

ligand, thereby generating a product with bridging SMe and carbyne (CSMe) groups.

If S lone-pair donation is important to the destabilization of $\mu\text{-C}(\text{SR})_2$ complexes, one might also expect O and N π -donation to destabilize complexes with $\mu\text{-C}(\text{OR})_2$ and $\mu\text{-C}(\text{NR})_2$ bridging groups; this appears to be the case. The dinuclear complex with a $\text{C}(\text{OR})_2$ ligand, $\text{Cp}_2\text{Fe}_2(\text{CO})[\text{C}(\text{OMe})(\text{O-c-Hex})](\mu\text{-CO})_2$,^{5c} has been assigned a structure in which the dioxycarbene ligand is in a terminal rather than a bridging position. Also, the di- and trinuclear complexes with dioxycarbene ligands, $\text{Mn}_2(\text{CO})_9[\text{C}(\text{OR})_2]$, $\text{Re}_2(\text{CO})_9[\text{C}(\text{OR})_2]$, $\text{Re}_2(\text{CO})_8[\text{C}(\text{OR})_2]_2$, $\text{Ru}_3(\text{CO})_{10}[\text{C}(\text{OR})_2]_2$,²⁵ and $\text{Os}_3(\mu_2\text{-H})(\mu_3\text{-CPh})(\text{CO})_9[\text{C}(\text{OR})_2]$,²⁶ have only terminal carbene groups.

The diamino carbene complexes $\text{Cp}_2\text{Fe}_2(\text{CO})[\overline{\text{CN}}(\text{R})\text{-CH}_2\text{CH}_2\text{N}(\text{R})](\mu\text{-CO})_2$, where R = Me or Et,²⁷ have also been

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assigned structures in which the carbene ligand is terminal. However, the carbene ligand in the more electron-rich $\text{Cp}_2\text{Ni}_2(\mu\text{-CO})[\overline{\mu\text{-CN}}(\text{Et})\text{CH}_2\text{CH}_2\text{N}(\text{Et})]$ complex is bridging.²⁷ Thus, in dinuclear complexes with diheteroatom carbene ligands $\text{C}(\text{YR})_2$, where R = O, S, or NR, the carbene ligand may be simply bridging (A), bridging with a sulfur atom coordinated to a metal (B), or terminal, depending upon the electron richness of the metals and possibly steric factors. The more electron-rich metals seem to favor structure A. The variety of structures observed for these diheteroatom carbene complexes contrasts with the situation for μ -alkylidene complexes ($\mu\text{-CR}_2$), where R = H or alkyl, which all have structure A.³

Registry No. Ia, 69532-11-2; Ib, 76136-38-4; Ic, 76136-40-8; Id, 61930-80-1; Ie, 102746-42-9; IIa, 77781-29-4; IIb, 102746-38-3; IIc, 102746-40-7; IId, 102746-45-2; III, 83043-22-5; IV, 102746-29-2; V, 102746-30-5; VI, 102746-31-6; VII, 102746-32-7; VIII, 102746-32-7; IX, 102746-33-8; X, 102746-34-9; XI, 102746-35-0; XII, 102746-36-1; $[\text{Cp}(\text{CO})_2\text{Ru}[(\text{C}(\text{SCH}_3)_2)]\text{SO}_3\text{F}]$, 102746-43-0; $\text{Na}[\text{Co}(\text{CO})_4]$, 14878-28-5; $\text{Cp}_2\text{Ru}_2(\text{CO})_4$, 12132-87-5; $\text{PPN}[(\text{CO})_3\text{Fe}(\text{NO})]$, 61003-17-6; $[\text{Cp}_2\text{Fe}]_2\text{FeCl}_4$, 1287-09-8; Fe, 7439-89-6; Ru, 7440-18-8; Co, 7440-48-4.

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Bidentate and Unidentate Formate Ligands in $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{O}_2\text{CH})_2$

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Syntheses and spectroscopic properties of complexes of the type $\text{M}(\text{CO})_2\text{L}_2(\text{B-B})\text{Y}$ are presented [M = Mo, W; L = PEt_3 , PPh_3 ; B-B = acetylacetonate (acac), 1,1,1,5,5,5-hexafluoroacetylacetonate (facfac), tropolonate (trop), carboxylate; Y = Cl, Br, O_2CR]. These products are derived from $\text{M}(\text{CO})_3\text{L}_2\text{X}_2$ reagents (X = Cl, Br). The X-ray diffraction structure of one member of this series, $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCH})_2$ (**2**), is described. The molecule crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.691$ (8) Å, $b = 12.250$ (9) Å, $c = 13.813$ (12) Å, $\beta = 90.85$ (6)°, and $Z = 4$. The structure was solved from 3410 reflections with $I > 3\sigma(I)$, with weighted and unweighted residuals of 5.4 and 4.1%, respectively. The formate ligands engage in different binding modes in the solid state. These ligands exchange unidentate and bidentate coordination modes rapidly in solution with an activation barrier too small to be readily measured by variable-temperature NMR techniques.

Introduction

Heptacoordinate carbonyl complexes of molybdenum(II) and tungsten(II) are numerous¹ in accord with effective atomic number rule expectations. In contrast to extensive studies of $\text{M}(\text{CO})_{3-n}\text{L}_n(\text{B-B})_2^2$ ($n = 0, 1$) or $\text{M}(\text{CO})_2\text{L}_2(\text{B-B})\text{X}^3$ compounds where B-B is a monoanionic sulfur-based chelate, reports of chelating oxygen donor ligands in carbonyl complexes of Mo(II) and W(II) are less common. Early reports of such complexes include ancillary η^3 -allyl ligands as in $(\pi\text{-allyl})\text{M}(\text{CO})_2(\text{B-B})\text{L}$ (L = THF, CH_3CN , $\text{C}_5\text{H}_5\text{N}$),⁴ $(\pi\text{-C}_6\text{H}_6)(\pi\text{-allyl})\text{Mo}(\text{B-B})$,⁵ and $[(\pi\text{-allyl})\text{M}(\text{CO})_2(\text{B-B})\text{X}]$,⁶ where M = Mo or W, B-B = acac or O_2CR , and X = halide. More recently, Archer and co-workers⁷ have reported tungsten quinolinolate (dcq) derivatives of the type $\text{W}(\text{CO})_2\text{L}_2(\text{dcq})\text{Cl}$, $\text{W}(\text{CO})\text{L}_2(\text{dcq})_2$, and $\text{W}(\text{CO})_2\text{L}(\text{dcq})_2$. An

early example of carbyne-carbonyl coupling was promoted with acetylacetonate as a reagent and resulted in $\text{W}(\text{acac})(\text{HOCCR})(\text{CO})_2\text{Cl}$ products.⁸ In this paper we describe the synthesis and spectroscopic properties of complexes of the type $\text{M}(\text{CO})_2\text{L}(\text{B-B})\text{Y}$ where M = Mo or W, L = PEt_3 or PPh_3 , B-B = acac, hexafluoroacetylacetonate (facfac), tropolonate (trop), or carboxylate, and Y = halide or carboxylate.

The role of formate as a ligand has assumed increasing importance as carbon dioxide chemistry has been promulgated.⁹ Of course, many carboxylate complexes have been studied and unidentate, bidentate, and bridging modes of coordination have been found for a variety of metals in a range of oxidation states.¹⁰ Wilkinson and Lyons¹¹ have recently reported the dynamic solution behavior of $\text{WH}_2(\text{PMe}_3)_3(\text{OOCH})_2$, an eight-coordinate d^2 complex with two formate ligands that exchange rapidly between unidentate and bidentate coordination modes. A similar dynamic process has been observed in six-coordinate d^6 carboxylate derivatives of Ru(II) and Os(II).^{12,13} One of the compounds we have prepared is a seven-coordinate d^4 bis(formate) derivative that is fluxional on the NMR time scale. In view of recent interest in formate chemistry⁹ we now report the crystal structure and

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Table I. Vibrational Data for Molybdenum(II) and Tungsten(II) Carbonyl Complexes (B-B = Oxygen Donor Ligand)

complex	$\nu(\text{MCO})$, cm^{-1}	$\nu(\text{B-B})$, cm^{-1}	note
$\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{O}_2\text{CH})_2$ (2)	1929 m, 1833	1627	a
$\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{O}_2\text{CCH}_3)\text{Br}$ (3)	1935 m, 1839		a
$\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{PMBA})_2$ (4) ^b	1926 m, 1827	1604	a
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{O}_2\text{CH})_2$ (5)	1955 m, 1870	1625	a
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{acac})\text{Cl}$ (6)	1933 m, 1832		a
$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{trop})\text{Cl}$ (7)	1910 m, 1808	1589, 1517	c
$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{acac})\text{Cl}$ (8)	1905 m, 1805	1590, 1521	c
$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{facfac})\text{Cl}$ (9)	1922 m, 1830		c
$\text{W}(\text{CO})_2(\text{PPh}_3)_2(\text{acac})\text{Cl}$ (10)	1923 m, 1818	1587, 1523	c
$\text{W}(\text{CO})_2(\text{PPh}_3)_2(\text{facfac})\text{Cl}$ (11)	1941 m, 1848		c

^a As KBr pellets. ^b PMBA = *p*-methoxybenzoate. ^c In methylene chloride solution.

dynamic solution properties of $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCH})_2$.

Experimental Section

All solvents and reagents were obtained from commercial sources. Methylene chloride was distilled over calcium hydride under a nitrogen atmosphere. Methanol was stored over molecular sieves. Atmospheric oxygen was expelled from all solvents by a nitrogen sparge before use. IR spectra were recorded with a Beckman 4250 spectrophotometer and were calibrated with polystyrene. NMR spectra were obtained on a Bruker WM250 spectrometer. Gas chromatograms were recorded on a Hewlett-Packard HP5890 gas chromatograph using a thermal conductivity detector and a Porapak Q column operated at 75 °C. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Aluminum trichloride was freshly sublimed and rigorously protected from the atmosphere. The sodium salts used in this work were prepared by treating the free organic acids with NaH in hexanes or diethyl ether, and they were recrystallized from ethanol/ethyl acetate or another suitable solvent pair before use. Potassium formate was prepared by titrating an aqueous solution of formic acid with potassium hydroxide and evaporating the solution nearly to dryness. $\text{W}(\text{CO})_3(\text{PEt}_3)_2\text{Cl}_2$ (**1a**) was prepared in 70% yield by a modification of the procedure used for the synthesis of the triphenylphosphine analogue (**1b**).^{2a} Two equivalents of PEt_3 were added to $\text{W}(\text{CO})_4\text{Cl}_2$ in methylene chloride at -78 °C. After being stirred 15 min, the solution was allowed to warm slowly to room temperature. After filtration, the solvent was removed under reduced pressure and the residue was washed with 15-mL portions of cold petroleum ether. Additional material may be recovered from the washings. The product is yellow or yellow-green. IR (CH_2Cl_2): 2002, 1922, 1877 (CO) cm^{-1} .

$\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCH})_2$ (2). A 200-mL Schlenk flask was charged with 1.3 g (2.9 mmol) of $\text{Mo}(\text{CO})_4(\text{PEt}_3)_2$ ¹⁴ and purged of atmospheric oxygen. Methylene chloride (15 mL) was introduced, and the solution was cooled to 0 °C. The metal reagent was titrated with a methylene chloride solution of bromine until a quantitative conversion to $\text{Mo}(\text{CO})_3(\text{PEt}_3)_2\text{Br}_2$ ¹⁵ was achieved as judged by the infrared spectrum of the reaction solution. A small lump of wet KOOCH was added; the solution liberated CO and became orange after being stirred approximately 10 min at room temperature. The solution was filtered after 5 h and stirred over MgSO_4 . Following solvent removal under reduced pressure, the residue was triturated with hexanes. The yellow powder was dried under a dry nitrogen stream and stored under dry carbon dioxide. IR (KBr): 1929, 1833 (strong, $\text{Mo}(\text{CO})$), 1627 (medium, $\text{O}=\text{C}$) cm^{-1} . ¹H NMR (CD_2Cl_2): δ 8.48 (s, 2 H, OOH), 2.10 (m, 12 H, PCH_2), 1.18 (m, 18 H, PCH_2CH_3). ³¹P NMR (CD_2Cl_2): δ 55.1. Anal. Calcd for $\text{MoC}_{16}\text{H}_{32}\text{O}_5\text{P}_2$: Mo, 20.14; P, 13.01; C, 40.35; H, 6.35; Br, 0.00. Found: Mo, 19.76; P, 13.16; C, 39.79; H, 6.51; Br, 1.37.

Decomposition Reaction of 2. A small sample of the complex was placed in a Schlenk tube and heated to 60 °C under a static vacuum. The solid turned brown, liquified, and liberated a gas. One decomposition product was carbon dioxide, identified by gas chromatography.

Molybdenum Complexes 3–6. These compounds were prepared by following the procedure below for 7, starting with $\text{Mo}(\text{CO})_3(\text{PEt}_3)_2\text{Br}_2$ ¹⁵ or $\text{Mo}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}_2$ ¹⁶ and the appropriate sodium carboxylate. The products were isolated following filtration of the reaction mixture by evaporating the solvent, washing with hexanes, and recrystallizing from

Table II. Phosphorus-31 NMR Data for Selected Molybdenum(II) and Tungsten(II) Carbonyl Complexes^a

complex	δ ($J(^{183}\text{W}-^{31}\text{P})$)
$\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{O}_2\text{CH})_2$ (2)	55.1
$\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{O}_2\text{CCH}_3)\text{Br}$ (3)	53.9
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{acac})\text{Cl}$ (6)	62.5
$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{trop})\text{Cl}$ (7)	22.6 (180)
$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{acac})\text{Cl}$ (8)	21.6 (180)
$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{facfac})\text{Cl}$ (9)	21.7 (190)
$\text{W}(\text{CO})_2(\text{PPh}_3)_2(\text{acac})\text{Cl}$ (10)	39.6 (175)
$\text{W}(\text{CO})_2(\text{PPh}_3)_2(\text{facfac})\text{Cl}$ (11)	33.6 (160)

^a Phosphorus chemical shifts relative to external 85% H_3PO_4 ; downfield is positive. $J(\text{W}-\text{P})$ is given in parentheses, expressed in Hz.

appropriate solvent pairs such as methylene chloride/diethyl ether. Yields were 60–80%. Infrared spectral data are collected in Table I, and ³¹P NMR chemical shifts are in Table II. Satisfactory elemental analyses were obtained for selected compounds.

$\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCCH}_3)\text{Br}$ (3). ¹H NMR (CDCl_3): δ 2.12 (m, 12 H, PCH_2), 1.88 (s, 3 H, OOCCH_3), 1.16 (m, 18 H, PCH_2CH_3).

$\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{PMBA})_2$ (4) (PMBA = *p*-Methoxybenzoate). ¹H NMR (CDCl_3): δ 7.83 (d, 4 H, C_6H_4), 6.71 (d, 4 H, C_6H_4), 3.76 (s, 6 H, OCH_3), 2.13 (m, 12 H, PCH_2), 1.19 (m, 18 H, PCH_2CH_3).

$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{OOCH})_2$ (5). ¹H NMR (CDCl_3): δ 8.14 (s, 2 H, OOH), 7.36 (m, 30 H, C_6H_5).

$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{acac})\text{Cl}$ (6). ¹H NMR (CDCl_3): δ 7.40–7.63 (m, 30 H, C_6H_5), 5.27 (s, 1 H, acac CH), 1.48 (s, 6 H, CH_3).

$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{trop})\text{Cl}$ (7). The synthesis of this compound is typical for the tungsten(II) complexes 8–11. A 200-mL Schlenk flask was charged with Na[trop] (0.30 g, 2.08 mmol) and **1a** (1.15 g, 2.00 mmol). The flask was purged of atmospheric oxygen, and the solids were dissolved in 30 mL of 1:1 v/v methylene chloride/methanol. The solution immediately became red and a gas evolved. After being stirred for 4 h, the burgundy solution was filtered and reduced to a gummy solid under reduced pressure. The residue was purified by Soxhlet extraction with diethyl ether. The product, $\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{trop})\text{Cl}$ (7), was recovered in analytically pure form as red plates from the ether extract: 0.91 g obtained, 72%. This is a typical yield for the other tungsten(II) complexes, 8–11, as well. Infrared spectral data are collected in Table I and ³¹P NMR data are in Table II. All compounds gave satisfactory elemental analyses.

$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{trop})\text{Cl}$ (7). ¹H NMR (CDCl_3): δ 7.1–6.7 (m, 5 H, trop), 2.12 (m, 12 H, CH_2), 1.08 (m, 18 H, CH_3).

$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{acac})\text{Cl}$ (8). ¹H NMR (CDCl_3): δ 5.44 (s, 1 H, acac CH), 2.06 (m, 12 H, CH_2), 1.93 (s, 6 H, acac CH_3), 1.08 (m, 18 H, CH_3).

$\text{W}(\text{CO})_2(\text{PEt}_3)_2(\text{facfac})\text{Cl}$ (9). ¹H NMR (CDCl_3): δ 6.36 (s, 1 H, facfac CH), 2.18 (m, 12 H, CH_2), 1.17 (m, 18 H, CH_3).

$\text{W}(\text{CO})_2(\text{PPh}_3)_2(\text{acac})\text{Cl}$ (10). ¹H NMR (CDCl_3): δ 7.7–7.1 (m, 30 H, phenyl), 5.35 (s, 1 H, acac CH), 1.44 (s, 6 H, acac CH_3).

$\text{W}(\text{CO})_2(\text{PPh}_3)_2(\text{facfac})\text{Cl}$ (11). ¹H NMR (CDCl_3): δ 7.8–7.1 (m, 30 H, phenyl), 5.61 (s, 1 H, facfac CH).

Attempted Preparation of $\text{W}(\text{CO})_2(\text{PPh}_3)_2(\text{trop})\text{Cl}$. A 200-mL Schlenk flask was charged with 1.95 g (2.0 mmol) of **1b**^{2a} and 0.48 g (2.0 mmol) of Na[trop]. After atmospheric oxygen was expelled, 25 mL of methanol was added to the flask. The slurry became blue-green with slow gas evolution. After being stirred overnight, the solution contained no carbonyl-containing species. The solid remaining in the flask was identified as unreacted **1b** from an infrared spectrum.

$[\text{W}(\text{CO})_2(\text{PEt}_3)_2\text{Cl}_2]_2$ (12). In the drybox (0.32 g, 0.50 mmol) and AlCl_3 (0.13 g, 1.0 mmol) were loaded into a 100-mL Schlenk flask and the flask was assembled with a magnetic stir bar, rubber septum, filter wand, and cannula as for a filtration. The exposed end of the cannula was inserted into a 200-mL Schlenk flask fitted with a rubber septum. The assembly was removed from the drybox, and 25 mL of methylene chloride was introduced into the reaction vessel via syringe. The mixture was stirred for 1 h at room temperature; a yellow solution formed. To the second flask was added 100 mL of hexanes, and the reaction solution was filtered into this flask while the hexanes were stirred. The hygroscopic white solid remaining behind displayed strong infrared absorptions (KBr pellet) at 1598, 1528, 1430, and 1360 cm^{-1} . The extremely air-sensitive yellow material that precipitated in the second flask was washed with hexanes and dried under high vacuum; this product, $[\text{W}(\text{CO})_2(\text{PEt}_3)_2\text{Cl}_2]_2$ (12), was recrystallized from methylene chloride/diethyl ether. Yield: 0.19 g, 68%. IR (CH_2Cl_2): 1940, 1855 cm^{-1} . ¹H NMR (CD_2Cl_2): δ 1.2 (m, 3 H, CH_3), 2.2 (m, 2 H, CH_2). ³¹P NMR (CD_2Cl_2): δ 22.8 ($J(\text{WP}) = 154$ Hz). Anal. Calcd for $\text{C}_{28}\text{H}_{60}\text{P}_4\text{O}_4\text{Cl}_4\text{W}_2$: P, 11.12; Cl, 12.73; W, 33.00. Found: P, 10.40; Cl, 16.98; W, 29.44. Molecular

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Table III. Collection and Refinement Parameters and Crystallographic Data for $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCH})_2$ (2)

mol formula	$\text{C}_{16}\text{H}_{32}\text{MoO}_6\text{P}_2$
formula wt	478.32
space group	$P2_1/n$
cell params	
<i>a</i> , Å	12.691 (8)
<i>b</i> , Å	12.250 (9)
<i>c</i> , Å	13.813 (12)
β, deg	90.85 (6)
vol, Å ³	2147.1
ρ(obsd) (ρ(calcd)), g/cm ³	1.38 (1.48)
<i>Z</i>	4
radiation (wavelength, Å)	Mo Kα (0.71073)
linear abs coeff, cm ⁻¹	7.77
scan type	ω/1.67θ
scan width	1.1 + 0.35 tan θ
bkgd	25% of full scan width on both sides
θ limits, deg	3.0 < θ < 27.0
quadrants colld	± <i>h</i> , + <i>k</i> , + <i>l</i>
no. of data with <i>I</i> > 3σ(<i>I</i>)	3410
<i>R</i> , %	4.1
<i>R</i> _w , %	5.4
largest param shift	0.80
error in observn of unit wt	2.29
no. of var	226

weight, determined in chloroform: 1045 (calcd: 1114).

Cleavage of $[\text{W}(\text{CO})_2(\text{PEt}_3)_2\text{Cl}_2]$. A stirred methylene chloride solution of **12** absorbed carbon monoxide overnight. The solution infrared spectrum of the product was identical with that of **1a**. This solution was treated with methanol and a slight excess of Na[trop] and worked up as described in the synthesis of **7**. The product was identified as **7** from its solid-state infrared spectrum.

Collection of Diffraction Data. Crystals of **2** suitable for the X-ray diffraction study were grown by diffusion of hexane into a tetrahydrofuran solution at -20 °C. An orange prism having approximate dimensions 0.40 × 0.35 × 0.20 mm was selected and mounted in a capillary under dry carbon dioxide. Diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 automated diffractometer.^{17a} A monoclinic cell was indicated from 25 centered reflections found in the region 20° < 2θ < 26° and refined by least-squares calculations. The cell parameters are listed in Table III.

Diffraction data were collected in the quadrant ±*h*, +*k*, +*l* under the conditions specified in Table III. Three reflections, chosen as intensity standards, were monitored every 5 h and showed no significant (≤1.5%) decay. The crystal orientation was checked every 300 reflections, and recentering was performed if the scattering vectors varied by more than 0.15°. ψ scans with nine reflections having 80° < χ < 90° were performed to provide an empirical correction for absorption, the calculated correction factors range from 0.98 to 1.00. In all, 3410 reflections having *I* > 3σ(*I*)^{17b} were used in the solution and refinement of the structure. The data were corrected for Lorentz-polarization effects prior to the solution of the structure.

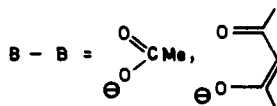
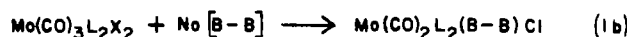
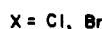
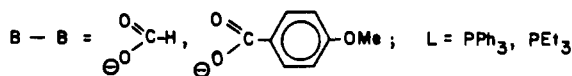
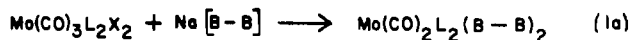
Solution and Refinement of the Structure. The structure solution was straightforward from the application of the heavy-atom method. The space group $P2_1/n$ was deduced from the systematic absences *h*0*l*, *h* ≠ 2*n*, and 0*k*0, *k* ≠ 2*n*. The molybdenum atom was located in a three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were obtained from the subsequent Fourier and difference Fourier calculations. The hydrogen atoms were not located.

Least-squares refinement of the non-hydrogen atoms allowing all positions to vary anisotropically produced unweighted and weighted residuals of 0.050 and 0.045, respectively. The positions of the hydrogen atoms were then calculated by using a C-H distance of 0.95 Å with the isothermal parameter set at 8.0 Å². Further full-matrix least-squares refinement converged with *R* = 0.041 and *R*_w = 0.054.^{17c} The final difference Fourier map contained no peaks with intensities greater than 0.50 e/Å³.

(17) (a) Programs utilized during solution and refinement were from the Enraf-Nonius structure determination package. (b) $I = S(C + RB)$ and $\sigma(I) = [s^2(C + R^2B) + (\rho I)^2]^{1/2}$, where *S* = scan rate, *C* = total integrated peak count, *R* = ratio of scan count time to background time, *B* = total background count time, and ρ = 0.03 is a correction factor. (c) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [2F_o/\sigma(F_o^2)]^2$ and $\sigma(F_o^2) = [\sigma^2(I) + \rho^2 I^2]^{1/2}$ with ρ assigned a value of 0.03. Expressions for residuals are $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o^2)]^{1/2}$.

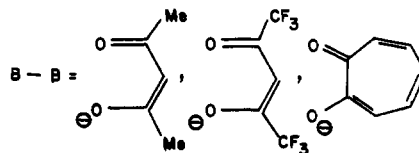
Results

Syntheses. Treating $\text{Mo}(\text{CO})_3\text{L}_2\text{X}_2$ with Na[B-B] (B-B = formate, acetate, *p*-methoxybenzoate, acetylacetonate; L = triethylphosphine, triphenylphosphine; X = chloride, bromide) at room temperature in methylene chloride/methanol mixtures resulted in smooth gas evolution and a color change from yellow to orange. The products of these reactions were formulated as bis(B-B) complexes of form $\text{Mo}(\text{CO})_2\text{L}_2(\text{B-B})_2$ or mono(B-B) complexes of form $\text{Mo}(\text{CO})_2\text{L}_2(\text{B-B})\text{X}$, from inspection of infrared spectra, proton and phosphorus NMR spectra, and elemental analyses (eq 1 and Tables I, II). (Elemental analyses are



available as supplementary material.) The complexes were stable as solids toward high vacuum and atmospheric oxygen except the bis(formate) complexes **2** and **5**. $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{O}_2\text{CH})_2$ readily liberated carbon dioxide under vacuum at slightly elevated temperatures. Good analytical data were not obtained for the bis-(formate) complex **2** (see Experimental Section), as evidenced by a trace of bromide ion found in a sample that appeared to be spectroscopically pure. When reaction times were curtailed during the generation of **2**, a second ¹H formate resonance was sometimes observed about 0.5 ppm upfield of that of the bis(formate) product. Though this material was not separated and independently characterized from the reaction mixture, it is likely that this second formate-containing compound is $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCH})\text{Br}$, analogous to the acetate derivative **3**.

No analogous tungsten complexes containing carboxylate ligands were isolated. Following procedures similar to those used to obtain the molybdenum complexes led to loss of all carbonyl ligands. However, clean reactions were observed with Na[acac], Na[facac], or Na[trop] as the chelating oxygen reagent. The products of these reactions were $\text{W}(\text{CO})_2(\text{PR}_3)_2(\text{B-B})\text{Cl}$, as judged by infrared spectra, proton and phosphorus NMR spectra, and elemental analyses (eq 2 and Tables I, II). (See supplementary material for analytical data.) A curious exception was that we were unable to prepare $\text{W}(\text{CO})_2(\text{PPh}_3)_2(\text{trop})\text{Cl}$.



Infrared and NMR Spectroscopic Results. Infrared spectra of the complexes prepared in this work (Table I) displayed normal absorptions due to $\text{M}(\text{CO})_2$ moieties. In some cases the vibrational modes of the bound oxygen donor ligands were also located. Medium-intensity bands at 1590 and 1525 cm⁻¹ in the spectra of acac complexes were assigned to symmetric CO and antisymmetric CC vibrations within the delocalized M(acac) grouping.¹⁸ A similar pattern was observed in the tropolonate derivative. In the infrared spectra of bis(carboxylate) complexes, a strong ab-

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Table IV. Final Positional Parameters for **2**

atom	x	y	z
Mo	0.18095 (3)	-0.22790 (3)	-0.01837 (3)
P(1)	0.21835 (8)	-0.39264 (9)	-0.12094 (9)
P(2)	0.27113 (10)	-0.16349 (11)	0.13082 (9)
O(1)	0.4192 (2)	-0.2232 (3)	-0.0649 (3)
O(2)	0.1432 (3)	-0.4192 (3)	0.1255 (3)
O(3)	0.1721 (3)	-0.0876 (3)	-0.1264 (3)
O(4)	0.1061 (2)	-0.0699 (3)	0.0174 (2)
O(5)	0.0269 (3)	-0.2449 (3)	-0.0836 (3)
O(6)	-0.0692 (4)	-0.2571 (4)	0.0484 (3)
C(1)	0.3316 (4)	-0.2260 (4)	-0.0427 (3)
C(2)	0.1591 (3)	-0.3482 (4)	0.0716 (3)
C(3)	0.1188 (4)	-0.0344 (4)	-0.0663 (4)
C(4)	-0.0532 (4)	-0.2532 (4)	-0.0375 (4)
C(5)	0.1022 (4)	-0.4781 (4)	-0.1404 (4)
C(6)	0.1098 (4)	-0.5656 (4)	-0.2184 (4)
C(7)	0.2598 (4)	-0.3536 (4)	-0.2426 (4)
C(8)	0.1774 (5)	-0.2912 (5)	-0.3002 (4)
C(9)	0.3270 (4)	-0.4870 (4)	-0.0905 (4)
C(10)	0.3109 (5)	-0.5645 (6)	-0.0081 (5)
C(11)	0.1869 (6)	-0.1317 (11)	0.2272 (5)
C(12)	0.0856 (5)	-0.1613 (7)	0.2458 (5)
C(13)	0.3469 (10)	-0.0425 (7)	0.1232 (7)
C(14)	0.3522 (5)	0.0350 (5)	0.0551 (6)
C(15)	0.3616 (8)	-0.2481 (9)	0.1936 (6)
C(16)	0.4160 (5)	-0.3362 (6)	0.1685 (5)

Table V. Complete Bond Distances (Å) for **2**

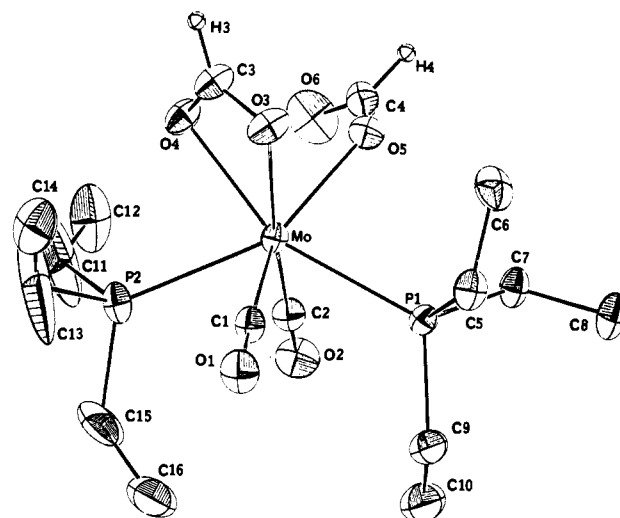
Mo-P(1)	2.516 (1)	O(1)-C(1)	1.155 (4)
Mo-P(2)	2.472 (1)	O(2)-C(2)	1.160 (4)
Mo-O(3)	2.281 (2)	O(3)-C(3)	1.263 (4)
Mo-O(4)	2.218 (2)	O(4)-C(3)	1.252 (4)
Mo-O(5)	2.148 (2)	O(5)-C(4)	1.210 (4)
Mo-C(1)	1.951 (3)	O(6)-C(4)	1.212 (4)
Mo-C(2)	1.954 (3)	C(5)-C(6)	1.525 (5)
P(1)-C(5)	1.826 (3)	C(7)-C(8)	1.507 (6)
P(1)-C(7)	1.836 (3)	C(9)-C(10)	1.505 (6)
P(1)-C(9)	1.844 (4)	C(11)-C(12)	1.355 (8)
P(2)-C(11)	1.757 (5)	C(13)-C(14)	1.335 (9)
P(2)-C(13)	1.774 (7)	C(15)-C(16)	1.318 (9)
P(2)-C(15)	1.779 (7)		

sorption near 1600 cm^{-1} indicated the presence of a unidentate O_2CR ligand.¹⁰ The assignment of bands arising from bidentate carboxylate groups was hampered due to interference from other low-frequency modes.

Proton NMR spectra of these complexes were first order and confirmed all product stoichiometries. A single sharp signal integrating for two protons was observed in the formate region of $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCH})_2$; the line width of this signal was unchanged when the NMR spectrum was obtained at -90°C . The ^{31}P NMR spectra (Table II) of eight complexes each displayed one resonance only. The five tungsten(II) complexes exhibited one-bond ^{31}P - ^{183}W couplings of 160–190 Hz.

Crystallographic Study. The positional parameters determined for all non-hydrogen atoms are collected in Table IV. All ligand bond distances within $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCH})_2$ were normal (Table V). Consequently, only the geometry of the inner coordination sphere and the structures of the two formate ligands will be described in detail.

The molecule adopts a 4:3 "piano stool" configuration (Figure 1). The hard oxygen atoms of the formate ligands occupy the triangular cap, and the soft ligands, carbon monoxide and triethylphosphine, form the rectangular base of the molecule. The molybdenum-formate oxygen distances are significantly different from one another. In the bidentate formate ligand, O3 lies 2.281 Å from molybdenum, while O4 is 2.218 Å from the metal (Table V). The metal-bound oxygen atom of the unidentate formate ligand is the closest to molybdenum at 2.148 Å. The noncoordinated oxygen atom is 3.338 Å away from Mo and exhibits the largest degree of thermal motion of the four formate oxygens. The carbon-oxygen bonds in the bidentate formate ligand are approximately equal in length, about 2.26 Å, and are significantly

**Figure 1.** Molecular structure of $\text{Mo}(\text{CO})_2(\text{PEt}_3)_2(\text{OOCH})_2$ showing the atomic labeling scheme.**Table VI.** Complete Bond Angles (deg) for **2**

P(1)-Mo-P(2)	129.5 (0)	O(5)-Mo-C(1)	145.0 (1)
P(1)-Mo-O(3)	104.2 (0)	O(5)-Mo-C(2)	93.0 (1)
P(1)-Mo-O(4)	155.9 (0)	C(1)-Mo-C(2)	105.6 (1)
P(1)-Mo-O(5)	82.2 (0)	C(5)-P(1)-C(7)	104.8 (1)
P(1)-Mo-C(1)	73.5 (1)	C(5)-P(1)-C(9)	106.1 (1)
P(1)-Mo-C(2)	77.5 (1)	C(7)-P(1)-C(9)	98.4 (1)
P(2)-Mo-O(3)	108.8 (0)	C(11)-P(2)-C(13)	101.7 (5)
P(2)-Mo-O(4)	74.3 (0)	C(11)-P(2)-C(15)	99.5 (5)
P(2)-Mo-O(5)	141.9 (0)	C(13)-P(2)-C(15)	99.7 (5)
P(2)-Mo-C(1)	72.3 (1)	O(3)-C(3)-O(4)	120.4 (3)
P(2)-Mo-C(2)	77.2 (1)	O(5)-C(4)-O(6)	131.7 (4)
O(3)-Mo-O(4)	58.0 (0)	P(1)-C(5)-C(6)	116.2 (2)
O(3)-Mo-O(5)	76.4 (1)	P(1)-C(7)-C(8)	114.0 (2)
O(3)-Mo-C(1)	85.5 (1)	P(1)-C(9)-C(10)	116.9 (3)
O(3)-Mo-C(2)	168.7 (1)	P(2)-C(11)-C(12)	131.8 (5)
O(4)-Mo-O(5)	77.7 (1)	P(2)-C(13)-C(14)	131.8 (6)
O(4)-Mo-C(1)	117.2 (1)	P(2)-C(15)-C(16)	132.6 (5)
O(4)-Mo-C(2)	116.6 (1)		

longer than the C-O distances in the monodentate formate ligand at 2.10 Å.

The structure and geometry of the rectangular base is typical for seven-coordinate Mo(II) complexes. The angle subtended by the carbonyl ligands is 105.6° , and the angle between the phosphines is 129.5° (Table VI). The plane formed by the carbonyl ligands and the metal center is perpendicular (89.8°) to the plane formed by the phosphorus atoms and molybdenum. Although the ethyl groups bound to P2 displayed much larger degrees of thermal motion than is usually observed, the fit was poor when "half-occupancy" disordered positions were entered for these atoms.

Discussion

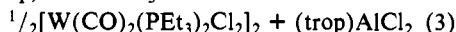
Molybdenum Complexes. Carboxylate complexes analogous to Archer's $(\text{dcq})_2$ species, $\text{Mo}(\text{CO})_{3-n}(\text{PPh}_3)_n(\text{dcq})_2$ ($n = 1, 2$),⁷ in which both dcq ligands are bidentate, were not prepared. Instead, Mo(II) bis(carboxylate) complexes that we synthesized were found to contain one bidentate and one unidentate O_2CR ligand. This conclusion is supported by the observation of a strong ketonic absorption in infrared spectra of the bis(carboxylates), which indicates the presence of an uncoordinated carboxylate oxygen.¹⁰ Accordingly, this band is absent in infrared spectra of **3** (Table I). The X-ray diffraction study of **2** confirms the presence of different coordination modes for the two formate ligands in the solid state.

In solution, a single ^1H formate signal is evidence for rapid exchange between the coordination modes (it is improbable that both formate protons would resonate at the same frequency). This rearrangement is not sufficiently slow for direct NMR detection of exchange even at -90°C . Similar observations have been made by Wilkinson and co-workers for the facile interchange between

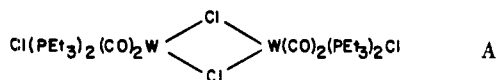
monodentate and bidentate coordination modes of the formato ligands in WH₂(PMe₃)₃(OOCH)₂.¹¹ An analogous process has also been reported for carboxylate ligands in Ru(O₂CMe)₂(CO)(PPh₃)₂¹² and related compounds M(O₂CR)₂(CO)(PPh₃)₂ (M = Ru, R = Me, CF₃, C₂F₅, C₆F₅; M = Os, R = Me, CF₃).¹³

Tungsten Complexes. Archer and co-workers⁷ found that 4,8-dichloroquinolinol (Hdcq) would react with **1b** under mild conditions to give a dcq product and two different (dcq)₂ products. Only a relatively weak base was required to obtain the bis(quinolinolates). In contrast, we found it necessary to prepare sodium or potassium salts of the ligands employed in this study before compounds analogous to Archer's dcq complexes⁷ could be synthesized. The difference presumably arises from the presence of a borderline base, the pyridine functionality, in dcq.⁷ The donor set in facfac, acac, or trop consists entirely of hard Lewis base oxygens, which are not expected to interact as favorably with a soft metal center such as W(II). The ability of soft or borderline basic ligands to promote the formation of stable W(II) carbonyl complexes has been studied by Archer.⁷ Nevertheless, the tungsten complexes and most of the molybdenum complexes prepared in this work are stable for prolonged periods in air, are easily handled, and are readily synthesized. A smooth trend in carbonyl stretching frequencies was observed in which the more highly donating ligand set (containing acac and PEt₃, for example) gave rise to lower energy CO bands (Table I).

Attempts to labilize chloride from W(CO)₂(PEt₃)₂(B-B)Cl using AlCl₃ were not successful, but in one instance the addition of AlCl₃ promoted the formation of a new dimer, [W(CO)₂(PEt₃)₂Cl₂]₂ (**12**; eq 3). This material is extremely air-sensitive, W(CO)₂(PEt₃)₂(trop)Cl + AlCl₃ →



perhaps accounting for the low accuracy of the analytical and molecular weight data. The spectroscopic behavior of the yellow compound is consistent with the dimeric assignment, but even more convincing is the successful generation of **1a** simply by adding CO gas to a solution of the dimer. The mechanism of the dimerization reaction was not determined, but the observation of stretches attributable to tropolonate in the infrared spectrum of the white precipitate formed during the reaction suggests that a simple metathesis occurs (eq 3). We presume that this yellow dimer is closely related to the well-known [W(CO)₄X₂]₂ family;¹⁹ Cotton et al. recently published the structure of [W(CO)₄Br₂]₂, confirming the presence of halide bridges and seven-coordinate metal centers.²⁰ Thus, it seems plausible that the dimer prepared in this study has a similar halide-bridged structure A. Colton



et al. briefly reported the preparation of another related compound, W(CO)₂(PPh₃)₂Cl₂, which they describe as blue.^{16c} This color is consistent with analogous 16-electron molybdenum(II) monomers,¹⁶ and though Colton considered both monomeric and dimeric formulations, no final conclusion concerning the molecularity of W(CO)₂(PPh₃)₂Cl₂ was reached. Unfortunately, we were unable to prepare [W(CO)₂(PPh₃)₂Cl₂]₂ by our method, due to our inability to synthesize W(CO)₂(PPh₃)₂(trop)Cl, and therefore we could not establish a molecular weight for the compound. We were also unable to prepare this material in a sufficiently pure form for analysis following Colton's method. The correct molecularity of complexes in this class merits further investigation.

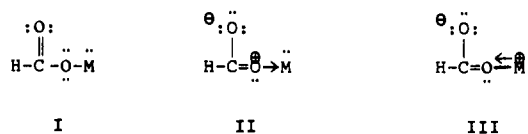
Molecular Structure of 2. The solid-state structure of Mo(CO)₂(PEt₃)₂(OOCH)₂ provides some interesting points of comparison with other formato structures. In particular, carbon-

Table VII. Metrical Data for Monodentate Formato Ligands

complex	M(O—C), C=O,		ref
	Å	Å	
CpFe(CO) ₂ (OOCH)	1.277	1.208	21
Pt[P(C ₆ H ₁₃) ₃] ₂ H(OOCH)	1.30	1.17	22
Ni[C ₆ H ₅ (CH ₂ NMe ₂) ₂](OOCH)	1.270	1.209	23
Mo(CO) ₂ (PEt ₃) ₂ (OOCH) ₂ (2)	1.210	1.212	this work

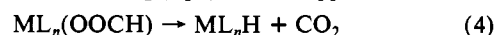
oxygen distances in unidentate formates normally differ significantly from one another with the longer C—O linkage associated with the metal-coordinated oxygen atom (Table VII).^{21–23} In contrast, within the unidentate formato ligand in **2** the C—O distances are nearly identical (Table VII), as the M(O—C) distance appears unusually short. Note that unidentate formato ligands would be expected to form shorter M—O bonds than bidentate analogues for both electronic and steric reasons.²⁴ We observe C—O distances within the bidentate formate that are nearly equal and significantly longer than those within the unidentate OOCH fragment (Table V). Our study appears to be the first in which a direct comparison can be made between the structure of formato ligands engaged in two different binding modes within the same coordination sphere.

The observation of unconventional binding modes for carboxylate ligands in low-valent group VI (6)²⁷ metals has been made before;²⁵ in particular, the M(O—C) distances in M(CO)₅(OOCH)[−] complexes (M = Cr, Mo, W) are slightly shorter than C=O distances in these molecules. As suggested by Cotton, Darensbourg, and Kolthammer,²⁵ we believe the electron density at the metal center here accounts for the similar C=O and C—OM distances in the monodentate formate ligand. As the electrophilicity of the metal decreases, resonance form I will become



less important and resonance form II will begin to shorten the C—OM distance and lengthen the C=O distance. More specifically overlap of the delocalized carboxylate pπ system with a filled metal dπ orbital can further favor a short C—OM distance as crudely reflected in resonance form III.

The presence of abnormally large thermal ellipsoids in the oxygens of unidentate formato ligands has been associated with a propensity to eliminate CO₂ (eq 4).²³ The appearance of such



an oxygen in **2** prompted us to attempt the formation of Mo(CO)₂(PEt₃)₂(OOCH)H by thermally decarboxylating the bis(formate) complex. This method has been successfully employed to produce metal hydride complexes in other systems.^{9c} The preparation by Wilkinson of W(PMe₃)₄(OOCH)H also made this transformation appear feasible.²⁶ Unfortunately, while mild

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(27) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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.

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

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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]·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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