

heating of **2** did liberate CO₂, gross decomposition also occurred and no metal hydride derivatives were isolated. Efforts continue to generate this hydrido-formate complex and studies of the reactivity of **2** are ongoing.

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Supplementary Material Available: Tables of analytical data, thermal parameters, calculated hydrogen positions, and values of observed and calculated structure factors (Tables VIII-XI) (31 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Brandeis University, Waltham, Massachusetts 02254

Cobalt(II) Cyanides in Aprotic Media: Effect of Varying Counterion and Solvent

Stephen J. Carter, Bruce M. Foxman, and Louis S. Stuhl*

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A spectroscopic, synthetic, and X-ray diffraction study of the species present in Co(II)-cyanide mixtures in polar aprotic solvents (acetonitrile, dimethylformamide) as a function of Co:CN ratio, counterion, and concentration is presented. Evidence is offered for the existence of species containing one to five cyanide ligands per cobalt, in some cases with additional coordinated solvent. Syntheses are reported for Li₃[Co(CN)₅] \cdot 3DMF and (PNP)₂[Co(CN)₄], as well as full details of the single-crystal X-ray structure determination of the last compound. Counterion effects on the stability of the species present in the Co(II)-CN system in aprotic solvents and on the reactivity of pentacyanocobaltate(II) in alkenyl halide cyanation are described. The nature of the decomposition pathways of the Co(II)-CN system is discussed.

Introduction

The pentacyanocobaltate(II) ion, [Co(CN)₅]³⁻, was one of the first homogeneous catalysts to be discovered and more recently has been shown to be of value as a reagent in organic synthesis.^{1,2} One particularly interesting recent application has been the catalytic cyanation of alkenyl halides by the pentacyanocobaltate(II)-derived [HCo(CN)₅]³⁻ anion to yield α,β -unsaturated nitriles, in most cases with excellent stereospecificity.³ Because of the high lattice energies and consequent restricted solubility of the alkali-metal cyanides employed in this study and the majority of other related studies, most of what is known of the chemistry of these cyanocobaltates relates to their behavior in aqueous or (less commonly) other protic solvents. Characterization of cobalt cyanides in aprotic solvents was achieved through the use of tetraalkylammonium counterions.^{4,5} It was of interest to determine if the alkenyl halide cyanation reaction could be performed under aprotic conditions both because of the potential utility of the reaction under such conditions and also because of what might be learned about the reaction mechanism from such studies. Work by L.S.S. has demonstrated that the cyanation reaction can occur under aprotic conditions where [HCo(CN)₅]³⁻ is not an accessible intermediate,⁶ indicating that an alternative mechanistic pathway can be operative besides the one described by Funabiki et al.⁷

In order to gain further insight into the cyanation process, we decided to initiate a study of the cobalt cyanide system alone, which would concentrate on the positive identification of species present in solution and their interrelationships as a function of the cyanide:cobalt ratio, henceforth referred to as R.⁸ There is

substantial spectroscopic evidence for the existence of at least three other species in solution besides [Co(CN)₅]³⁻ as R is increased from 2 to 6 in aprotic solvents.^{4,5,9-11} In work recently communicated, we were able to identify one of these species as the low-spin square-planar [Co(CN)₄]²⁻ ion.¹² In the present paper we present further spectroscopic results confirming the identity of the two other species, consider the possible presence of additional species, and demonstrate that the choice of counterion and solvent has a profound effect on the equilibria between these species and their stabilities. We also report some observations concerning the effect of counterion choice on the alkenyl halide cyanation reaction. In addition, full details of the X-ray diffraction study of (PNP)₂[Co(CN)₄]¹³ are presented.

Experimental Section

Solvents and Starting Materials. All work with air- or moisture-sensitive materials was performed in a Vacuum Atmospheres Dri-Lab glovebox or by Schlenk techniques. Dichloromethane and acetonitrile were distilled from phosphorus pentoxide (acetonitrile was predried with anhydrous potassium carbonate). Ether and THF were distilled from sodium benzophenone ketyl. DMF (Burdick and Jackson) was stirred with activated 4A molecular sieves for 3 days, filtered and passed through a column of freshly opened neutral Super alumina (I) (Woelm). Deuterioacetonitrile was dried with 4A sieves before distillation in vacuo.

18-Crown-6-ether (Aldrich), henceforth abbreviated crown, was recrystallized from acetonitrile and dried for 2 days in vacuo. Potassium cyanide (Fisher) was purified by a literature method,¹⁴ washed several times with ether, and dried as for the crown ether. Tetrabutylammonium cyanide (Fluka) was recrystallized from hot THF and dried in vacuo for 24 h at 50 °C (mp 95-96 °C [lit.⁴³ mp 92-93 °C]). (PNP)CN was prepared by a published method¹⁵ (except that procedures were con-

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ducted under nitrogen) (mp 247.5–249.5 °C [lit.¹⁵ mp 212–214 °C]; Cl < 0.01%). Triethylmethylammonium cyanide and pentacyanocobaltate(II) were obtained as previously reported.⁶ Potassium hexacyanocobaltate(III) (Schlesinger Chemicals) was heated to 120 °C in vacuo for 12 h before use. Alkenyl halides were distilled in vacuo before each experiment. Other materials were used as received. Elemental analyses were performed by Pascher Mikroanalytische Laboratorium, Bonn, West Germany, or Galbraith Labs, Knoxville, TN.

Preparation of (PNP)₂[Co(CN)₄].¹⁶ A 0.13-g (1-mmol) sample of CoCl₂ was dissolved in 9 mL of warm DMF and slowly added to a stirred solution of 2.26 g (4 mmol) of (PNP)CN dissolved in 6 mL of DMF. A deep blue color finally formed after the CoCl₂ addition. The solution was left to stand for 30 min before cooling to –35 °C for 24 h. The pale blue crystals were collected by filtration, washed successively with 1 × 5 mL of cold DMF and 2 × 5 mL of ether, and dried in vacuo at 90 °C for 24 h to afford the anhydrous material (1.00 g, 81%; mp 226.5–228.5 °C). Anal. Calcd for C₇H₆₀N₈P₄Co: C, 73.60; H, 4.88; N, 6.78; Co, 4.75. Found: C, 73.24; H, 4.89; N, 6.87; Co, 4.80.

Preparation of Li₃[Co(CN)₃·3DMF]. A 0.625-g (4.8-mmol) sample of CoCl₂ was dissolved in 15 mL of warm DMF and added to a stirred solution of 50 mL of 0.5 M (25 mmol) LiCN in DMF (Aldrich 0.5 M solution, used as received). The resulting deep yellow solution was left to stand until crystals appeared, at which time it was cooled to –35 °C for 1 day. The pale green crystals were collected by filtration and washed successively with 2 × 5 mL of DMF and 2 × 10 mL of ether before drying in vacuo at 75 °C for 15 h. The washings were discarded. When the filtrate had reached room temperature, 10 mL of ether was added and the solution cooled again to yield a second crop of crystals. The crystals were stirred in 30 mL of warm (ca. 50 °C) DMF for 30 min before collection, washing, and drying as described for the first batch (total 1.98 g, 96%). A small portion was recrystallized from DMF/ether (1:1 v/v) and dried as above for elemental analysis. Anal. Calcd for C₁₄H₂₁N₈O₃Li₃Co: C, 39.19; H, 4.93; N, 26.11. Found (different single determinations of two preparations): (1) C, 38.68; H, 5.21; (2) C, 37.31; H, 4.67; N, 25.58.¹⁷ IR (mineral oil mull): 2127 (m), 2097 (s) cm⁻¹.¹⁸

Spectroscopic Measurements. Infrared spectra were recorded on a Perkin-Elmer 683 spectrometer interfaced to a Perkin-Elmer 3500 data station. Calibration of the monochromator was achieved initially with polystyrene and checked frequently in the cyanide region with K₃[Co(CN)₆]. The precision of wavenumber measurements averaged ±2 cm⁻¹.

Electronic spectra were measured on a Perkin-Elmer 552A UV/visible spectrometer calibrated with a holmium oxide filter. Near-infrared spectra (1000–2000 nm) and kinetic data (rate measurements) were obtained on a Perkin-Elmer 323 spectrometer that was equipped with a temperature-controlled cell enclosure maintained at 30 °C for the kinetic measurements.

Reaction of Alkenyl Halides with [Co(CN)₄]²⁻ and [Co(CN)₅]³⁻ Ions. In a typical reaction, 105 mg (84.6 μmol) of (PNP)₂[Co(CN)₄] was dissolved in 0.5 mL of CD₃CN (to give a ~1.7 × 10⁻¹ M solution) that was transferred to a NMR tube and capped with a septum. An 8.35-μL (85-μmol) sample of isocrotyl chloride that had been degassed by the freeze-pump-thaw technique was then injected into the solution. An NMR spectrum was immediately obtained, and then the contents of the tube were warmed to 45 °C and maintained at this temperature. Further spectra were taken at specific time intervals.

X-ray Diffraction Study of (PNP)₂[Co(CN)₄]. Single crystals of the complex were grown by cooling from DMF and sealed inside thin-walled quartz capillaries under nitrogen. Operations with the Syntex P2₁ diffractometer and XTL Structure Determination System following mounting of the crystal were carried out as previously described.^{19,20} Absences in 0k0 (*k* = 2*n* + 1) and h0l (*l* = 2*n* + 1) established the space group P2₁/c. Intensity data generated from θ–2θ scans out to 2θ = 40° were collected and empirical absorption corrections made (see Table I; a preliminary X-ray photographic examination of the crystal indicated that there would be few data with *I*/σ(*I*) > 2 at Bragg angles >20°). The location of the cobalt and phosphorus atoms were obtained from an unsharpened three-dimensional Patterson map. Solution of the structure showed the *y* coordinates of both phosphorus atoms to be ~0, and thus

Table I. Data for X-ray Diffraction Study of (PNP)₂[Co(CN)₄]·4DMF

(A) Crystal Data ^a	
cryst syst: monoclinic	Z = 2
space group: P2 ₁ /c [C ₂ ^v ; No. 14]	cryst size: 0.4 × 0.3 × 0.08 mm
a = 11.188 (3) Å	fw = 1496.55
b = 12.426 (4) Å	ρ(calcd) = 1.27 g cm ⁻³
c = 29.142 (9) Å	ρ(obsd) ^a = 1.26 (1) g cm ⁻³
β = 98.31 (3)°	μ = 3.6 cm ⁻¹
V = 4008.8 Å ³	
(B) Measurement of Intensity Data	
radiation: Mo Kα, graphite monochromator	
reflens measd: + <i>h</i> , + <i>k</i> , ± <i>l</i> (to 2θ = 40°)	
scan type: speed: θ–2θ; vbl, 2.46–4.50°/min	
scan range: sym, [1.7 + Δ(α ₂ – α ₁)]°	
no. of reflens measd: 4007; 3750 in unique set	
std reflens: 013̄, 214̄, 508; period, 60	
abs cor: empirical, transmissn factors 0.885–1.000	
data redn: as before ^b	
statistical information: ^c R _s = 0.047; R _{av} = 0.031 (0kl reflens)	
(C) Refinement	
refinement: ^d 2025 data for which F > 3.92 σ(<i>F</i>)	
weighting of reflens: as before, ^b p = 0.05	
full-matrix least squares: anisotropic temp factors for Co atom;	
isotropic temp factors for all other atoms; R = 0.084; R _w = 0.105;	
SDU = 1.488	
struct factor calcn, all 3750 unique data: R = 0.170, R _w = 0.106	
final diff map: 8 peaks 0.40–0.54 e/Å ³ near DMF molecules; other	
peaks random, <0.39 e/Å ³	
weighting scheme anal.: no systematic dependence on magnitude of	
F _o (sin θ)/λ, or indices	

^a Determined by neutral buoyancy in 1-bromopentane/2-bromopropene. ^b Foxman, B. M.; Goldberg, P. L.; Mazurek, H. *Inorg. Chem.* **1981**, *20*, 4381. ^c R_s = Σ(σ|F_o|)/Σ|F_o|; R_{av} = Σ(|I – I_{av}|)/Σ|I|. ^d R = Σ||F_o| – |F_c||/Σ|F_o|; R_w = {Σ[|F_o| – |F_c||²]/Σw|F_o|²}^{1/2}; SDU = {Σw[|F_o| – |F_c||²]/(m – n)}, where m (=2025) is the number of observations and n (=223) is the number of parameters. ^e Cell constant determination: 10 pairs of ±(*hkl*) and refined 2θ, ω, and χ values in the range 23° < |2θ| < 24° (λ(Mo Kα) = 0.71073 Å).

the cobalt and two phosphorus atoms are pseudo-A-centered. The pseudosymmetry was “broken” by manually adjusting the *y* coordinates of the phosphorus atoms and observing the effect on *R*. Once this was completed, the structure was solved from successive difference Fourier maps. All non-hydrogen atoms were then refined to convergence by using full-matrix least squares after introducing the disordered-DMF model (see Results and Discussion). Phenyl-carbon-bound hydrogen atoms were placed at ideal distances (0.95 Å) and their positions updated after each cycle of refinement.

Results and Discussion

Crystal Structure of (PNP)₂[Co(CN)₄]·4DMF. A perspective view of the [Co(CN)₄]²⁻ anion and its associated DMF molecules is available.¹² Atomic coordinates are listed in Table II; selected bond lengths and angles and nonbonded contacts in Table III.

The molecular structure of the anion consists of a crystallographically centrosymmetric square-planar unit with a pair of axially situated disordered DMF molecules. The disorder results from the fact that each molecule can occupy two alternate sites of equal probability in which, for each molecule, the carbon-nitrogen framework is similar but the position of the oxygen atom is quite different.¹² While the longer Co–O(A) distance (5.89 Å) precludes any interaction, the shorter Co–O(B) distance (2.64 Å) suggests a fractional but perhaps significant bond order, which can be quantified in the manner elaborated by Jurnak et al.²¹ Its calculated value (approximately 0.1), when considered with O–Co–CN angles and type of disorder, indicates that the square-planar [Co(CN)₄]²⁻ entity should be best described as coordinating very weakly to one or a pair of DMF molecules along its longitudinal axis (the results cannot differentiate between equal populations of [Co(CN)₄]²⁻ units associated with either one DMF

(16) Spectroscopic data on this compound have already been published.¹²

(17) The formula of this compound is best represented as Li₃Co(CN)₃·3DMF. Reproducibility of elemental analyses on this compound is poor. If, after preliminary drying, the material is further dried before elemental analysis, some loss of DMF solvents may occur. We have not been able to further purify this material. There are no extraneous bands in the cyanide stretching region of the IR.

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Table II. Atomic Coordinates^a for (PNP)₂[Co(CN)₄]-4DMF

atom	x	y	z
Co	0.0000	0.0000	0.0000
P(1)	0.2375 (3)	-0.0129 (3)	0.71872 (11)
P(2)	0.4685 (3)	-0.0287 (3)	0.68076 (11)
O(1A)	-0.249 (3)	-0.333 (3)	0.0948 (12)
O(1B)	-0.085 (3)	-0.174 (3)	0.0359 (11)
O(2)	0.3080 (14)	0.3491 (13)	0.0465 (5)
N(1)	-0.1936 (12)	0.1369 (11)	0.0327 (5)
N(2)	-0.1509 (11)	-0.0384 (10)	-0.0943 (5)
N(3)	0.3715 (8)	0.0135 (8)	0.7106 (3)
N(4)	-0.106 (2)	-0.341 (2)	0.519 (7)
N(5)	0.398 (2)	0.199 (2)	0.0177 (8)
C(1)	-0.1214 (13)	0.0834 (12)	0.0201 (5)
C(2)	-0.0947 (12)	-0.0217 (11)	-0.0578 (5)
C(3)	0.2273 (10)	0.0081 (10)	0.7788 (4)
C(4)	0.1395 (11)	-0.0422 (10)	0.8003 (5)
C(5)	0.1357 (12)	-0.0266 (11)	0.8467 (5)
C(6)	0.2143 (13)	0.0373 (11)	0.8728 (5)
C(7)	0.3050 (14)	0.0906 (13)	0.8526 (6)
C(8)	0.3098 (13)	0.0740 (11)	0.8054 (5)
C(9)	0.1308 (10)	0.0716 (9)	0.6846 (4)
C(10)	0.1598 (11)	0.1201 (10)	0.6464 (4)
C(11)	0.0761 (12)	0.1858 (11)	0.6173 (4)
C(12)	-0.0361 (12)	0.1965 (11)	0.6283 (5)
C(13)	-0.0680 (12)	0.1490 (11)	0.6666 (5)
C(14)	0.0156 (12)	0.0841 (11)	0.6960 (5)
C(15)	0.1897 (10)	-0.1482 (9)	0.7067 (4)
C(16)	0.2422 (11)	-0.2299 (11)	0.7359 (4)
C(17)	0.2143 (13)	-0.3366 (11)	0.7275 (5)
C(18)	0.1364 (13)	-0.3632 (11)	0.6888 (5)
C(19)	0.0840 (14)	-0.2885 (12)	0.6589 (5)
C(20)	0.1117 (12)	-0.1763 (11)	0.6691 (5)
C(21)	0.5940 (11)	-0.0827 (9)	0.7196 (4)
C(22)	0.5991 (12)	-0.0759 (10)	0.7653 (5)
C(23)	0.7020 (13)	-0.1128 (12)	0.7953 (5)
C(24)	0.7960 (13)	-0.1520 (11)	0.7775 (5)
C(25)	0.7971 (13)	-0.1596 (11)	0.7311 (5)
C(26)	0.6943 (13)	-0.1246 (11)	0.7014 (5)
C(27)	0.4162 (10)	-0.1298 (10)	0.6395 (4)
C(28)	0.3554 (12)	-0.0994 (11)	0.5955 (5)
C(29)	0.3020 (13)	-0.1822 (12)	0.5654 (5)
C(30)	0.3079 (13)	-0.2855 (12)	0.5792 (5)
C(31)	0.3640 (13)	-0.3139 (12)	0.6212 (5)
C(32)	0.4213 (12)	-0.2362 (11)	0.6519 (4)
C(33)	0.5271 (10)	0.0827 (9)	0.6510 (4)
C(34)	0.5090 (12)	0.1862 (11)	0.6662 (4)
C(35)	0.5602 (13)	0.2727 (11)	0.6442 (5)
C(36)	0.6250 (13)	0.2545 (12)	0.6084 (5)
C(37)	0.6450 (13)	0.1534 (12)	0.5942 (5)
C(38)	0.5921 (12)	0.0665 (11)	0.6151 (5)
C(39)	-0.042 (2)	-0.274 (2)	0.0241 (9)
C(40)	-0.076 (3)	-0.444 (3)	0.0468 (13)
C(41)	-0.182 (3)	-0.312 (3)	0.0820 (13)
C(42)	0.451 (3)	0.254 (3)	-0.0108 (11)
C(43)	0.404 (3)	0.085 (3)	0.0307 (10)
C(44)	0.330 (2)	0.251 (2)	0.0470 (9)

^a Estimated standard deviations for the least significant digits appear in parentheses in this and subsequent tables.

molecule above and the other below the square plane or equal populations of [Co(CN)₄]²⁻ units associated either with a pair of DMF molecules or with none at all).

A comparison of the average Co-CN bond length in the [Co(CN)₄]²⁻ anion (1.872(10) Å) with Co-CN bond lengths of other cobalt(II) complexes containing a pentacyanocobaltate subunit reveals that although the average Co-CN distance is one of the shortest values observed, it is not significantly different from those previously published.²²⁻²⁶

Table III. Selected Bond Lengths (Å), Angles (deg), and Intramolecular Nonbonded Contacts (Å) for (PNP)₂[Co(CN)₄] and Associated DMF Molecules^a

Co-C(1)	1.869 (15)	O(1A)-C(41)	0.912 (51)
Co-C(2)	1.875 (14)	O(1B)-C(39)	1.385 (45)
Co-O(1A)	5.892 (35)	P(1)-N(3)	1.585 (10)
Co-O(1B)	2.643 (34)	P(2)-N(3)	1.576 (10)
C(1)-N(1)	1.147 (20)	Co-P(1)	8.91
C(2)-N(2)	1.174 (19)	Co-P(2)	9.03
N(4)-C(39)	1.424 (34)	Co-N(3)	9.17
N(4)-C(40)	1.345 (47)	N(1)-C(30)	3.46
N(4)-C(41)	1.356 (42)	N(2)-C(23)	3.52
C(1)-Co-C(2)	91.1 (6)	Co-O(1B)-C(39)	118.3 (22)
Co-C(1)-N(1)	178.1 (14)	C(39)-O(1B)-N(4)	99.2 (24)
Co-C(2)-N(2)	177.3 (13)	C(41)-O(1A)-N(4)	144.7 (43)
P(1)-N(3)-P(2)	139.0 (7)	C(1)-Co-O(1B)	90.6 (8)
C(39)-N(4)-C(40)	110.3 (24)	C(2)-Co-O(1B)	92.8 (8)
C(39)-N(4)-C(41)	129.1 (24)	N(1)-Co-O(1A)	80.7
C(40)-N(4)-C(41)	120.5 (27)	N(2)-Co-O(1A)	94.3

^a Other distances and angles whose determined values lie very close to expected values are listed in supplementary tables.

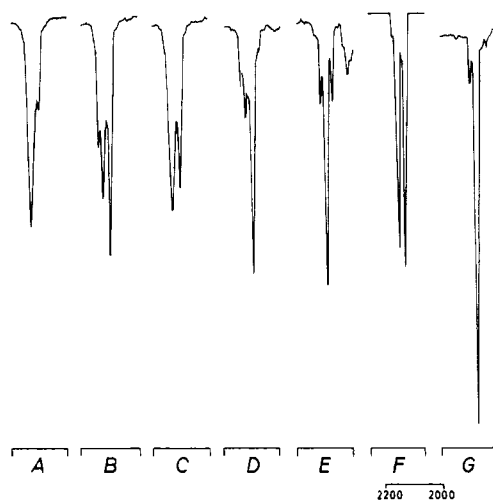


Figure 1. Infrared spectra obtained in the region 2200–2000 cm⁻¹ for solutions of CoCl₂ plus Bu₄N⁺CN⁻ in acetonitrile ([Co] = 4.7 × 10⁻² M): A, R = 2; B, R = 2.5; C, R = 3; D, R = 3.5; E, R = 4; F, R = 4.6; G, R = 6.

The crystal packing is completed by two *unassociated* DMF molecules and two PNP cations (per cobalt atom) whose bond lengths and angles are normal. The absence of strong ion pairing in the crystal is apparent from the distances between the cobalt, cyanide nitrogen, and PNP nitrogen atoms.

Spectroscopic Studies of CoCl₂/Cyanide Solutions. As increasing amounts of cyanide are added to CoCl₂ solutions, the presence of different species can be detected by observing the ν(CN) region of the IR spectrum. Table IV summarizes some IR data obtained at different R values in acetonitrile and DMF with a variety of counterions. No experimental difficulties were encountered except in the K-crown system, where it proved difficult to reproduce R due to the nonstoichiometric quantities of crown ether required to dissolve KCN in a given amount of solvent. The problem was more acute in acetonitrile and necessitated the filtering of (K-crown)CN solutions before use. Above 4, R could be assessed by spectrophotometric measurement of [Co(CN)₅]³⁻ content. With regard to the lithium system, it should be noted that above R = 4.6 solutions are supersaturated with respect to [Co(CN)₅]³⁻ when [Co] ≥ 2 × 10⁻² M. At these concentrations, precipitation of the salt can be expected within 1 h of formation.

Figure 1 depicts the abbreviated IR spectra obtained for the Bu₄N⁺ system at discrete values of R between 2 and 6 (see Table IV for associated numerical values of the bands) with acetonitrile

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Table IV. Infrared Data (cm^{-1}) Obtained for $\text{CoCl}_2 + \text{MCN}$ Solutions ($M = \text{Counterion}$) in (A) Acetonitrile and (B) DMF ($[\text{Co}] = 2 \times 10^{-2} M$ Unless Stated Otherwise)

counterion	R						
	2	3	3.5	4	4.6	5	6-8
(A)							
Bu_4N^a	2134 (sh) ^b	2134 (m)	2136 (m) ^c				
	2128 (s)						
		2121 (s)	2120 (m)				
	2112 (sh)	2112 (sh)		2112 (m) ^c	2112 (sh) ^c	2112 (vw) ^c	
	2098 (m)	2096 (s)	2096 (sh)	2096 (sh)	2097 (sh)		
PNP^a			2091 (s)	2090 (s)	2091 (s)	2090 (w)	
			2071 (w)	2070 (m)	2071 (s)	2070 (s)	2070 (s)
				2015 (w)			
	2130 (sh)	2134 (m) ^c	2135 (m) ^c				
	2121 (s)	2120 (s)	2120 (m)				
K-crown				2111 (w) ^c		2111 (m) ^c	
				2097 (sh)			
			2070 (vw)	2070 (w)	2070 (s)	2089 (w)	
	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>f</i>	2082 (m)	
						2070 (s)	2070 (s)
(B)							
Bu_4N	2126 (s)	2130 (m)	2130 (m)				
		2117 (m)	2115 (m)				
	2102 (sh)	2098 (s)	2098 (s)	2099 (s)	2100 (m)	2100 (vw)	
			2089 (sh)				
			2083 (sh)	2083 (m)	2082 (m)	2082 (w)	2082 (vw)
PNP					2067 (s)	2067 (s)	2067 (s)
	2131 (sh)	2130 (m)	2131 (m)				
	2125 (s)	2116 (m)	2116 (m)				
	2101 (m)	2098 (s)	2099 (s)	2100 (s) ^g	2100 (m) ^{d,h}	2100 (w)	
			2089 (sh)	2089 (sh)	2090 (sh)		
Li			2082 (m)	2082 (m)	2082 (m)	2082 (w)	
					2068 (s)	2067 (s)	2067 (s)
	2125 (s)						
	2110 (sh)	2113 (s)		2107 (sh)	2110 (sh) ^c	2110 (sh)	
				2100 (sh)			
K-crown				2092 (s)	2090 (sh)	2092 (sh)	
					2084 (s)	2083 (s)	2083 (s)
	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	2100 (w)		
					2085 (sh)		
					2073 (s)		2073 (s)

^a $[\text{Co}] = 4.7 \times 10^{-2} M$; spectra for $2 \times 10^{-2} M$ Co are similar.¹² ^b IR data for $R = 2.5$: 2132 (sh), 2122 (s), 2112 (sh), 2097 (s) cm^{-1} . ^c Spectra change with time. ^d $[\text{Co}] = 1.7 \times 10^{-2} M$. ^e R is not experimentally reproducible. ^f Change of spectra with time is too fast to record initial spectrum. ^g Spectra for $(\text{PNP})_2[\text{Co}(\text{CN})_4]$ are similar. ^h Compare IR data for $(\text{PNP})_2[\text{Co}(\text{CN})_4] + 0.5$ equiv of $(\text{PNP})\text{CN}$: 2100 (w), 2089 (sh), 2082 (vw), 2068 (s) cm^{-1} .

as solvent. In DMF, there are only slight changes in IR frequencies (see Figure 2). The major difference resulting from the switch of solvents is a substantial change in band intensities, best understood in terms of changes in equilibrium constants. In DMF, at a given R value, the equilibrium between any two cyanocobaltate species lies more toward the complex possessing the lesser number of bound cyanide ligands. The temperature dependence of the equilibria is much greater in DMF and is greatest at an R value of ~ 4.5 , where the typical deep green color turns blue on heating and yellow on cooling.

Only one IR band is observable in solution at $R \geq 6$, and this can be attributed to the $[\text{Co}(\text{CN})_5]^{3-}$ ion. While the frequency of the cyanide stretch is identical in acetonitrile regardless of the counterion (excluding the Li^+ salt, which is too insoluble to measure), there are differences in DMF.²⁷ If the changes in $\nu(\text{CN})$ are listed in descending order, then the arrangement of the corresponding counterions, $\text{Li} > \text{K-crown} > \text{PNP}, \text{Bu}_4\text{N}$,

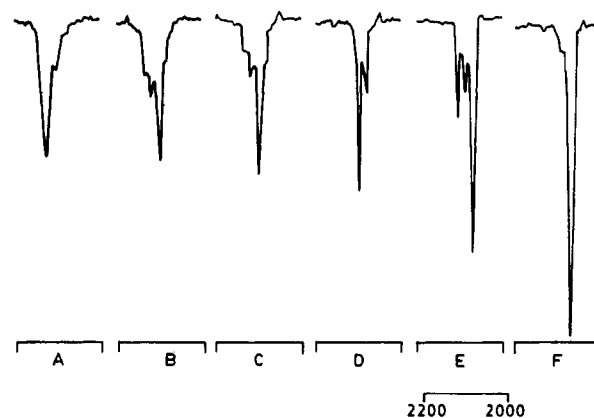


Figure 2. Infrared spectra obtained in the region $2200\text{--}2000 \text{ cm}^{-1}$ for solutions of CoCl_2 plus Bu_4NCN in DMF ($[\text{Co}] = 2 \times 10^{-2} M$): A, $R = 2$; B, $R = 3$; C, $R = 3.5$; D, $R = 4$; E, $R = 4.6$; F, $R = 6$.

(27) While it has previously been reported that $\nu(\text{CN})$ for $(\text{Et}_4\text{N})_3[\text{Co}(\text{CN})_5]$ is 2080 cm^{-1} (mull and DMF solution),⁵ we believe that our recent measurements are more accurate and that representative values of $\nu(\text{CN})$ for tetraalkylammonium pentacyanocobaltate salts are 2065 (s) cm^{-1} (mineral oil mull), 2067 (s) cm^{-1} (DMF), and 2070 (s) cm^{-1} (acetonitrile) ($\pm 2 \text{ cm}^{-1}$).

parallels the expected decrease in ion pairing under these conditions. The reason for the increase in $\nu(\text{CN})$ in contact ion pairing (as opposed to a decrease for $\nu(\text{CO})$ in carbonylates) is believed to result from kinematic coupling.²⁸ Another indication of the

Table V. Electronic Spectra for the $[\text{Co}(\text{CN})_3]^{3-}$ Ion^a

PNP ⁺ (R = 8; acetonitrile)		Li ⁺ (R = 8; DMF)		K ⁺ (H ₂ O) ³⁰	
λ	ϵ	λ	ϵ	λ	ϵ
		284	4675	280	5200
332 (sh)	540	314 ^b	1025	315	540
427	58	423	61	428	46
654	6.5	639	6.2	619	6.3
1080	303	1055	277	970	270

^a For the spectra with PNP as counterion, $[\text{Co}] = 1.75 \times 10^{-2}$ M for $\lambda = 400\text{--}800$ and $[\text{Co}] = 3.6 \times 10^{-3}$ M for other ranges. Concentrations for Li are 2×10^{-2} and 4×10^{-4} M, respectively. λ = wavelength in nm, sh = shoulder, ϵ = molar extinction coefficient. ^b No shoulder discernible.

Table VI. Visible Spectra of $(\text{PNP})_2[\text{Co}(\text{CN})_4]$ in Different Solvents

solvent	concn, M	λ_{max} , nm (ϵ)
DMF	1.3×10^{-2}	617 (158), 598 sh (114), 581 sh (66)
	1.3×10^{-3}	617 (17), 601 (126), 582 (74)
acetonitrile	1.2×10^{-2}	668 sh (21), 602 (118), 558 sh (33)
	1.3×10^{-3}	602 (120)
dichloromethane	5.8×10^{-3}	594 (50), 563 sh (28)
	5.8×10^{-4} ^a	591 (53), 560 sh (29)

^a Error in the calculation of values for ϵ is estimated at least $\pm 5\%$ due to the poor S/N ratio.

presence of contact ion pairs in the lithium system is the observation that $\nu(\text{CN})$ is unaltered by the addition of excess 12-crown-4 ether²⁹ or tetrabutylammonium bromide (i.e. transmetalation does not occur).

At $R \geq 6$, solutions of CoCl_2 and added cyanide are yellow and extremely air sensitive irrespective of aprotic solvent or counterion. Electronic spectra taken at $R = 8$ resemble those published in the literature.^{5,30-32} Two tabulated examples (different counterions and solvent) are presented in Table V together with some published data for aqueous $\text{K}_3[\text{Co}(\text{CN})_5]$ ³¹ as a comparison. There are some differences when anhydrous aprotic solvents are substituted for water. The major changes are limited to the bathochromic shift of two absorptions: the band in the visible region at ca. 600–650 nm (${}^2A_1 \rightarrow {}^4E + {}^2A_1 \rightarrow {}^4A_2$) and the near IR band (${}^2A_1 \rightarrow {}^2B_1$).^{33,34} Recent experimental and theoretical studies have concluded that there is little or no interaction with the sixth, uncoordinated position of the pentacyanocobaltate anion by water or aprotic solvents such as acetonitrile or DMF.³²⁻³⁶ The observed differences in spectra could be attributed at least in part to the hydrogen bonding of water to coordinated cyanide, which should produce a noticeable perturbation in the electron distribution within the complex.

As R is lowered from 6 to 4, two other species begin to predominate: the square-planar $[\text{Co}(\text{CN})_4]^{2-}$ and the tetrahedral $[\text{Co}(\text{CN})_3(\text{solvent})]^-$ anions. In the IR spectrum, the bands at 2090 (acetonitrile), 2082 (PNP/Bu₄N, DMF), 2090 (K-crown, DMF), and 2092 cm^{-1} (Li, DMF) are assigned to the former moiety. Values of $\nu(\text{CN})$ for unsolvated $(\text{PNP})_2[\text{Co}(\text{CN})_4]$ in a mull and in dichloromethane solution are 2100 (sh), 2095 (s), and 2096 (s) cm^{-1} , respectively, as previously reported.¹² Since dichloromethane is not known to coordinate to cobalt, the results may be explained by some degree of coordination by DMF in the vacant axial position, assuming some ion-pair effects are still in operation in the lithium and K-crown salts in this solvent. Some

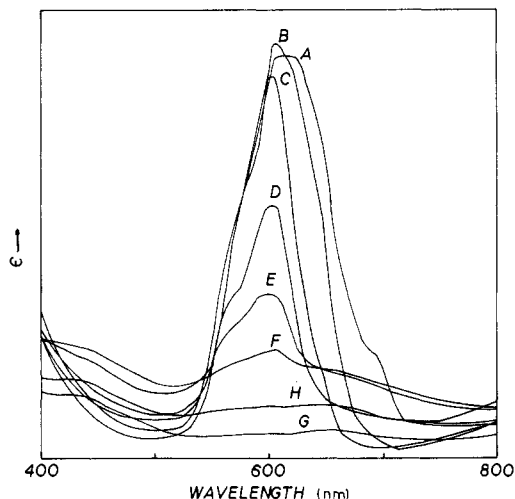


Figure 3. Electronic spectra obtained from solutions of CoCl_2 and $(\text{PNP})\text{CN}$ in acetonitrile with R from 2.5 to 10 ($[\text{Co}] = 3.05 \times 10^{-3}$ M): A, $R = 2.5$; B, $R = 3$; C, $R = 4$; D, $R = 5$; E, $R = 6$; F, $R = 7$; G, $R = 8$; H, $R = 10$.

support for this rationale is derived from measurements of $\nu(\text{CN})$ in the species $[\text{Co}(\text{CN})_2(\text{solvent})_2]$ and $[\text{Co}(\text{CN})_3(\text{solvent})]^-$, where there is much less variation between the two solvents. In addition, any further solvent coordination to a tetrahedrally configured species would substantially perturb the electronic spectrum, an effect not observed (see below).

A summary of the visible spectra obtained from $(\text{PNP})_2[\text{Co}(\text{CN})_4]$ in different solvents appears in Table VI. There is a paucity of information available on the electronic spectra of d^7 cobalt square-planar complexes, and their theoretical basis is poorly understood. In general, they consist of a narrow but weak band in the 1100–1200-nm region accompanied by a stronger broader band centered around 500 nm.³⁷⁻³⁹ The visible and near-infrared bands for $(\text{PNP})_2[\text{Co}(\text{CN})_4]$ in dichloromethane occur at 563 (sh, 28), 593.5 (50), and 1095 (12) nm (ϵ) (estimated half-width 500 nm). Both the infrared data and Beer's law dependence support the contention that the $[\text{Co}(\text{CN})_4]^{2-}$ anion is the only species present in solution. It should be noted that Gutmann and Wegleitner⁹ had proposed earlier the existence of the anion based on visible spectra (which are virtually identical with those reported here) obtained from solutions of $\text{Co}(\text{ClO}_4)_2$ and $(\text{Et}_4\text{N})\text{CN}$ in nitromethane at $R = 4$.

As alluded to earlier, the tricyano species is present in coordinating solvents. Its visible region band maximum occurs at 602 nm in acetonitrile and 617 nm in DMF, and as can be seen from the data in Table VI, its apparent molar extinction coefficient rises as the Co concentration falls. Evidence that the $[\text{Co}(\text{CN})_3(\text{solvent})]^-$ anion is tetrahedral is quite compelling.^{5,11} It is therefore not surprising that the visible bands of the square-planar complex are obliterated since it is well-known that the extinction coefficients of tetrahedral anions are typically 1 order of magnitude larger. The peak in the infrared spectrum at 2096 cm^{-1} (acetonitrile) or 2100 cm^{-1} (DMF) (2113 cm^{-1} for Li) at $R = 4$ can therefore be reasonably assigned to the tricyano compound.

Previous workers^{4,5} have also pointed to the existence of another cobalt cyanide at lower R values: $[\text{Co}(\text{CN})_2(\text{solvent})_2]$ based on magnetic moment data and electronic spectra. An examination of the infrared data at $R = 2$ reveals that the formation of the tricyano cobalt complex has already taken place to some extent. It can be inferred from this result that the remainder of the cobalt in solution is not entirely in the form of the proposed dicyano species since there is clearly a cyanide deficit. Our interpretation of the infrared spectra is that the bands at 2134 and 2121 cm^{-1} (acetonitrile) or 2130 and 2117 cm^{-1} (DMF) are attributable to

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a tetrahedrally configured $[\text{Co}(\text{CN})_2(\text{solvent})_2]$ moiety and that at $R = 2$ the bands in the region $2125\text{--}2128\text{ cm}^{-1}$ indicate the presence of a monocyanocobalt species. The true identity of this compound cannot be ascertained at present due to the complexity of the interaction between CoCl_2 and solvent,⁴⁰ although a reasonable candidate might be tetrahedral $[\text{Co}(\text{CN})\text{Cl}(\text{solvent})_2]$. Where lithium is the counterion, it would appear that the dicyanocobalt species is absent, assuming that the two infrared bands assigned to $\nu(\text{CN})$ of the complex do not collapse to a single peak under these conditions.

Figure 3 shows how bands in the visible portion of the electronic spectrum change as R is varied in the PNP system with acetonitrile as solvent. While considerable dissociation is apparent at this cobalt concentration, the important feature to note is the appearance of a new band at $\sim 625\text{ nm}$ and an associated shoulder at 690 nm as R is reduced from 3 to 2.5. This peak is undoubtedly due to the increased formation of the dicyanocobalt species. White et al.⁵ listed peak maxima of the $[\text{Co}(\text{CN})_2(\text{CH}_3\text{CN})_2]$ and $[\text{Co}(\text{CN})_3(\text{CH}_3\text{CN})]^-$ complexes as 605 and 590 nm, respectively. As these absorptions are broad and somewhat overlapping, the wavelengths of their apparent maxima are somewhat concentration-dependent as well as very sensitive to the value of R . We thus consider the band at $\sim 625\text{ nm}$ to be within experimental error the same as that at 605 nm reported previously.⁵

Stability of Cobalt Cyanide Complexes in Solution. In Table IV it is implied that, under certain circumstances, solutions of CoCl_2 and added cyanides are not stable. The fastest rate of decomposition (at $20\text{--}30\text{ }^\circ\text{C}$) was found at $R \sim 4.6$. Solutions containing the PNP or Bu_4N cation at this R value were found to be indefinitely stable in DMF. Those of K-crown showed slow decomposition while in the case of lithium substantial reaction was seen after 24 h. Destruction of pentacyanocobaltate in acetonitrile occurred regardless of the counterion, although the reaction slowed progressively as the limits of R were expanded beyond the 4–5 range. In order to discover if a rate law was applicable to the circumstances, the kinetics of the decomposition process were studied by monitoring the disappearance of the $[\text{Co}(\text{CN})_5]^{3-}$ ion at 430 nm for different cobalt concentrations at $30\text{ }^\circ\text{C}$. While the results could not be subsequently used for this purpose because of interference from other ions and nonlinear rate variations (see below), a qualitative ordering of the decomposition rate according to counterion was possible: K-crown \gg PNP $>$ Bu_4N . This order holds for the concentration range $[\text{Co}] = 5 \times 10^{-3} - 4 \times 10^{-2}\text{ M}$. Above the upper limit, the rate increases dramatically, while below $5 \times 10^{-3}\text{ M}$, the rate slows sufficiently to define the solutions as stable in the short term. These findings can be illustrated by quoting some results from the K-crown system: at $R = 6$ and $[\text{Co}] = 4.7 \times 10^{-2}\text{ M}$, it takes about 11 days to attain $t_{1/2}$ for the decomposition reaction, while at $R = 4.6$, it is estimated that the decomposition process is complete within 10–15 min.

An examination of IR solution spectra following decomposition suggests that there are a number of products. In the K-crown system there is formed additionally another compound that gives rise to a broad band in the infrared spectrum at $\sim 1970\text{ cm}^{-1}$. Experiments involving the reduction of $(\text{K-crown})[\text{Co}(\text{CN})_5]$ by potassium amalgam in acetonitrile or DMF suggest this is a polymeric potassium cyanocobaltate(I) species.⁴¹ Figure 4 illustrates some solution IR spectra taken before and after decomposition. Examination of both the IR and UV/visible spectra indicate the virtual absence of pentacyanocobaltate(II). The new bands are at 2113, 2092, and 2083 cm^{-1} (average values) with the middle peak often obscuring the latter, which is shown arrowed in Figure 4. Exposure of the final solutions (usually light blue) to air does not result in spectral changes. It can be concluded therefore that the band at 2092 cm^{-1} is not due to any remaining $[\text{Co}(\text{CN})_4]^{2-}$ ions. It is possible to partially purify some of the material from the lithium system, which has the following infrared spectrum: 2146 (s), 2123 (sh), 2116 (sh), 2105 (s), 2098 (sh),

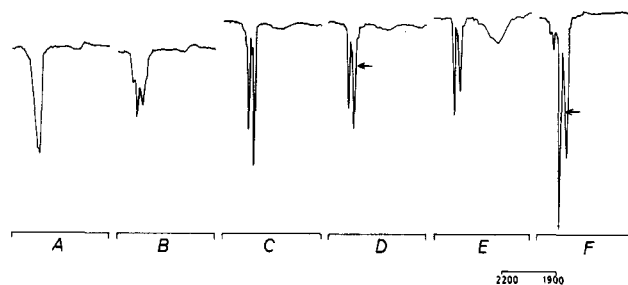


Figure 4. Infrared spectra ($2200\text{--}1900\text{ cm}^{-1}$) of cobalt cyanide solutions ($R = 4.6$) in DMF/acetonitrile, before ($t = 10\text{ min}$) and after ($t = 24\text{--}48\text{ h}$) decomposition. (A) Li/DMF, $[\text{Co}] = 2 \times 10^{-2}\text{ M}$, $t = 10\text{ min}$. IR: 2090 (sh), 2084 (s) cm^{-1} . (B) Conditions of A + 48 h. IR: 2134 (m), 2119 (s), 2096 (s), 2083 (sh) cm^{-1} . (C) PNP/acetonitrile, $[\text{Co}] = 1.7 \times 10^{-2}\text{ M}$, $t = 10\text{ min}$. IR: 2091 (s), 2071 (s) cm^{-1} . (D) Conditions of C + 24 h. IR: 2113 (s), 2091 (s) cm^{-1} . (E) K-crown/acetonitrile, $[\text{Co}] = 1.7 \times 10^{-2}\text{ M}$, $t = 24\text{ h}$. IR: 2114 (s), 2090 (s), 1971 (m, br) cm^{-1} . (F) Bu_4N /acetonitrile, $[\text{Co}] = 3.8 \times 10^{-2}\text{ M}$, $t = 24\text{ h}$. IR: 2151 (w), 2139 (w), 2112 (s), 2085 (s) cm^{-1} .

1890 (w) , $778\text{ (w)}\text{ cm}^{-1}$. This spectrum has some features in common with the infrared spectrum of an impure form of $\text{Li}_3\text{[Co}(\text{CN})_5\text{H]}$ reported earlier,¹⁸ in particular those peaks at 2123, 2116, 1890, and 778 cm^{-1} , the latter two of which are assigned to $\nu(\text{CoH})$ and $\delta(\text{CoH})$ vibration modes. While the evidence is strong for the formation of this compound in the Li/DMF system, there is no convincing data to support such an identification where the other cations are concerned. Infrared spectra of partially purified material from the PNP system have consistently failed to show any peaks attributable to a $\nu(\text{CoH})$ band, and $^1\text{H NMR}$ spectra have not detected a hydride resonance, although residual Co(II) material may have broadened the peak beyond recognition. After decomposition has taken place in the K-crown or Bu_4N systems, UV spectra show typical maxima at 236 and 313 nm ($\epsilon \sim 4600$ and 600 , respectively). While the higher wavelength band is close to that of $(\text{K-crown})_3[\text{Co}(\text{CN})_6]$ (see Experimental Section), its extinction coefficient is substantially larger. In addition, there are intricately structured bands from 500 to 700 nm (ϵ ranges $90\text{--}120$) in the visible region and a very broad peak at $\sim 1150\text{ nm}$ in the near-IR region that cannot be accounted for by any remaining known cobalt(II) cyanides.

There are some other significant factors that have a bearing on the identity of the decomposition products: (1) Since no spectral changes accompany exposure to oxygen, it seems likely that the products are Co(III) compounds although the positions of the bands at 2092 and 2083 cm^{-1} are indicative of Co(II) species. (2) At $R \geq 6$, pentacyanocobaltate(II) solutions are quite stable, but below this figure, where small amounts of tetracyanocobaltate(II) become available, decomposition occurs. This suggests that decomposition involves interaction of the different anions. (3) Apart from the lithium/DMF combination, significant decomposition only takes place in acetonitrile. The $\text{p}K_a$ of this solvent is lower than that of DMF, and thus if a strong base were formed during the reaction, it would be more likely to deprotonate acetonitrile.⁴²

The failure of pentacyanocobaltate(II) to react with alkenyl halides in acetonitrile when the counterion is PNP or K-crown is perhaps due to the competing decomposition pathway already discussed. This likelihood is further increased when the solutions are more concentrated (with regard to cobalt) or the reaction is run at higher temperatures. Nevertheless, the reason why this should be is not clear. Solutions of $(\text{Et}_3\text{MeN})_3[\text{Co}(\text{CN})_5]$ in acetonitrile at concentrations of $\sim 5 \times 10^{-2}\text{ M}$ are indefinitely stable and their $\nu(\text{CN})$ frequency under these conditions is within experimental error of those reported in Table IV ($R = 6$). Thus, it would seem that there is no variation in ion pairing, although it should be stressed that infrared spectroscopy cannot differentiate between solvent-separated ion pairs and salts in which there is

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no interaction between cations and anions in solution ("free ions").

There are two observations that might shed some light on the problem. The first is that below $R = 4$ precipitation of material occurs in the triethylmethylammonium system and is rapid below $R = 3.5$. This may be an indication that tetracyanocobaltate(II), which was implicated in the mechanism of decomposition earlier, is ion-paired quite differently relative to those systems using other counterions. The second point is that at $R = 5$ solutions are yellow when the cation is triethylmethylammonium and not green. This is best interpreted as a change in the equilibrium constant favoring less dissociation of the pentacyanocobaltate complex. It is unfortunate that infrared measurements cannot resolve this matter since pentacyanocobaltates show weak bands in the region 2110-2090 cm^{-1} and thus it becomes difficult to assess $[\text{Co}(\text{CN})_5]^{3-}:[\text{Co}(\text{CN})_4]^{2-}$ ratios accurately when the former ion is in large excess. There are clearly some subtle nuances between the behavior of the triethylmethylammonium system and those employing other counterions that cannot be detected by infrared spectroscopy but perhaps might be resolved by extensive conductivity measurements.

On the basis of the presented data, a switch from acetonitrile to DMF might eliminate the problem with the cyanation reaction

when the counterion is PNP, K-crown, or Bu_4N . Indeed, reaction starts to occur when the solvent composition is 1:1 DMF- d_7 /acetonitrile- d_3 for the K-crown system at 45 °C. Since in some situations DMF may present a problem in workup, the original combination of acetonitrile and triethylmethylammonium cation still remains the best choice for the cyanation reaction.

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Registry No. (PNP) $_2$ [Co(CN) $_4$]-4DMF, 102746-96-3; $\text{Li}_3[\text{Co}(\text{CN})_5]$, 24803-72-3; $[\text{Co}(\text{CN})_5]^{3-}$, 14971-18-7; $[\text{Co}(\text{CN})_4]^{2-}$, 18901-67-2; $[\text{Co}(\text{CN})_3(\text{CH}_3\text{CN})]^-$, 38141-16-1; $[\text{Co}(\text{CN})_3(\text{DMF})]^-$, 102746-97-4; $\text{Co}(\text{CN})_2(\text{CH}_3\text{CN})_2$, 38141-15-0; $\text{Co}(\text{CN})_2(\text{DMF})_2$, 102746-98-5; PNP $^+$, 48236-06-2; Bu_4N^+ , 10549-76-5; K-crown $^+$, 31270-13-0; Li^+ , 17341-24-1; $\text{Li}_3[\text{Co}(\text{CN})_5\text{H}]$, 24803-73-4; Et_3MeN^+ , 302-57-8; isocrotyl chloride, 513-37-1.

Supplementary Material Available: Tables of hydrogen atom atomic coordinates, temperature factors, and nonessential bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Deprotonation of $[\text{HMo}(\text{CO})_2(\text{P}^{\wedge}\text{P})_2]\text{BF}_4$ Complexes: Hard Anions as Proton Carriers

Marcetta Y. Darensbourg* and Maria M. Ludvig

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Reported are kinetic studies of the deprotonation of $[\text{HMo}(\text{CO})_2(\text{P}^{\wedge}\text{P})_2]\text{BF}_4$ complexes ($\text{P}^{\wedge}\text{P} = 1,2$ -bis(diphenylphosphino)ethane, dppe; $\text{P}^{\wedge}\text{P} = 1,2$ -bis(dimethylphosphino)ethane, dmpe; $\text{P}^{\wedge}\text{P} = 1,2$ -bis(diethylphosphino)ethane, depe). Amine bases deprotonated the metalloacids slowly, $t_{1/2}$ typically being days, following the rate expression $\text{rate} = k_2[\text{MoH}^+][\text{amine}]$. Deprotonation rates were dependent on the size of the amine bases and were greatly enhanced by the addition of salts of hard anions such as halides and acetate. The rate expression for deprotonation by mixed-base systems loses dependence on [amine], substituting instead a dependence on $[\text{X}^-]$. The dependence of rate on the steric and electronic nature of the $\text{P}^{\wedge}\text{P}$ ligand was interrelated with similar features of the base. Activation energy parameters, H/D kinetic isotope effects, and solvent effects suggest Mo-H bond breaking as well as coordination sphere rearrangement in the transition state.

Introduction

The protonation/deprotonation reactions of transition-metal hydride complexes as well as carbon acids undergo electronic, and hence geometric, changes that are not found in protonation/deprotonation of nitrogen and oxygen acids. Heterolytic cleavage of an M-H bond generating M^- and H^+ requires an oxidation state change of two units for each. Although this formal view exaggerates the actual changes in charge distributions, the deprotonation of the M-H bond involves extensive polarization of electron density.

Our studies in this area are based on the well-known $\text{HMo}(\text{CO})_2(\text{P}^{\wedge}\text{P})_2^+$ cations. Earlier we reported the X-ray crystal structure of $\text{HMo}(\text{CO})_2(\text{dppe})_2^+$ (IH^+ (dppe = 1,2-bis(diphenylphosphino)ethane) as its AlCl_4^- salt and suggested the unlocated hydride ligand to be in or near the girdle of a pentagonal bipyramid, largely flanked by phenyl rings of the dppe ligands.¹ Consistent with this view, rates of deprotonation by amine bases (pyridine, py; NEt_3 ; NHET_2) were very slow and were found to be greatly enhanced upon addition of salts of small hard anions such as F^- and Cl^- . The hypothesis was advanced that the small, largely unsolvated anion assisted Mo-H $^+$ bond cleavage by its ability to penetrate the outer coordination sphere of IH^+ , polarize the hydride ligand toward H^+ in a preamble to H-bonding, and carry the proton to the amine base. To further examine this claim,

we have extended studies of $\text{HMo}(\text{CO})_2(\text{P}^{\wedge}\text{P})_2^+$ deprotonation, varying the steric and electronic nature of $\text{P}^{\wedge}\text{P}$, as well as studying solvent effects and H/D kinetic isotope effects.

Experimental Section

Materials. All solid reagents and ligands were obtained from standard vendors and used as received. The acid $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (Aldrich) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich; see Table II footnotes for formula) were sealed with a septum and stored under a positive pressure of argon. Bis(triphenylphosphine)nitrogen(1+) acetate (PPN^+OAc^-), PPN^+F^- , and PPN^+I^- were synthesized by ion exchange with PPN^+Cl^- as described in the literature.² All solvents and bases were distilled under N_2 from appropriate drying agents (THF, Na^0 /benzophenone; CH_2Cl_2 , P_2O_5 ; $\text{Me}_2\text{C}=\text{O}$, MgSO_4 ; CH_3CN , CaH_2 followed by P_2O_5 ; Me_2SO , py, NEt_3 , and lutidine (2,6-dimethylpyridine), BaO) and degassed with argon before use.

Preparation. The $[\text{HMo}(\text{CO})_2(\text{P}^{\wedge}\text{P})_2]^+\text{BF}_4^-$ (IH^+BF_4^- , $\text{P}^{\wedge}\text{P} = 1,2$ -bis(diphenylphosphino)ethane, dppe; $2\text{H}^+\text{BF}_4^-$, $\text{P}^{\wedge}\text{P} = 1,2$ -bis(dimethylphosphino)ethane, dmpe) salts were synthesized as previously described by substituting HBF_4 as protonating agent and recrystallizing from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$.^{3,4} The 1,2-bis(diethylphosphino)ethane (depe) derivative (3H^+) was prepared in a manner similar to the case of the dppe derivative. That is, $\text{Mo}(\text{N}_2)_2(\text{depe})_2$ was synthesized according to the method of George and Noble⁵ and converted to $\text{Mo}(\text{CO})_2(\text{depe})_2$ (3) following the same procedure as described for $\text{Mo}(\text{CO})_2(\text{dppe})_2$. The

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