. *n*-Butyronitrile (Aldrich) was purified by a published procedure.[42] Other solvents (with the exception of chloroform) were HPLC grade. DMF-d_7 and CD_3CN were stirred with 3-Å sieves for 2 days and distilled in vacuo. THF-d_8 was dried as for the protio form but distilled in vacuo. C_6D_6 was dried with CaH_2.

18-Crown-6 ether (Aldrich) was recrystallized from acetonitrile and dried for 2 days in vacuo. KCN (Fisher) was purified by a literature method,[43] washed several times with ether, and dried in vacuo for 2 days at 60°. $(Bu_4N)CN$ (Fluka) was recrystallized from hot THF and dried in vacuo for 24 h at 50 °C. $(Et_3MeN)CN$,[44] (K-crown)CN,[45] and (PPN)CN[46] were prepared by published procedures ((PPN)CN: mp 247.5–249.5 °C;[16] Cl, <0.01%). Tosyl chloride (Aldrich), triphenyltin chloride (Alfa), and triphenylphosphine (Strem) were recrystallized from chloroform, toluene/*n*-hexane (1:1, v/v), and ether respectively. Trimethylamine *N*-oxide dihydrate (Aldrich) was dried by heating to reflux in benzene for 18 h (removing the water by use of a Dean-Stark trap) with subsequent cooling to 4 °C for 8 h. After the anhydrous material was collected by filtration, it was sublimed (110 °C, 2×10^{-2} Torr). Activated zinc was prepared by either acid washing of the powder[47] or reduction of $ZnBr_2$ by potassium.[48] Pivaloyl chloride, acetyl chloride, and benzyl bromide (all from Aldrich) were distilled in vacuo prior to use. Collidine (Aldrich) was stirred over KOH for 3 days and distilled in vacuo. Octadecylsilica and cyanopropylsilica (flash chromatography grade) were obtained from Baker. (K-crown)CN–silica was prepared by a published method.[49] $CpCo(\eta^2-C_2H_4)$,[50] $CpCo(CO)_2$,[51] and $CpCo(CO)(PPh_3)$[52] were synthesized by literature procedures (in the preparation of the latter compound, *n*-heptane was substituted for methylcyclohexane which with additional cooling to −35 °C after the reaction provided a yield of 94%). $CpCo(PPh_3)_2$ and $P(OCH_2)_3CCH_3$ were gifts from Prof. A. Stolzenberg and Prof. M. Rosenblum (Brandeis University), respectively. All other chemicals were commercial products, used as received.

Caution: Most cyanides are severe poisons. Gloves must be worn and an efficient hood used when handling these materials. Cleanup of glassware and disposal of reaction wastes and washings should be done carefully with emphasis on the avoidance of HCN generation by keeping the pH of washing liquids in the alkaline range. Consult with pertinent officials to arrange for safe disposal of residues.

Synthesis of (K-crown)[Cp(CN)(CO)] (1a). A solution of 6.9 g (38.3 mmol) of $CpCo(CO)_2$, 3.75 g (57.45 mmol) of KCN and 12.14 g (45.96 mmol) of crown ether in 100 mL acetonitrile was stirred for 2 days and then filtered. The filtrate was reduced in volume until crystals appeared, at which point about 5–10 mL of acetonitrile was added (until all the crystals were dissolved). Ether (100 mL) was then added slowly and the solution cooled to −35 °C. After 24 h the dark red crystals were collected by filtration, washed with 3 × 20 mL of ether, and allowed to dry on the frit for 5 min: yield, 15.22 g (82.5%); mp 197–199 °C; IR 2066 (s), 1885 (s), 1841 (w), 1411 (w)*, 1368 (sh)*, 1350 (s)*, 1285 (m)*, 1250 (m)*, 1238 (m)*, 1150 (sh), 1135 (sh)*, 1105 (vs)*, 1060

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(39) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(40) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(41) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(42) Coetzee, J. F.; Padmanacham, G. R. *J. Phys. Chem.* **1962**, *66*, 1708. As for acetonitrile purification, method C, Experimental Section.

(43) Brown, G. H.; Adisech, S. R.; Taylor, J. E. *J. Phys. Chem.* **1962**, *66*, 170.

(44) Kobler, H.; Munz, R.; Gasser, G. A.; Simchen, G. *Liebigs Ann. Chem.* **1978**, 1937.

(45) Livinghouse, T. *Org. Synth.* **1981**, *60*, 126.

(46) Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 645.

(47) Shriner, R. L.; Neumann, F. W. *Organic Syntheses*; Wiley: New York, 1965; Coll. Vol. 3, p 73.

(48) Riecke, R. D.; Uhm, S. J.; Hadnall, P. M. *J. Chem. Soc., Chem. Commun.* **1973**, 269.

(49) Carter, S. J.; Stuhl, L. S. *J. Chromatogr.* **1984**, *291*, 348.

(50) Jonas, V. K.; Deffense, E.; Habermann, D. *Angew. Chem. Suppl.* **1983**, 1005.

(51) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888.

(52) King, R. B. *Inorg. Chem.* **1966**, *5*, 82.

(sh), 1022 (w), 992 (w), 968 (s)*, 842 (m)*, 800 (m), 772 (w), 608 (m), 587 (m), 538 (w)*, 520 (m), 462 (w), 438 (w) cm^{-1} (frequencies with an asterisk assigned to crown ether). IR (acetonitrile) 2066 (ν_{CN}, s), 1891 (ν_{CO}, s) cm^{-1}; ^{1}H NMR (CD_3CN) δ 4.61 (s, 5 H, Cp), 3.63 (s, 24 H, crown ether); $^{13}C\{^1H\}$ NMR (DMF-d_7, -45 °C) δ 70.4 (s, crown), 81.4 (s, Cp), 145.0 (s, br, CN), 211.5 (s, br, CO). Anal. Calcd for $C_{19}H_{29}O_7NKCo$: C, 47.40; H, 6.07; N, 2.91. Found: C, 47.24; H, 6.18; N, 3.00.

Synthesis of (PPN)[Cp(CN)(CO)] (1b). $CpCo(CO)_2$ (1.75 g, 9.70 mmol) and 6.56 g (11.62 mmol) of (PPN)CN were dissolved in 50 mL of acetonitrile and left to stand for 2 days. The solvent was removed and the residue crystallized from acetonitrile/ether (approximately 1:1.5, v/v) by cooling to -35 °C for 1 day. The red-brown crystals were collected by vacuum filtration and washed with 3 × 10 mL of ether before drying on the frit for 5 min: yield 6.16 g (88.6%); mp 189–190 °C; IR 2062 (s), 1893 (s) cm^{-1}; ^{1}H NMR (CD_3CN) δ 7.7–7.4 (m, 30 H), 4.59 (s, 5 H). Anal. Calcd for $C_{43}H_{35}ON_2P_2Co$: C, 72.02; H, 4.92; N, 3.90. Found: C, 71.49; H, 4.98; N, 4.16.

Synthesis of (K-crown)[CpCo(CN)PPh$_3$] (4). A solution of 0.53 g (0.82 mmol) of $CpCo(PPh_3)_2$ and 285 mg (0.86 mmol) of (K-crown)CN in 20 mL of acetonitrile was stirred for 2 h. The solvent was then removed by reduced pressure until a thick oil remained, at which point 30 mL of toluene was added. The flask was swirled for 30 s and then cooled to -35 °C for 15 min. The crude product was collected by vacuum filtration, washed with 2 × 5 mL of ether, and recrystallized from acetonitrile/ether in two successive batches by cooling to -35 °C. Each batch of crystals was washed with 1 × 5 mL ether, and dried on the frit for 5 min; total yield, 390 mg (75%) of purple-black crystals; mp 169–171 °C; IR 2014 (s), 1353 (m)*, 1284 (w)*, 1251 (w)*, 1103 (s)*, 1028 (w), 1008 (w), 962 (s)*, 863 (w)*, 836 (s), 753 (s), 743 (m), 698 (s), 538 (s), 524 (s), 492 (m), 473 (w), 453 (w), 444 (w), 426 (w) cm^{-1} (the asterisk denotes bands assignable to crown ether); ^{1}H NMR (CD_3CN) δ 7.7 (m, 6 H, *o*-Ph), 7.2 (m, 9 H, *m,p*-Ph), 4.09 (s, 5 H, Cp), 3.59 (s, 24 H, crown). Anal. Calcd for $C_{36}H_{44}O_6NPKCo$: C, 60.41; H, 6.20; N, 2.00. Found: C, 60.37; H, 6.24; N, 1.98.

Reaction of (PPN)[Cp(CN)(CO)] with Tosyl Chloride: Isolation of (PPN)[CpCo(CN)$_2$(η^1-SO$_2$C$_6$H$_4$CH$_3$)] (5a). A cooled solution (-20 °C) of 0.84 g (4.39 mmol) of tosyl chloride in 100 mL of THF was transferred to a flask containing 3 g (4.19 mmol) of (PPN)[Cp(CN)(CO)]. After being stirred for 2 h at this temperature (-20 °C), the flask contents were allowed to rise to room temperature. Stirring was continued for another hour before cooling the reaction mixture to -35 °C. Vacuum filtration a day later gave a red solution and a green viscous oil which solidified when washed with 2 × 10 mL of ether. The solid material was washed with successive 3-mL portions of acetonitrile until an orange residue remained, which was finally washed with 1 × 5 mL of ether and dried on the frit. Weight: 250 mg (7%). A small portion of the orange crystals was recrystallized by cooling from hot acetonitrile, followed by ether addition, for elemental and spectroscopic analysis: mp 214–216 °C; IR 2117 (m), 1587 (w), 1187 (m), 1041 (s), 842 (w), 829 (w), 814 (w) cm^{-1} (bands arising from phenyl groups are omitted); ^{1}H NMR (CD_3CN) δ 7.3–7.7 (m, 32 H, Ph), 7.12 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, $SO_2C_6H_4$), 5.02 (s, 5 H, Cp), 2.35 (s, 3 H, CH_3). Anal. Calcd for $C_{50}H_{42}N_3O_2PSCo$: C, 69.04; H, 4.87; N, 4.83; S, 3.69. Found: C, 69.24; H, 4.99; N, 5.03; S, 3.76.

Synthesis of CpCo(CO)(CNSnPh$_3$)·(PPN)Cl (6). THF was precooled to -30 °C, and 60 mL was added to a flask containing 2 g (2.79 mmol) of (PPN)[Cp(CN)(CO)] and 1.13 g (2.93 mmol) of $SnPh_3Cl$ cooled to the same temperature. The reaction mixture was stirred for 1 h as the temperature was slowly raised to -20 °C and then a further hour as the temperature was raised to room temperature. A pale red solution with a white precipitate formed during this time. The contents of the flask were then cooled to -35 °C for 1 day before filtering. The solvent was stripped from the filtrate and the residue dissolved in hot THF. The cloudy solution was slowly cooled to room temperature and filtered and 10 mL of ether added before cooling to -35 °C. Vacuum filtration 24 h later yielded 1.32 g of orange microcrystals. The mother liquor was concentrated, more ether added, and the solution cooled again to produce a second crop of crystals (0.16 g). The material was combined, recrystallized again from hot THF, and dried at 50 °C for 1 day in vacuo. Yield, based upon a [CpCo(CO)(CNSnPh$_3$)]·(PPN)Cl formulation, was 49%: mp 161–163 °C. IR 2053 (s), 1904 (s). ^{1}H NMR (THF-d_8) δ 8.3 (m, 6 H), 7.7–7.3 (m, 30 H), 7.1 (m, 9 H), 4.58 (s, 5 H). Anal. Calcd for $C_{61}H_{50}N_2OClP_2SnCo$: C, 66.48; H, 4.57; N, 2.54; Cl, 3.22. Found: C, 66.40 (duplicate analyses: 65.06, 67.73); H, 4.51 (duplicate analyses: 4.05, 4.96); N, 2.24; Cl, 3.15.

Reaction of (K-crown)[Cp(CN)(CO)] with Pivaloyl Chloride: Isolation of CpCo(CNCOC$_4$H$_9$)$_2$ (11a). A solution of 0.4 g (3.28 mmol) of pivaloyl chloride in 50 mL of THF that had been purged with nitrogen for 20 min was brought into the glovebox and added to 1.5 g (3.12 mmol) of (K-crown)[CpCo(CO)(CN)]. The reactants were stirred for 5 h and then cooled to -35 °C for 16 h. Filtration gave a red solution which was stripped of solvent. The residue was dissolved in toluene and applied to a 2.2 × 20 cm column packed with silica. When toluene had eluted a faint red-brown band, the solvent composition was switched to toluene/ether (2:1, v/v). A deep red-brown band then eluted which was collected until the color of the band at the bottom of the column was green-brown. The solvent was removed from the fraction and the material dissolved in *n*-hexane and applied to a 2.2 × 20 cm column packed with cyanopropylsilica (FC). *n*-Hexane eluted a pale orange followed by a pale green band after which the solvent composition was changed to *n*-hexane/toluene (2:1, v/v). A red band then eluted, which was stripped of solvent, and the material left crystallized from ether by cooling to -35 °C. One day later, orange-red crystals were collected by vacuum filtration and dried in vacuo for 18 h: yield, 95 mg (9.5%); mp 63–64 °C; IR 2017 (s), 1922 (s), 1716 (s), 1700 (s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.70 (s, 5 H), 1.09 (s, 18 H); CIMS (CH_4), *m/z* (relative intensity) 375 [11.7, $(M + C_2H_5)^+$], 347 [100, $(M + H)^+$], 346 [54.2, $(M)^+$], 290 [1.0, $(M + H - C_4H_9)^+$], 263 [15.5, $(M + 2H - COC_4H_9)^+$ or $(M - C_4H_9 - CN)^+$]. Anal. Calcd for $C_{17}H_{23}N_2O_2Co$: C, 58.96; H, 6.69; N, 8.09. Found: C, 59.13; H, 6.72; N, 8.05.

Reaction of (K-crown)[,cp(CN)(CO)] with 1-Adamantanecarbonyl Chloride: Isolation of CpCo(CNCOAd)$_2$ (11b). In 50 mL of acetonitrile were dissolved 1.5 g (3.12 mmol) of (K-crown)[CpCo(CO)(CN)] and 0.62 g (3.12 mmol) of 1-adamantanecarbonyl chloride. The reaction mixture was stirred for 8 h. The solvent was removed by reduced pressure and the residue extracted with 3 × 15 mL of *n*-hexane. After concentration, the *n*-hexane extract was diluted with an equal volume of toluene and applied to a 2.2 × 20 cm column packed with silica. A dark red band eluted with *n*-hexane/toluene (1:1, v/v). Collection of the fraction was terminated when the color of the band at the bottom of the column had turned brown. The solvent from this fraction was removed and the material redissolved in *n*-hexane. The solution was chromatographed down a 2.2 × 20 cm cyanopropylsilane–silica column (FC). Elution with *n*-hexane yielded a pale orange followed by a pale green band, at which point the eluant was switched to *n*-hexane/toluene (2:1, v/v). A red band was then collected that was subsequently stripped of solvent. The material was crystallized from ether by cooling to -35 °C for 1 day to yield 110 mg of red-brown microcrystals (7%): mp 130–131 °C; IR 2032 (sh), 2011 (s), 1913 (s), 1708 (s), 1688 (s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.78 (s, 5 H), 1.89 (s, 18 H), 1.53 (s, 12 H); CIMS (CH_4), *m/z* (relative intensity) 531 [0.3, $(M + C_2H_5)^+$], 503 [4.1, $(M + H)^+$], 502 [2.0, $(M)^+$], 341 [16.7, $(M + 2H - COAd)^+$ or $(M - Ad - CN)^+$], 163 [44.1, $AdCO^+$], 135 [100, Ad^+]. Anal. Calcd for $C_{29}H_{35}N_2O_2Co$: C, 69.31; H, 7.01; N, 5.57; Co, 11.72. Found: C, 68.85; H, 7.07; N, 5.52; Co, 11.45.

Synthesis of (K-crown)[CpCo(CN)$_3$]. Five grams (10.38 mmol) of (K-crown)[Cp(CN)(CO)], dissolved in 70 mL of acetonitrile, was slowly added dropwise over a period of 5 min to a warm solution (~40 °C) of 2.62 g (10.38 mmol) of $Hg(CN)_2$ in 75 mL of acetonitrile, contained in a 250-mL Schlenk flask under nitrogen. After the addition, the flask was flushed with nitrogen for 5 min to remove any traces of CO before opening to the atmosphere (provision for a nitrogen inlet and check valve must be made to vent the CO formed during the reaction). After the mixture was filtered to separate the mercury, 100 mL ether was added and the solution cooled to -20 °C for 1 day. The yellow precipitate was collected by vacuum filtration, washed with 2 × 20 mL of ether, and dried on the frit for 20 min. The mother liquid was concentrated until crystals appeared, at which point 100 mL of more ether was added and the cooling process repeated to produce a second crop of microcrystals: total yield, 4.96 g (94.6%); mp 246 °C dec; IR 2117 (s, ν_{CN}) cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.20 (s, 5 H), 3.63 (s, 24 H). Anal. Calcd for $C_{20}H_{29}N_3O_6CoK$: C, 47.52; H, 5.78; N, 8.31. Found: C, 47.47; H, 5.73; N, 8.27.

Synthesis of $CpCo(CN)_2PPh_3$. A solution of 20 g (48.3 mmol) of $CpCo(CO)PPh_3$ in 150 mL of acetonitrile was loaded into a 500-mL three-necked round-bottomed flask equipped with stir bar, nitrogen inlet adapter, septum, and Schlenk addition tube containing 12.23 g (48.3 mmol) of $Hg(CN)_2$. After the nitrogen inlet adapter was connected to a standard nitrogen/vacuum manifold/oil bubbler/check valve assembly, the mercuric cyanide was added over a period of 15 min so as to ensure steady CO evolution. Nitrogen was then swept through the flask to remove any CO remaining before the flask was opened to the atmosphere. The solvent was removed by reduced pressure and the brown residue extracted with successive portions of boiling methanol (5 × 200 mL), filtering each portion to separate any mercury. The filtrates were combined, reduced in volume to about 800 mL, and cooled to −20 °C for 1 day. This process yielded 16.785 g of yellow-orange needlelike crystals that were collected by filtration, washed with ether, and dried on the frit for 15 min. A second batch of crystals (1.2 g) was afforded by concentrating the mother liquor to 100 mL, heating to redissolve any precipitated solids, and cooling to −20 °C: total yield, 85%; IR 2123 (s), 2117 (s) cm^{-1} (lit.[13a] 2120, 2110 cm^{-1}).

Attempted Acetylation of $CpCo(CN)_2PPh_3$: Isolation of $CpCo(CN)(CN{\cdot}BF_3)PPh_3$. In 100 mL of dichloromethane under nitrogen, 0.8 g (1.82 mmol) of $CpCo(CN)_2PPh_3$, 2.0 g (25.2 mmol) of acetyl chloride, and 0.9 g (4.56 mmol) of $AgBF_4$ were heated to reflux for 36 h. After the solution was cooled to room temperature, the solvent was removed and the residue extracted with 2 × 25 mL of hot acetonitrile. The extract was filtered, concentrated to about 15 mL, and heated to redissolve any precipitated material. After the solution was cooled to −20 °C for 18 h, 0.73 g of orange crystals was collected by filtration, washed with a little ether, and dried on frit for 10 min. The crystals were identified as $CpCo(CN)(CN{\cdot}BF_3)PPh_3$ by spectroscopy and elemental analysis (yield 79%, based on cobalt): mp 230 °C dec; IR 2204 (s), 2126 (m), 1306 (w), 1190 (w), 1165 (sh), 1122 (s), 1090 (s), 1030 (sh), 998 (m), 908 (sh), 882 (s), 858 (w), 834 (w), 765 (w), 749 (m), 709 (m), 698 (m), 560 (m), 536 (s), 516 (m), 508 (w), 477 (w), 456 (w), 426 (vw) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.7–7.4 (m, 15 H), 5.24 (s, 5 H). Anal. Calcd for $C_{25}H_{20}N_2PBF_3Co$: C, 59.32; H, 3.98; N, 5.53; P, 6.12; Co, 11.64. Found: C, 59.66; H, 3.94; N, 5.62; P, 6.35; Co, 11.47.

Synthesis of (K-crown)[$CpCo(CN)_2$] (10a). One gram (2.28 mmol) of $CpCo(CN)_2PPh_3$ and 0.605 g (2.28 mmol) of crown ether were stirred in 50 mL of acetonitrile to give a yellow suspension. Following the addition of 0.095 mg (2.4 mmol) of potassium (as a 1% amalgam) to the suspension, an almost immediate darkening in color took place. The color intensified concomitant with clearing to give a dark brown solution. After 90 min, the mercury was separated, the solution filtered, and solvent removed from the filtrate. The residue was washed with 2 × 10 mL of ether and 1 × 10 mL of acetonitrile. The acetonitrile fraction was filtered and the solvent removed by reduced pressure. The crude material was crystallized from 3–4 mL of hot acetonitrile by cooling to −35 °C. One day later, the dark brown crystals were collected by vacuum filtration and washed with 1 × 2 mL of acetonitrile/THF (1:2, v/v) and 1 × 5 mL of ether before drying on the frit for 5 min. The mother liquor was concentrated and cooled again to give a smaller second crop of crystals. Total weight: 0.84 g (76%). A small portion of the compound was recrystallized from acetonitrile for elemental analysis and magnetic moment determination: mp 190–192 °C; IR 2098 (vs), 815 (s), 790 (w), 408 (w) cm^{-1}; magnetic susceptibility (CD_3CN), 3.03×10^{-6}, $\mu_{eff} = 1.86\ \mu_B$ (25 °C). Anal. Calcd for $C_{19}H_{29}N_2O_6CoK$: C, 47.59; H, 6.10; N, 5.84. Found: C, 47.61; H, 6.26; N, 5.95.

Reaction of (K-crown)[$CpCo(CN)_2$] and Potassium Anthracene Radical Anion. In 40 mL of THF were stirred 0.445 g (2.28 mmol) of anthracene and 0.09 g (2.28 mmol) of potassium for 16 h, creating a dark blue solution. A solution of 0.5 g (1.04 mmol) of (K-crown)[$CpCo(CN)_2$] and 0.275 g (1.04 mmol) of crown ether in 50 mL of DMF was cooled to −40 °C. The radical anion solution was then added dropwise over a period of 20 min to the stirred DMF solution (a dark black-brown color formed initially) until the color of the DMF solution changed to deep blue, at which point the addition was terminated. The solvent was immediately removed. The oily residue was extracted with 3 × 10 mL of THF. The extracts were filtered and cooled to −35 °C. Filtration gave 300 mg of a purple-black powder tentatively identified as K_2[$CpCo(CN)_2$]: IR 3080 (sh), 2003 (vs), 1950 (vs), 768 (w) cm^{-1}.

Reaction of (K-crown)[Cp(CN)(CO)] with Triphenylphosphine. Under nitrogen, 500 mg (1.04 mmol) of (K-crown)[Cp(CN)(CO)] and 275 mg (1.14 mmol) of triphenylphosphine were dissolved in 75 mL of *n*-butyronitrile and heated to reflux for 30 h. After solvent removal, the residue was extracted with 3 × 15 mL of toluene and recrystallized from 4 mL of *n*-hexane at −35 °C. Filtration yielded soft red crystals of $CpCo(CO)PPh_3$ and large off-white crystals of triphenylphosphine which were manually separated. Weight of $CpCo(CO)PPh_3$: 20 mg (4%). An IR spectrum of the red crystals verified the material as the expected product.

Reaction of (K-crown)[Cp(CN)(CO)] and 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane. Under nitrogen, 500 mg (1.04 mmol) of (K-crown)[Cp(CN)(CO)] and 170 mg (1.14 mmol) of $P(\mu\text{-}OCH_2)_3CCH_3$ were heated to reflux in 50 mL of toluene for 24 h. The reaction mixture was cooled to −35 °C for 1 day and filtered. The product was isolated by evaporation of the filtrate and characterized by ^{1}H NMR. The yield of $CpCo(CO)(P(\mu\text{-}OCH_2)_3CCH_3)$ was 85 mg (27%).

Synthesis of $CpCo(CO)(P(\mu\text{-}OCH_2)_3CCH_3)$. Under nitrogen, 1 g (5.55 mmol) of $CpCo(CO)_2$ and 0.87 g (5.83 mmol) of $P(\mu\text{-}OCH_2)_3CCH_3$ were heated to reflux in 40 mL of *n*-heptane for 3 h. Crystallization of the product was completed by cooling to −35 °C for 16 h to yield red, needle-shaped crystals which were washed with 1 × 5 mL of ether and dried in vacuo for 16 h at 45 °C. Weight: 1.68 g (98%). A small portion was recrystallized from hot THF for elemental analysis: mp 204–206 °C; IR 1944 (s), 1929 (s), 1400 (w), 1190 (w), 1172 (m), 1012 (s), 955 (s), 928 (m), 861 (s), 822 (m), 805 (w), 777 (s), 768 (sh), 658 (s), 559 (m), 501 (m), 415 (w), 377 (vw), 361 (vw) cm^{-1}; IR (acetonitrile) 1947 cm^{-1}; ^{1}H NMR (CD_3CN) δ 4.84 (s, 5 H), 4.17 (d, $^3J_{PH} = 5.4$ Hz, 6 H), 0.72 (s, 3 H); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 75.7 (d, $^2J_{PC} = 8$ Hz, OCH_2), 83.0 (s, Cp). Anal. Calcd for $C_{11}H_{14}O_4PCo$: C, 44.01; H, 4.70; P, 10.32. Found: C, 44.10; H, 4.73; P, 10.46.

Reaction of $CpCo(CO)PPh_3$ and (K-crown)CN. To a filtered solution of 400 mg (1.21 mmol) of (K-crown)CN in 50 mL of acetonitrile was added 500 mg (1.21 mmol) of $CpCo(CO)PPh_3$. After standing at room temperature for 10 days, a small aliquot of the solution was worked up and subjected to ^{1}H NMR analysis. The composition of the reaction mixture was ~1:1 $CpCo(CO)PPh_3$/(K-crown)[Cp(CN)(CO)].

Reaction of (K-crown)[Cp(CN)(CO)] with Diphenylacetylene. Under nitrogen, 1 g (2.08 mmol) of (K-crown)[Cp(CN)(CO)] and 0.74 g (4.16 mmol) of diphenylacetylene were dissolved in 50 mL of *n*-butyronitrile and heated to reflux for 2 days. The product was extracted successively with 3 × 10 mL of toluene, 1 × 10 mL of THF, and 3 × 15 mL of acetonitrile, leaving some deep red-purple crystals and a small amount of gray powder which was mechanically removed. The crystals (weight 360 mg) were identified as $CpCo(\eta^4\text{-}C_4Ph_4CO)$ from their melting point, IR spectrum, and EI mass spectrum. The various extracts were chromatographed as described in the Ph.D. thesis of S.J.C.[2] Crystalling $CpCo(\eta^4\text{-}C_4Ph_4)$ was identified by IR spectroscopy and high-resolution EI-MS. Yield: 3%. In addition, another 95 mg of $CpCo(\eta^4\text{-}C_4Ph_4CO)$ was isolated. Total yield: 43%.

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Registry No. **1a**, 91946-70-2; **1b**, 93473-81-5; **4**, 114928-60-8; **5a**, 114944-18-2; **6**, 114928-61-9; **10a**, 114928-64-2; **11a**, 93473-83-7; **11b**, 93473-84-8; $CpCo(CO)_2$, 12078-25-0; (PPN)CN, 65300-07-4;

$CpCo(PPh_3)_2$, 32993-07-0; $SnPh_3Cl$, 639-58-7; (K-crown)[$CpCo(CN)_3$], 93473-86-0; $CpCo(CN)_2PPh_3$, 38531-03-2; $Hg(CN)_2$, 592-04-1; $CpCo(CO)PPh_3$, 12203-85-9; $CpCo(CN)(CN{\cdot}BF_3)PPh_3$, 114928-62-0; $K_2[CpCo(CN)_2]$, 114928-65-3; $P(\mu\text{-}OCH_2)_3CCH_3$, 1449-91-8; $CpCo(CO)(P(\mu\text{-}OCH_2)_3CCH_3)$, 93473-82-6; K-crown)CN, 42860-64-0; $CpCo(\eta^4\text{-}C_4Ph_4CO)$, 12119-11-8; pivaloyl chloride, 3282-30-2; 1-adamantanecarbonyl chloride, 2094-72-6; diphenylacetylene, 501-65-5.

Mass Spectrometry of Organo-f-Element Systems. 1. Electron-Impact-Induced (C_5-to-C_6) Ring Enlargement in Various Tris(methylcyclopentadienyl)lanthanoid(III) Systems[†]

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The complete mass spectrometric (MS) fragmentation pattern common to base-free organolanthanoid(III) complexes of the type $(CH_3C_5H_4)_3Ln$ (Ln = La, Pr, Nd, Tm, and Yb) has been determined by using B/E- and B^2/E-linked scans as well as CAD MIKE techniques. Apparently six different fragments lose, inter alia, one benzene molecule, the occurrence of any other C_6H_6 isomer (e.g. of fulvene) being ruled out by detailed collisional activation MS including the partially deuteriated complex $(CD_3C_5H_4)_3Pr$. Unlike for other metal-assisted $C_5H_4R \rightarrow C_6H_5R'$ ring enlargement processes, the generation of C_6H_6 is not necessarily preceded by the complete separation of at least one H atom (or another fragment) from the cationic complex. Instead, facile intramolecular migration of one ring methyl H atom either to the central metal atom or to a likewise metal-bonded C_5H_4 fragment (as created by preceding CH_3 radical abstraction from another $CH_3C_5H_4$ ligand) appears to be essential to initiate the final release of C_6H_6.

Introduction

While the mass spectrometric behavior of isoleptic cyclopentadienyl complexes of the trivalent rare-earth elements $(RC_5H_4)_3Ln$ with R = H[1-4] or C_nH_{2n+1} with $n \geq 2$[5-7] has been studied in some detail, the corresponding tris(methylcyclopentadienyl) complexes have so far received less attention. According to several more detailed studies of methylmetallocenes of d-transition metals where inter alia fragments of the type $[C_6H_6M]^+$ were observed,[8-10] metal complexes with more than two $CH_3C_5H_4$ ligands might be particularly attractive for further investigations of metal-assisted $CH_3C_5H_4$ ligand rearrangements induced by electron impact. Some earlier MS studies of organouranium(IV) complexes of the type $(CH_3C_5H_4)_3UX$[11] suggest that the number of molecular fragments capable of corresponding rearrangements would in such cases be more numerous. For the present study, isoleptic $(CH_3C_5H_4)_3Ln$ systems with Ln = La (1), Pr (2), Nd (3), Tm (4), and Yb (5) were selected in order to account for appropriate variation of electron configuration, ionic radii, and redox potentials, respectively, within the Ln^{3+} series.

Results and Discussion

The fragmentation pattern principally common to all five homologues, 1–5,[12a] is shown in Scheme I, the relative abundance[12b] of each individual fragment being listed in Table I.

In analogy to the unmethylated compounds Cp_3Ln,[1-4] the base peak of all metal-containing fragments of 1–4 is $[Cp'_2Ln]^+$ ($Cp' = CH_3C_5H_4$); only in 5 is the base peak $[Cp'Yb]^{\bullet+}$. While one possible sequence of fragmentation:

[†] Also part 6 of the series "Coordination Behaviour in Base-Free Tris(cyclopentadienyl) Complexes of Rare Earth Elements". For part 5 see ref 31.

(1) Müller, J. *Chem. Ber.* **1969**, *102*, 152.

(2) Thomas, J. L.; Hayes, R. G. *J. Organomet. Chem.* **1970**, *23*, 487.

(3) Devyatykh, G. G.; Krasnova, S. G.; Borisov, G. K.; Larin, N. V.; Gaivoronskii, P. E. *Dokl. Akad. Nauk SSSR* **1970**, *193*, 1069.

(4) Devyatykh, G. G.; Gaivoronskii, P. E.; Larin, N. V.; Borisov, G. K.; Krasnova, S. G.; Zyuzina, L. F. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1974**, *19*, 496.

(5) Druzhkov, O. N.; Andrianov, Yu. A.; Dyagileva, L. N. *Zh. Obshch. Khim.* **1977**, *47*, 1836.

(6) Andrianov, Yu. A.; Druzhkov, O. N.; Smirnov, A. S.; Perevozchikova, N. V.; Zhil'tsova, E. E.; Dodonov, V. A. *Zh. Obshch. Khim.* **1978**, *48*, 2097.

(7) Gaivoronskii, P. E.; Gavrishchuk, E. M.; Chernyaev, N. P.; Zverev, Yu. B. *Russ. J. Inorg. Chem.* (Engl. *Transl.*) **1978**, *23*, 1742.

(8) Spilners, I. J.; Larson, J. G. *Org. Mass Spectrom.* **1970**, *3*, 915.

(9) Zhuk, B. V.; Domrachev, G. A.; Semenov, N. M.; Mysov, E. I.; Materikova, R. B.; Kochetkova, N. S. *J. Organomet. Chem.* **1980**, *184*, 231.

(10) Müller, J.; Lüdemann, F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 74 and further references therein.

(11) Sienel, G. R. Doctoral Dissertation, Universität Erlangen, Erlangen, FRG 1976, pp 33, 112, 124.

(12) (a) Occasionally observed ions whose m/z exceeds that of **a**, as well as ions with probably CH_2-interlinked ring ligands, have been omitted in Table I and will be discussed in a different context elsewhere. (b) In some instances, the most intense peak appears at m/z 79 ($[CH_3C_5H_4]^+$). This may be due to thermal decomposition as the source temperature (200 °C) approaches that of the melting (or decomposition) points of the samples. The intensity ratio $m/z(C_6H_6^{\bullet+})/m/z(\mathbf{a})$ remains almost unchanged when the ion source temperature is varied between 80 and 200 °C.

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