Synthesis of Group 6 Metal Carbonyls with Hybrid P-Donor Crown Ether and Aza-Crown Ether Ligands and the Effect of Phosphorus Substituents on Their Reaction with RLi Reagents

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A series of α, ω -di-P-donor ligands of the type X-XP-OO-PX-X {P₂ \supset ; X-X = MeNCH₂CH₂NMe, MeN(CH₂)₃NMe, 1,2-O₂C₆H₄, OCH₂CH₂O; OO = O(CH₂)₂₍₃O(CH₂)₃O, O(CH₂)₂A(CH₂)₂₍₃A(CH₂)₂₍₃O) (A = 0, NMe), MeN(CH₂)₃N(Me)(CH₂)₃NMe) have been prepared from the reaction of 2 equiv of X-XPCI

with the appropriate α, ω -diol (or diamine) in the presence of Et₃N. Complexation of these ditopic ligands to $M(CO)_4$ (norbornadiene) (M = Mo, Cr, W) using high dilution techniques has been used to synthesize 19 11-crown-3, 12C3, 13C4, and 14C4 metalla-(aza)-crown ether tetracarbonyl complexes, cis-M(CO)₄P₂ \supset .

The complexes containing "MeNCH₂CH₂N(Me)PO" donor groups react with RLi (R = Ph, Me) to give isolable benzoylate/acylate complexes of the type $M(CO)_3(RCOLi)P_2 \supset$ in which the Li⁺ cation is en-capsulated by the benzoylate/acylate oxygen, the two "PO" oxygens, and the O(NMe) donor groups of the di-P-donor ligand. Equilibrium studies of the reaction $M(CO)_4P_2 \supset$ + PhLi $\rightleftharpoons M(CO)_3(PhCOLi)P_2 \supset$ indicate that Li⁺ binding and benzoylate stabilization (i) is greatest for 12C3 and 13C4 metalla-crown ether rings and (ii) is very constitute to the besisity of the "PO" oxygens documents in the order $P_2 \supset P_2 \supset M_2$ rings and (ii) is very sensitive to the basicity of the "PO" oxygens decreasing in the order R_2P = Me- $NCH_2CH_2N(Me)P > Ph_2P \gg (1,2-O_2C_6H_4)P \ge OCH_2CH_2OP$. This decrease in stability is opposite to that predicted on the basis of the $\nu(CO)$ stretching frequencies of the $M(CO)_4P_2$ complexes. A qualitative comparison of the kinetic stability of the benzoylate complexes $M(CO)_3(PhCOLi)P_2$ in CH_2Cl_2 and in 0.044 M H₂O in THF is also consistent with the above stability sequence. The "(1,2-O_2C_6H_4)P" complexes $M(CO)_4P_2$ react with RLi to give highly reactive " $M(CO)_4P_2$ react with a complexe to H_2O or MeOH rapidly revert to $M(CO)_4P_2$. Evidence suggests that these adducts involve complexation of the Li by an oxygen atom of the 1,2-O_2C_6H_4 substituent on each phosphorus together with one or more

ether oxygens of the ligand "backbone". The " OCH_2CH_2OPO " complexes are the least reactive toward RLi forming small amounts of " $M(CO)_4P_2$)-LiR" adducts and very small amounts of benzoylate/acylate as assessed by IR monitoring of the $\nu(CO)$ region.

Introduction

A simple approach to the synthesis of heterodinuclear complexes containing low oxidation state transistion metals and cations of groups 1A and 2A involves the synthesis of ditopic ligands that combine a subunit containing a "soft" binding site with one bearing a "hard" site.¹⁻¹⁵ Of particular relevance to this paper are ligands that combine a crown ether or cryptand functionality with one or more P-donor groups.^{4,10-18} Of interest with respect to the

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chemistry of heterobimetallic complexes derived from hybrid P-donor crown ether ligands is the possible effect(s) that the presence of a proximal class 1A/2A cation may have on the reactivity of ligands coordinated to the transition metal.¹⁰⁻¹⁵ For group 1A cations Li⁺ has the most pronounced effect.^{15,19}

In the preceding paper we have reported the synthesis of a range of ditopic α, ω -bis(diphenylphosphinito) polyether ligands and amino analogues {e.g. Ph_2POCH_2 -(CH_2ACH_2)_n CH_2OPPh_2 (1) (A = O, NMe; n = 1-4); $Ph_2PO(CH_2)_3A(CH_2)_3OPPPh_2$ (A = O, NMe), etc.].¹⁵ The cis chelation of these ligands to group 6 metal carbonyls gave complexes of the type $cis-M(CO)_4$ Ph₂POCH₂- $(CH_2ACH_2)_nCH_2OPPh_2$ (2) (A = 0, NMe) in which M is incorporated into the crown ether backbone (eq 1). While



 $M(CO)_4(PR_3)_2$ complexes are unreactive toward RLi reagents,^{20,21} the addition of RLi to a coordinated carbonyl

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Table I. Analytical and IR Data for the Group 6 Metalla-Crown-Ether Complexes 6-16

	metalla-		element	al anal. calcd	(found)		vield.]	IR ν(CO), cm ⁻¹
complex	crown ether		С	Н	N	mp, ±1 °C	%		(CH ₂ Cl	2 soln)
6 a	11C3	C17H30M0N4O7P2	36.43 (36.95)	5.36 (5.45)	10.00 (9.90)	170d	20	2019	1904	1886
7a	12C3	$C_{18}H_{32}M_0N_4O_7P_2$	37.64 (37.97)	5.58 (5.59)	9.76 (9.73)	163	46	2020	1905	1878
8 a	13C4	C18H32MoN4O8P2	36.60 (36.64)	5.40 (5.57)	9.49 (9.43)	162	21	2021	1908	1883
9a	13C4	C ₁₈ H ₃₂ N ₄ O ₈ P ₂ W	31.90 (32.18)	4.73 (4.81)	8.27 (8.24)	170	17	2016	1888	1878
10a	13C4	C ₁₈ H ₃₂ CrN ₄ O ₈ P ₂	39.56 (40.71)	5.86 (6.15)	10.26 (10.24)	173	29	2009	1898	1878
11 a	14C4	C10H34MoN4O9P2	37.75 (37.80)	5.63 (5.97)	9.27 (9.19)	193	37	2021	1908	1885
12a	13C4(NMe) ₂	C ₂₀ H ₃₈ MoN ₆ P ₂	38.96 (39.19)	6.17 (6.10)	13.60 (13.55)	130	43	2020	1906	1883
13 a	14C4(NMe) ₂	C ₂₁ H ₄₀ MoN ₆ O ₆ P ₂	40.00 (40.97)	6.53 (6.57)	13.33 (12.81)	143	18	2020	1908	1885
14a	13C4	C ₂₀ H ₂₀ MoN ₄ O ₈ P ₂	38.83 (39.09)	5.82 (5.84)	9.06 (9.05)	187	37	2014	1901	1872
6b	11C3	$C_{21}H_{12}M_0O_{11}P_2$	41.74 (42.02)	3.00 (2.76)		144	11	2050	1966	1946 (br)
7b	12C3	$C_{22}H_{20}M_0O_{11}P_2$	42.74 (43.19)	3.26 (3.28)		81	53	2050	1965	1945 (br)
8b	13C4	C ₂₂ H ₂₀ MoO ₁₂ P ₂	41.66 (41.69)	3.18 (3.05)		121	36	2050	1965	1945 (br)
15b	12C3(NMe),	CarHaoMoNaOaPa	45.63 (45.72)	4.45 (4.38)	6.39 (6.39)	163	38	2042	1952	1933 (br)
16		CieHi MoOinP	39.44 (39.43)	2.57 (2.26)		118	20	2053	1966	1949 (br)
-6c	11C3	C ₁₀ H ₁₀ M ₀ O ₁₁ P ₀	30.73 (30.89)	3.57 (3.41)		135	35	2040	1945	1925 (br)
7c	12C3	C ₁ ,H ₀ M ₀ O ₁ P ₀	32.20 (32.02)	3.86 (3.80)		114	35	2039	1945	1927 (br)
8c	13C4	C ₁ H ₀ M ₀ O ₁₀ P ₀	31.24 (31.23)	3.75 (3.63)		81	36	2040	1946	1927 (v br)
11c	14C4	C ₁ H ₀₀ M ₀ O ₁₀ P ₀	32.63 (32.86)	4.02 (3.90)		107	41	2040	1945	1925 (br)
12c	13C4(NMe)。	C10HooMoNoO10Po	34.06 (34.20)	4.64 (4.72)	4.96 (4.88)	84	20	2040	1944	1925 (v br)
15c	12C3(NMe) ₃	$C_{17}H_{29}M_0N_3O_8P_2$	36.38 (36.54)	5.21 (5.26)	7.49 (7.45)	111	38	2028	1928	1913

group of these metalla-crown ether complexes gave acylate/benzoylate complexes "fac-M(CO)₃(RCOLi)P₂ \supset " (e.g. 3, eq 2). The ease of isolation of these complexes was



<u>3a</u>, A=O; <u>3b</u>, A=NMe

found to be highly sensitive to the structural and bonding features of the crown ether, the stability of the products being determined by the ease/degree of "preferential Li⁺ cation binding". It was found that the metalla-12C3, 13C4, and 14C4 "M(CO)₃(RCOLi)P₂ \supset " complexes were particularly stable as assessed by K (eq 2) and k_d values for the reaction of the benzoylate complexes with H₂O in THF (eq 3). In this paper we describe the preparation of 11C3,

$$\begin{array}{c} \begin{array}{c} Ph \\ C = 0 \\ C \\ C \\ C \\ Ph_{2} \end{array} \xrightarrow{(Ph_{2})} 0.22 \text{ MH}_{2} O \text{ in THF, } 26^{\circ}C \\ C \\ C \\ C \\ Ph_{2} \end{array} \xrightarrow{(Ph_{2})} 0.22 \text{ MH}_{2} O \text{ in THF, } 26^{\circ}C \\ C \\ C \\ C \\ Ph_{2} \end{array} \xrightarrow{(Ph_{2})} + \text{LiOH} + \text{C}_{6}\text{H}_{6} \\ C \\ C \\ Ph_{2} \\ C \\ Ph_{2} \end{array} \xrightarrow{(eq. 3)}$$

12C3, 13C4, and 14C4 group 6 metalla-crown ether tetracarbonyl complexes of the general type 4, which are structural analogues of 2 etc., and report on the effects that the replacement of the Ph₂ substituents at phosphorus (2) by MeNCH₂CH₂CMe, OCH₂CH₂O, and 1,2-O₂C₆H₄ has on the reaction of the metalla-crown ether tetracarbonyls (4) with RLi.



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Results

The reaction of the appropriate α,ω -diol with 2 molar equiv of the chlorophosphorus reagents ClP(X₂) (X₂ = MeNCH₂CH₂NMe, MeNCH₂CH₂CH₂NMe, OCH₂CH₂O, 1,2-O₂C₆H₄) in the presence of base yielded the α,ω -bis-P-donor ligands 5 as viscous colorless oils (eq 4). As these

$$HO OH + 2 CI - P_{X}^{X} \xrightarrow{2NE_{1_{3}}} (X - P - O - P_{X}^{X}) + 2E_{1_{3}}NH^{+}CI^{-} \downarrow (eq, 4)$$

$$X = OCH_{2}CH_{2}O \qquad O = O(CH_{2})_{2(3)}O(CH_{2})_{3}O$$

$$I,2 - O_{2}C_{6}H_{4} \qquad O(CH_{2})_{2(3)}A(CH_{2})_{2(3)}O$$

$$MeN(CH_{2})_{2(3)}NMe \qquad A = 0, NMe$$

compounds were not easily purified, care was taken to use freshly distilled, dry reagents and the ligands 5 were used "as is" subject to satisfactory NMR characterization. Reaction of the ligands 5 with a molar equivalent of M-(CO)₄(norbornadiene) (M = Cr, Mo, W) using high dilution conditions gave the metalla-crown ether complexes "M-(CO)₄P₂ \supseteq " (6-15, eq 5). Reactions were run in CH₂Cl₂



solutions at room temperature for M = Mo and in refluxing benzene solution for M = Cr and W. High-dilution conditions were used to ensure maximization of ring formation relative to the competition reaction of polymerization. After chromatographic workup the metalla-crown ether complexes were obtained as white (M = Mo) or yellow (M = Cr, W) crystalline materials in yields of 10–55%. The complex *cis*-Mo(CO)₄{P(OMe)(1,2-O₂C₆H₄)}₂ (16) was prepared for reference purposes. Complexes 6–16 were characterized by elemental analysis and IR [ν (CO) region) (Table I) and ¹H and ³¹P{¹H} NMR spectroscopy (e.g. Table II and Figure 1a).

Reaction of the Bis(1,3-dimethyl-1,3,2-diazaphospholidine)-Metalla-Crown Ether Tetracarbonyl Complexes (6a-13a) with RLi. The "Me NCH_2CH_2N -(Me)P-" complexes 6a-13a and the "Me $N(CH_2)_3N$ -(Me)P-" complex 14a reacted with a slight excess of RLi







Synthetically, benzene was the solvent of choice as the benzoylate/acylate products rapidly precipitated as yellow-orange powders. Recrystallization from CH₂Cl₂/hexane often resulted in much decomposition of the benzoylate/acylate product. Once recrystallized however, the complexes were stable in dry CH₂Cl₂ for fairly long periods of time. If PhLi, freshly prepared from Ph₂Hg and Li metal, was used instead of commercially supplied PhLi, the resulting benzoylate was far more easily recrystallized from dry CH_2Cl_2 with very little decomposition. IR data and elemental analyses on a few selected complexes are given in Table III. The complexes exhibit three strong ν (CO)'s of approximately equal intensity at ca. 1927, 1835, and 1825 cm⁻¹, and the ¹H NMR spectra exhibit two NCH₃ resonances consistent with the structure "fac-M(CO)₃- $(PhCOLi)P_2 \supset$ " (see Table II and Figure 1b). The molecular structure of the $[2.3.2(NMe)_2]$ benzoylate 21a, as determined by single-crystal X-ray diffraction, is reported in detail elsewhere.²² However, the basic molecular features are given in Figure 2. The coordination geometry about the encapsulated Li⁺ approximates a square pyramid with the benzoylate carbon atom occupying the apical position and the P-O and NMe groups forming the basal plane. While the structural features of the Mo(PhCO)-Li⁺ unit and the benzoylate O…Li⁺ distance of 1.899 (8) Å are similar to those of previously studied benzoylate systems.^{11,14,28} the PO…Li⁺ distances are significantly longer. Structural analogues of 21a include M(CO)₃(PhCOLi)- ${Ph_2PO(CH_2)_3N(Me)(CH_2)_3OPPh_2}^{15,22}$ and $Mo(CO)_3$ -(PhCOLi){(Ph2POCH2CH2)2NCH2CH2OMe}¹⁴ which have Li⁺ in approximately tetrahedral and trigonal-bipyramidal



environments, respectively. As with previous studies in 21a the oxygen atoms attached to phosphorus are trigonal planar (POC $\approx 121^{\circ}$) consistent with O \rightarrow P π -donation of one of the oxygen "lone pairs".

As an assessment of the relative stabilities of the acylate/benzoylate metalla-crown ether lithium salts 17-25, the equilibrium constant $K = [M(CO)_3(RCOLi)P_2]/[M (CO)_4P_2$ [RLi] (eq 6) was determined by IR studies (Table IV and Figure 3a). It should be noted that RLi reagents exist in THF solution as oligomers (e.g. Me₄Li₄, Ph₂Li₂) and that the presence of LiX salts (e.g. X = Cl, OH) can result in the formation of less reactive mixed aggregates.²³ For the purpose of obtaining a comparative scale of the relative Li⁺ complexing abilities of the metalla-crown ether acylate/benzoylate anions the concentration term [RLi] (reflective of total "R⁻ concentration") is used rather than the more appropriate, but difficult to assess terms, such as $[R_n Li_n]^{1/n}$. Values of K (eq 6) are given in Table IV. The percentage experimental error in K varies from ± 15 to $\pm 50\%$ with the largest errors being for very large or very small values of K. The major sources of error in the measurements resulted from (i) the necessity/difficulty of working with dilute solutions of organolithium reagents $(<10^{-2} \text{ M})$, (ii) difficulties associated with obtaining a completely dry apparatus (glassware + IR cell), and (iii) decomposition problems. For example, if the addition of a second molar equivalent of RLi resulted in a dramatic increase in the concentration of the $M(CO)_3(RCOLi)P_2$ product, it was assumed that some of the original RLi had been decomposed by trace amounts of H_2O and the result was not used for K measurements. Attempts to measure K in benzene solutions resulted in the acylate/benzoylate products being precipitated from solution in the IR cell.

A second approach that we have previously used to assess the relative kinetic stabilities of lithium benzoylate/acylate complexes is to compare their relative rates of decomposition in dry CH₂Cl₂ or H₂O/THF solution (e.g. k_d , eq 3) to regenerate the tetracarbonyl.¹⁶ In dry CH₂Cl₂ solution at 20 °C the benzoylate complexes 17a-25a are quite stable with respect to decomposition to the tetracarbonyl complexes 6a-14a and presumably "PhLi + CH₂Cl₂ decomposition products". After 9 days in dry CH₂Cl₂ solution less than 1% of the 11C3 benzoylate complex 17a has been converted to the tetracarbonyl

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Table II.	¹ H and ²	^H P[¹ H] NM	IR Data ^a o	of the l	Bis(1,3-dime	t hyl-1,3,2	-diazapho	spholidine)–Metalla-Cr	own-Ether (Complexes

		1	H NMR recorde	d in CD ₂ Cl ₂ soln	(δ, ppm; J,	Hz)		
			PR ₂					
	metalla-	$\delta(CH_3-N)$			crown	ether back	bone	
complex	crown ether	wn ether $({}^{3}J_{31}P^{-1}H)$	$\delta(CH_2N)$	$\delta(CH_2O)$	$-CH_2-$	CH3-N	$-CH_2N$	$\delta(\mathbf{P}), \mathbf{ppm}$
6 a	11C3	2.84 (b d, 10.8)	3.03-3.33 (m)	3.33-3.80 (m)	1.7 (qn)			$146 (d, {}^{2}J_{31P} = 50)$
7a	12C3	2.79 (vc, ^b 11.4)	3.00-3.37 (m)	3.61 (t)	1.7 (qn)			145 (s)
8a.	13C4	2.87 (vc, ^b 10.8)	3.05-3.43 (m)	3.61 (s)				145 (s)
9a	13C4	2.83 (vc, b 10.8)	3.02-3.42 (m)	3.59 (b s)				123 (s, ${}^{1}J_{183}W_{31P}$ not resolved)
10a	13C4	$3.02 (vc, ^{b} 9.0)$	3.22-3.47 (m)	3.73 (d)	1.64 (qn)			154 (s)
11a	14C4	2.79 (d, 10.2)	2.93-3.29 (m)	3.75 (t) 3.57 (b s) 3.49 (b s)				145 (d), 144 (d, ${}^{2}J_{31P}=48$)
12a 13a 14a	13C4(NMe) ₂ 14C4(NMe) ₂ 13C4	2.86 (vc, ^b 10.2) 2.87 (vc, ^b 10.8) 2.26 (vc, ^b 12.6)	3.00-3.43 (m) 3.05-3.42 (m) 3.00 (q)	3.48-3.82 (m) 3.42-3.80 (m) 3.37-3.93 (m)	1.57 (qn) 1.85 (qn)	2.25 (s) 2.23 (s)	2.60 (t) 2.47 (t)	145 (s) 145 (s) 154 (s)

^aAbbreviations: b, broad; d, doublet; m, multiplet; q, quartet; qn, quintet; s, singlet; t, triplet. ^bvc = virtually coupled ³¹P nuclei; gives distinctive ¹H NMR pattern for NCH₃ groups (see Figure 1). Quoted ²J_{³¹P-1H} is the separation of the "outer resonances". ^cNonequivalent ³¹P nuclei—no virtual coupling.





Figure 1. (a) ¹H NMR spectrum of the 12C3 complex Mo-(CO)₄{MeNCH₂CH₂N(Me)PO(CH₂)₃O(CH₂)₃OPN(Me)-CH₂CH₂NMe] (7a) in CD₂Cl₂ solution. (b) ¹H NMR spectrum of the benzoylate 18a derived from the addition of PhLi to 7a (Ph resonances not shown).



Figure 2. The basic structural features of the $14C4(NMe)_2$ benzoylate complex $21a.^{22}$

complex 6a [as judged by IR monitoring, $\nu(CO)$ region]. The benzoylate complexes were also quite stable for short periods of time in THF solutions that were 0.044 M in H₂O. Figure 4 shows the change in the concentration of the 11C3 complex Mo(CO)₃(PhCOLi){MeNCH₂CH₂N-(Me)PO(CH₂)₂O(CH₂)₃OPN(Me)CH₂CH₂NMe} (17a) with time (0.044 M H₂O/THF/26 °C). For comparison

Table III. IR Data and Elemental Analyses (see Footnotes a-f) for the Benzoylate and Acylate Complexes 17-25

М	metalla- crown ether	R	ν(C	0), cm ⁻¹ (Tl	HF soln)
Mo	11C3	Ph	1926	1837	1818
Mo	11C3	Me	1930	1837	1830
Mo	12C3	Ph	1931	1842	1829
Mo	12C3	Me	1931	1841	1828
Mo	13C4	Ph	1927	1836	1825
Mo	13C4	Me	1928	1835	1825
Mo	$13C4(NMe)_2$	Ph	1926	1835	1822
Mo	$13C4(NMe)_2$	Me	1925	1833	1822
Mo	$14C4(NMe)_2$	Ph	1926	1832	1824 (br)
Mo	14C4	\mathbf{Ph}	1927	1834	1823
\mathbf{Cr}	13C4	Ph	1919	1820 (br)	
\mathbf{Cr}	13C4	Me	1918	1819 (br)	
W	13C4	Ph	1910	1805 (br)	
Mo	13C4	Ph	1918	1827	1813
Mo	13C4	Me	1920	1826	1815
	M Mo Mo Mo Mo Mo Mo Cr Cr Cr W W Mo Mo	metalla- crown ether Mo 11C3 Mo 11C3 Mo 12C3 Mo 12C3 Mo 13C4 Mo 13C4(NMe)_2 Mo 13C4(NMe)_2 Mo 13C4(NMe)_2 Mo 14C4(NMe)_2 Mo 14C4 Cr 13C4 W 13C4 W 13C4 Mo 13C4	metalla- crown ether R Mo 11C3 Ph Mo 11C3 Me Mo 12C3 Ph Mo 12C3 Me Mo 12C3 Me Mo 13C4 Ph Mo 13C4 Me Mo 13C4(NMe)2 Ph Mo 13C4(NMe)2 Me Mo 13C4(NMe)2 Ph Mo 14C4(NMe)2 Ph Mo 14C4 Ph Cr 13C4 Me W 13C4 Ph Mo 13C4 Me	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

^aElemental Anal. Calcd (Found) for $C_{22}H_{35}LiMoN_4O_7P_2$: C, 50.76 (50.51); H, 6.44 (6.23); N, 10.30 (10.14). ^b For $C_{24}H_{37}LiMoN_4O_7P_2$: C, 51.64 (51.25); H, 6.63 (6.58); N, 10.04 (9.87). ^c For $C_{24}H_{37}LiMoN_4O_8P_2$ ·CH₂Cl₂: C, 39.57 (39.12); H, 5.17 (5.58); N, 7.39 (7.67). ^d For $C_{26}H_{43}LiMoN_6O_6P_2$ ·CH₂Cl₂: C, 41.32 (40.66); H, 5.10 (4.29); N, 10.71 (11.15). ^e For $C_{21}H_{41}LiMoN_6O_6P_2$ · $^1/_2$ CH₂Cl₂: C, 38.39 (38.33); H, 6.25 (6.16); 12.50 (11.81). ^l fstructure determined by single-crystal X-ray diffraction²²—see Figure 2.

Table IV. Equilibrium Constant Data^a for the Reaction of the "MeNCH₂CH₂CH₂N(Me)P-" "M(CO)₂P." Complexes 6a-14a

ιne			2 Complexes	04-144
	with RLi in TH	F at 26 °C	(Eq 7) ^b	

M- (CO) ₄ P ₂	metalla- crown ether	М		benzoylate K(PhLi)	acylate K(MeLi)
6a	11C3	Mo	17	680 (~60)	33 000 (45)
7a	12C3	Mo	18	8000 (500)	$>2 \times 10^5$ (6700)
8 a	13C4	Mo	19	2500 (2500)	>10 ⁵ (44 200)
9a	13C4	W	23	3000 (100)	(16 000)
10a	13C4	Cr	24	15 (100)	500 (220)
11a	14C4	Mo	22	35 (25)	(2400)
12a	13C4(NMe) ₂	Mo	20	32 000 (50 000)	$>1.2 \times 10^5 (>10^5)$
13 a	$14C4(NMe)_2$	Mo	21	200	
1 4a	13C4	Mo	25	ppts	ppts

^a $[M(CO)_4P_2 \supset]_0 = 7.25 \times 10^{-3} M.$ ^bK = $[(OC)_3M(RCOLi)P_2 \supset]/[M(CO)_4P_2 \supset] \times [RLi]$ (L·mol⁻¹). The corresponding data for the "PPh₂" analogues (eq 2) are given in parentheses.

purposes the change in the concentration of several "Ph₂P" analogues, and $Mo(CO)_5$ (PhCOLi), with time (eq 3) under identical conditions are also given in Figure 4.¹⁵ Complex 17a is quite stable for ca. 12 min at which time there is



Figure 3. IR spectra ν (CO) region for a series of Mo(CO)₄P₂ complexes and spectra after addition of a molar equivalent of PhLi recorded as THF solutions: (a) (-) Mo(CO)₄[MeNCH₂CH₂N-(Me)PO(CH₂)₃O(CH₂)₃OPN(Me)CH₂CH₂NMe] (7a) and (---) the benzoylate 18a; (b) (-) Mo(CO)₄(1,2-O₂C₆H₄)PO(CH₂)₃O(C-H₂)₃OP(1,2-O₂C₆H₄)] and (---) after addition of PhLi; (c) (-) Mo(CO)₄[P(OMe)(1,2-O₂C₆H₄)]₂ and (---) after addition of PhLi; (d) (-) Mo(CO)₄[(1,2-O₂C₆H₄)]₂ and (---) after addition of PhLi; (d) (-) Mo(CO)₄[(1,2-O₂C₆H₄)]₂ and (---) after addition of PhLi; (d) (-) Mo(CO)₄[(1,2-O₂C₆H₄)]₂ of (--) Mo(CO)₂CH₂OP(1,2-O₂C₆H₄)] (8a) and (---) +PhLi; (e) (-) Mo(CO)₄ {OCH₂CH₂OPOCH₂(CH₂N(Me)CH₂)₂CH₂OPOCH₂CH₂O} and (---) +PhLi.

a sudden and rapid reaction to give new and as yet unidentified products (eq 7). No tetracarbonyl complex was formed in this reaction. Similar results were observed with the 12C3 and 13C4 systems 18a and 19a, respectively. The *major* ν (CO) stretches for the products of eq 7 are at 1898 (s) and 1764 (s, br) cm⁻¹ which are at lower frequency than



the starting benzoylate complexes. This suggests that the major product is possibly an anionic tricarbonyl complex. The occurrence of this presumed autocatalytic reaction, which is under further investigation,²⁴ prevented the measurement of the decomplexation rate constant k_d (see eq 3) for complexes 17a-25a.

Reaction of the Bis(*o*-phenylene phosphito)-Metalla-Crown Ether Tetracarbonyl Complexes (6b-15b) with RLi. Addition of RLi (R = Ph, Me) to benzene or THF solutions of the " $(1,2-O_2C_6H_4)P$ -" complexes 6b-15b results in the immediate precipitation of the adduct compounds "M(CO)₄P₂ \supset ·RLi" as white, insoluble, highly reactive solids (e.g. 26, eq 8). Addition of MeOH to these



adducts resulted in the rapid regeneration of "M- $(CO)_4P_2$. The IR [$\nu(CO)$ region] of a 7.25 × 10⁻³ M solution of the 12C3 complex 7b in THF, before and after the addition of a molar equivalent of PhLi (Figure 3b). clearly indicates that the product of PhLi addition is still a tetracarbonyl complex. Adduct formation is also observed on addition of PhLi to the non-crown system cis- $M_0(CO)_4 \{P(OMe)(1,2-O_2C_6H_4)\}_2$ (Figure 3c). The IR spectrum of the 13C4 complex 8b before and after PhLi addition (Figure 3d) suggests the probable formation of three isomeric " $M(CO)_4P_2$ ·RLi" adducts. The 12C3 $(NMe)_3$ complex 15b also formed a 1:1 adduct with PhLi. The IR data for the PhLi adducts are given in Table V together with an estimate of the equilibrium constant K'= $[M(CO)_4P_2 \supset RLi]/[M(CO)_4P_2 \supset] \times [RLi]$ (eq 8). In the case of "7b + PhLi" the IR also contains ν (CO) absorptions at 1883 and 1873 cm⁻¹ which are tentatively assigned to a small quantity of the benzoylate Mo(CO)₃(PhCOLi)- $\{(1,2-O_2C_6H_4)PO(CH_2)_3O(CH_2)_3OP(1,2-O_2C_6H_4)\}$ (see Figure 3b). The adducts formed from the addition of MeLi to THF solutions of 6b-15b precipitate in the IR cell, and these systems were not studied to the same degree as the PhLi systems.

Reaction of the Bis(ethylene phosphito)-Metalla-Crown Ether Tetracarbonyl Complexes (6c-15c) with RLi. IR monitoring of the addition of a molar equivalent of RLi to 7.25×10^{-3} M THF solutions of the " OCH_2CH_2OP -" complexes 6c-15c provided the following observations: for the 12C3(NMe)₃ system 15c, no RLi adduct formation and no benzoylate (no reaction); for the 11C3 and 12C3 systems 6c and 7c, a relatively small amount (ca. 15%) of "M(CO)₄P₂ \supset ·RLi" adduct formation occurs together with a small amount of benzoylate (tentative identification); for the 13C4 complex 8c, small amounts (ca. 15% total) of two adducts are obtained (new bands at 2032 and 2018 cm⁻¹—compare with absorption

⁽²⁴⁾ Powell, J. et al., work in progress.

Table V. IR Data [ν(CO) Region] for the "Mo(CO)₄P₂⊃•RLi" Adducts Formed from the Addition of a Molar Equivalent of PhLi to a 7.25 × 10⁻³ M THF Solution of "(1,2-O₂C₆H₄)P-" Tetracarbonyl Complexes "M(CO)₄P₂⊃", Recorded at 26 °C

M(CO)₄P₂⊃	metalla-crown ether		K'(PhLi)," L·mol ⁻¹			
16		2037 (s)	1950 (s)	1925 (s) 1883 (m)	1873 (m) ^b	1200
7b	12C3	2034 (s)	1948 (s)	1928 (s br)	1010 ()	45 000
80	13C4	2035 (m) 2023 (m) 2013 (m)	1948 (s)	1929 (s)	1912 (s) 1886 (s) ^c	$1.2 \times 10^{\circ}$
15 b	$12C3(NMe)_3$	2034 (s)	1944 (s)	1925 (s)	1902 (s) ^d	14 000

 ${}^{a}K' = [M(CO)_{4}P_{2} \rightarrow PhLi]/[M(CO)_{4}P_{2}] \times [PhLi]$ monitored by following the change in intensity of the high-frequency $\nu(CO)$ absorption of $M(CO)_{4}P_{2}$ (ca. 2050 cm⁻¹—see Table I). The term $[M(CO)_{4}P_{2} \rightarrow PhLi] \equiv$ total concentration of adducts + benzoylate product. ^bAbsorptions at 1883 (m) and 1873 (m) cm⁻¹ are tentatively assigned to the 12C3 benzoylate product " $M(CO)_{3}(PhCOli)P_{2} \supset$ " [third $\nu(CO)$ at higher wavenumber is masked by adduct absorptions). ^cPossible formation of a small quantity of benzoylate is masked by the broadness of the $\nu(CO)$ absorptions. ^dNo absorptions below 1900 cm⁻¹ is taken to infer the absence of any benzoylate.



Figure 4. Changes in the concentration (%) with time for the benzoylate complexes 17a (eq 7) and $Mo(CO)_5(PhCOLi)$, "Ph₂P" 11C3, and 12C3 benzoylates (eq 3) on exposure to 0.044 M H₂O in THF solution at 26 °C.¹⁵

at 2035, 2023, and 2013 for the "8b-PhLi" adducts—Table V); and for the $13C4(NMe)_2$ system, large amounts of "12c-PhLi" adducts are obtained (see Figure 3e). Possible formation of a benzoylate product is masked by the broadness of the $\nu(CO)$ absorptions.

Discussion

The high-dilution reaction procedures that we have previously used to prepare "Ph₂P-" bis(diphenylphosphinito)-metalla-crown ether complexes (eq 1)¹⁵ have been used to synthesize a series of bis(1,3-dimethyl-1,3,2diazaphospholidine)-, bis(o-phenylene phosphito)-, and bis(ethylene phosphito)-metalla-crown ether tetracarbonyl analogues 6-15. Isolated yields (10-55%) were lower than those obtained for the "Ph₂P-" complexes (usually isolated in 60-85% yields), and this may reflect a decrease in the steric bulk of the R₂P group, vis à vis Ph₂P which may decrease the probability of ring closing vs polymer formation. 15,25

Complexes 6-15 and the previously reported " Ph_2P " analogues allow one to assess the effects of phosphorus substituents on the role of preferential Li⁺ cation binding in promoting RLi addition to a coordinated CO of these tetracarbonyl complexes. Equilibrium constant data for the reaction of RLi with the "MeNCH₂CH₂N(Me)P-" complexes 6a-13a and the "MeN(CH₂)₃N(Me)P-" complex 14a (eq 6) give values of K {= $[M(CO)_3(RCOLi)P_2]$ $]/[M(CO)_4P_2] \times [RLi]$ that vary from 15 (10a) to values in excess of 10^5 L·mol⁻¹ (Table IV). Although the experimental errors (reproducibility) in individual K may be $\pm 50\%$, it seems likely, given that most of the experimental problems result in loss of acylate/benzoylate product (e.g. reaction with trace H_2O , that the experimental K values in Table IV are *less* than the "true K value" and should only be used as a qualitative guide. The large variation in the experimental K is reflective of the relative Li^+ ligating abilities of the product molecules and clearly indicated that 12C3 and 13C4 metalla-crown ether systems are the most effective. The data also suggest that the "MeNCH₂CH₂N(Me)P" benzoylate/acylate complexes 17-25 are more stable than the corresponding " Ph_2P " complexes (e.g. K_{PhLi} , "MeNCH₂CH₂N(Me)P", vs K_{PhLi} , "Ph₂P", are as follows: 11C3, 680, vs 60; 12C3, 8000 vs 500). Further support for this conclusion comes from a study of the stability of the 11C3 benzoylate complexes Mo- $(CO)_3(PhCOLi)\{R_2PO(CH_2)_2O(CH_2)_3OPR_2\}$ where $R_2P =$ MeNCH₂CH₂NMeP (17a) and Ph₂P in 0.044 M H₂O/ THF solution. A comparison of the relative stabilities of a series of benzoylate complexes with respect to reaction with water to give $M(CO)_4P_2$, LiOH, and benzene (Figure 4 and eq 3) indicates that in the initial stages the "Me-NCH₂CH₂N(Me)P-" 11C3 system 17a is, kinetically, considerably more stable than both 11C3 and 12C3 "Ph₂P' analogues. One can estimate that for eq 3 k_d (17a) is $<10^{-2}k_{\rm d}$ for the "Ph₂P-11C3" analogue. Assuming that $k_{\rm f}$, the rate constant for formation of the benzoylate complexes, is determined primarily by the energetics of R^{-} addition to CO and is relatively insensitive to the crown ether component, it follows that the replacement of Ph_2P by MeNCH₂CH₂N(Me)P- significantly increases the stability of the benzoylate product consistent with the more qualitative conclusions obtained from the K data (Table IV). Previous kinetic studies of crown ether-cation

and cryptand-cation²⁶ complexation reactions have shown

⁽²⁵⁾ Shaw, B. L. J. Am. Chem. Soc. 1975, 97, 3856.

Table VI. IR Data $[\nu(CO) \text{ region } (cm^{-1})]$ for the 12C3 Tetracarbonyl Mo(CO)₄P₂ \supset and the 12C3 Benzoylate Mo(CO)₅(PhCOLi)P₂ \supset as a Function of the R₂P Substituents (Recorded in THF Solution)

R ₂ P		ν(CO) {Ι	$Mo(CO)_4P_2 \supset $		ν(CO) {Ν	fo(CO) ₃ (PhCO	$DLi)P_2 \supset i$
$MeNCH_2CH_2N(Me)P$ Ph_2P	2020 2025	1916 1930	1903 1917	1884 1903	1931 1936	1842 1854	1829 1833
$\begin{array}{c} \overrightarrow{\text{OCH}_2\text{CH}_2\text{OP}^b} \\ (1,2-\overrightarrow{O}_2\text{C}_6\text{H}_4)\text{P}^b \end{array}$	2039 2050	1945 1965		1927 (br) 1945 (br)	a a	1881 1883	1855 1873

^a High-frequency absorption masked by overlap with $M_0(CO)_4P_2 \supset RLi$ and/or $M_0(CO)_4P_2 \supset carbonyl stretches$. ^bPresence of benzoylate inferred from the IR. The benzoylate products could not be isolated on workup.

that in general,²⁷ though not always,²⁸ the decomplexation rate constant is a dominant factor controlling the ligating abilities of crown ethers. The onset of a very fast and presumably autocatalytic reaction for the "Me- $NCH_2CH_2N(Me)P$ -" benzoylates $[Mo(CO)_3(PhCOLi)P_2]$] in H_2O/THF (eq 7) prevents a more detailed study of the decomplexation reactions of complexes 17-25. (The nature of this reaction is under investigation.²⁴) A comparison of benzoylate stabilities in dry CH₂Cl₂ at 20 °C shows complex 17a to be notably stable. Percent decomposition to $M(CO)_4P_2$ and presumed "PhLi + CH_2Cl_2 decomposition products" after 200-h reaction time are as ~1%, 17a; ~50% for $Mo(CO)_3(PhCOLi)$ follows: $\{Ph_2PO(CH_2)_3NMe(CH_2)_3OPPh_2\}; >95\% \text{ for } Mo(CO)_3-$ (PhCOLi){(Ph₂POCH₂CH₂)₂NMe}.

The " $(1,2-O_2C_6H_4)P$ -" and " OCH_2CH_2OP -" phosphito-metalla-crown systems **6b**-15b and **6c**-15c contrast with the "MeNCH₂CH₂N(Me)P-" and "Ph₂P" systems in that they do not readily react with RLi to give benzoylate/ acylate products. Instead, highly reactive $M(CO)_4P_2$ ·RLi adducts are obtained (eq 8). Adduct formation is considerably greater for the $(1,2-O_2C_6H_4)P$ systems (Table V), vis à vis " OCH_2CH_2OP " systems which are relatively insensitive with respect to both adduct and benzoylate formation. The relative stabilities of benzoylate complexes as a function of phophorus substituent decreases in the order "MeNCH₂CH₂N(Me)P-" > Ph₂P \gg "(1,2-O₂C₆H₄)- $P^{*} \approx "OCH_2CH_2OP"$. This is the opposite to the trend predicted on the basis of $\nu(CO)$ stretching frequencies (Table VI). The " $(1,2-O_2C_6H_4)P$ -" complexes, having ν (CO)'s 30-50 cm⁻¹ higher than those of the "Me- $NCH_2CH_2N(Me)P$ -" systems, would, on the basis of simple bonding arguments, be expected to be the most reactive.²¹ The observed effect is clearly a consequence of the degree/stability of Li⁺ cation binding in the benzoylate products. A rationalization of the observed trend can be obtained by assessing the relative basicity of the "P-O oxygen" and its effect on Li⁺ cation binding. The electronegative oxygen substituents in the bis(phosphito) systems should result in increased $O \rightarrow P \pi$ -donation and a decrease in the basicity and Li⁺ binding capacity of these oxygens.²⁹ The absence of benzoylate formation in $12C3(NMe)_3$ systems (e.g. 15c) is due to the nonbasic nature of the P–NMe– nitrogen which is a consequence of N–>P π -donation.^{15,29}

The formation of a relatively strong $Mo(CO)_4P_2 \supset RLi$ adduct in the reaction of the "(1,2- $O_2C_6H_4$)P-" complexes **6b-16b** was at first rather surprising. The formation of PhLi adducts from $Mo(CO)_4[P(OMe)(1,2-O_2C_6H_4)]_2$ and the "all aza" 12C3(NMe)₃ complex 15b indicates that a crown ether functionality is not essential for adduct formation and implicates the oxygens of the "(1,2- $O_2C_6H_4$)P" unit in LiR adduct binding. (The "PNMe" nitrogens in 15b are nonbasic.^{15,29}) It should be noted that the Mo-(CO)₄[P(OMe)(1,2- $O_2C_6H_4$)]₂·RLi adducts are considerably more soluble than the analogous "crown ether·RLi" adducts. A possible structure for this adduct is 27. Owing



to the rigidity and planarity of the " $(1,2-O_2C_6H_4)P$ " ring system the "POLi⁺OP" unit in 27 will be approximately planar with the net result being that the Mo…Li⁺ separation is too great to accommodate a "PhCO" bridge. For the 12C3 "Mo(CO)₄P₂ \supset ·PhLi" adduct "7b·PhLi", coordination of the ether oxygen is also possible. On the basis of molecular models a possible structure is 28. Involve-



ment of the ether oxygens in adduct stabilization is suggested by the large K' for "8b-PhLi" adduct formation (Table V) and the observation of isomeric forms for this 13C4 adduct. Also, adduct formation with the " OCH_2CH_2OP -" systems is relatively weak except for the diaza-13C4(NMe)₂ system 12c for which strong adduct formation is observed. It should be noted that chelating amines such as tetramethylethylenediamine are known to form LiR adducts.³⁰ It seems likely that the rigidity of

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the cis-"(1,2-O₂C₆H₄)P-" units and possibly ring strain effects in the "(1,2-O₂C₆H₄)P" unit enhance Li⁺ chelation in the "**6b**-15**b**·PhLi" systems. The increased flexibility in the "OCH₂CH₂OP-" systems may account for their poorer chelation properties and the decrease in adduct stability. Organolithium adducts of transition-metal complexes are relatively rare. One example involves U-(OⁱPr)₆ which forms an adduct with MeLi formulated as $U(OⁱPr)_6(LiMe)_3$ (29).³¹ An unusual feature of adduct



formation is the shift in $\nu(CO)$'s to *lower* frequencies (Tables I and V and Figure 3) since removal of electron density by association with the LiR would, on the basis of simple arguments, be expected to decrease the electron density at Mo and increase $\nu(CO)$. One possible explanation is that the oxygen lone pairs on the relatively rigid " $(1,2-O_2C_6H_4)P$ -" units are directed toward and have an antibonding effect on the M-CO bonds. This effect, if present, would be reduced by RLi adduct formation. The possibility of a Li…OC interaction in these adducts, similar to that observed in alkali-metal salts of carbonylate anions, seems unlikely in that all the $\nu(CO)$'s are moved to lower frequency while $M(CO)_x$ -…Li⁺/Na⁺ interactions result in shifts to both higher and lower frequencies.³²

Conclusions

Previous studies have shown that preferential Li⁺ cation binding in benzoylate/acylate complexes of 12C3 and 13C4 bis(diphenylphosphinite) metalla-(aza)-crown ether systems (e.g. $2 \rightleftharpoons 3$, eq 2) can provide an additional 9 kcal-mol⁻¹ of stabilization, vis à vis systems that are unable to complex Li⁺ (e.g. the 12C3(NMe)₃ system 15c).¹⁵ The current study suggests that an additional stabilization of ca. 1–3 kcal·mol⁻¹ can be achieved by replacing the "Ph₂P" with "MeNCH₂CH₂N(Me)P" units. However, the utility of this modification is greatly offset by the tendency of the "MeNCH₂CH₂N(Me)P-" benzoylate complex to react with H_2O by a rapid autocatalytic process to give an as yet unidentified product. The bis(phosphito)-metalla-crown ether tetracarbonyl complexes, which on $\nu(CO)/bonding$ considerations, might be expected to be more reactive toward nucleophilic addition to CO, are less reactive. This decrease in reactivity has been ascribed to a decrease in the basicity of the P-O oxygen and a consequent decrease in Li⁺ ligation.

Experimental Section

¹H,¹³C{¹H}, and 31P{¹H} NMR spectra were recorded on one of the following instruments: Varian T-60, CFT-20, XL-200, or XL-400 spectrometer. Infrared spectra were recorded on Nicolet 5DX, 10DX, and 7000 series Fourier Transform infrared spectrometers using 0.5-mm NaCl solution cells. Elemental analyses were done by Canadian Microanalytical Laboratories, Vancouver, British Columbia, Canada. All reactions were carried out under a nitrogen atmosphere. Dichloromethane was distilled from P_2O_5 ; pyridine was distilled over KOH; triethylamine (Et₃N) was distilled over LiAlH₄; diethyl ether, tetrahydrofuran (THF), and benzene were distilled from sodium benzophenone ketyl. The chlorophosphorus derivatives

 OCH_2CH_2OPCl and $(1,2-O_2C_6H_4)PCl$ were purchased from Ald-

rich Chemical Co. and distilled prior to use. $MeNCH_2CH_2N-(Me)PCl$ was prepared from the reaction of N,N'-dimethyl-1,2-

diaminoethane with PCl₃ in benzene at 5 °C in the presence of $2 \text{ molar equiv of Et}_3$ N and distilled prior to use.³³ The compound

MeN(CH₂)₃N(Me)PCl was similarily prepared by using N,N'-dimethyl-1,3-diaminopropane. (Considerable care should be taken in handling these compounds.³³) Phenyllithium and methyllithium solutions were purchased from the Aldrich Chemical Co. and standardized with diphenylacetic acid prior to use. Triethylene glycol, 1,3-propanediol, N,N'-dimethyl-1,2-diaminoethane, N,N'-dimethyl-1,3-diaminopropane, and 3,3'-methyliminobis(N-methylpropylamine) were purchased from the Aldrich Chemical co., dried over K₂CO₃, and distilled under reduced pressure prior to use. Published methods were used to prepare [(2,5-norbornadiene)M(CO)₄] (M = Mo,³⁴ Cr,³⁴ W³⁵), 3-oxa-1,6hexanediol,¹⁵ 4-oxa-1,7-heptanediol,³⁶ 3,6-dioxa-1,9-nonanediol,¹⁵ N,N'-bis(2-hydroxyethyl)-N,N'-dimethyl-1,3-diaminopropane.¹⁵

Preparation of the α,ω -Di-P-Donor Ligands 5 (Eq 4). A typical procedure is illustrated for the synthesis of 4-oxa-1,7heptanediylbis(o-phenylene phosphite). To a solution of 2.4 g (0.02 mol) of 4-oxa-1,7-heptanediol and 5.8 mL (0.04 mol) of Et₃N in 125 mL of dry benzene, cooled to +5 °C in an ice bath, was added 7.0 g (0.04 mol) of (1,2-O₂C₆H₄)PCl in 5 mL of benzene, dropwise with stirring. A white precipitate (triethylammonium hydrochloride) slowly formed. After being stirred for 1 h, the mixture was filtered under nitrogen via a Schlenk tube to remove [Et₃NH]Cl. Evaporation of the filtrate yielded the product as a colorless, viscous oil, 92% yield. The oil was characterized by 'H and ³¹P{¹H} NMR spectroscopy. If the spectrum integration was not close to that expected, the oil was not used in subsequent reactions and the synthesis repeated.

The metalla-crown ether complexes were prepared as outlined in eq 5. Typically a solution of ca. 5 g of $Mo(CO)_4(NBD)$ was dissolved in 250 mL of dry CH₂Cl₂ and loaded into a 250-mL Marriotte-type pressure-equalizing constant addition funnel. Exactly 1 equiv of the α, ω -di-P-donor ligand was dissolved in 250 mL of dry CH₂Cl₂ and placed in a second Marriotte-type pressure-equalizing constant addition funnel. The two solutions were then added simultaneously and dropwise to 3500 mL of dry CH_2Cl_2 over a period of 15-20 h. The whole apparatus was shielded from light as much as possible. After the addition of the two reactant solutions was complete, the mixture was stirred for 72 h at 20 °C. The solvent was then concentrated to ca. 50 mL on a rotary evaporator. Acid-washed cellulose powder (100 mL) was then stirred into the concentrated reaction mixture. The solvent was removed by rotary evaporator. The "cellulose powder/reaction residue" was dried in vacuo and added to the top of a 30-mm diameter column packed with glass wool, sand, a 60-cm column length of "Florisil" (magnesium silicate), and more sand (bottom to top description of column packing) filled with hexanes. The column was eluted with ca. 1 L of ACS hexanes, 2 L of 1:1 hexanes/CH₂Cl₂, and 2 L of CH₂Cl₂ and then stripped by using 500 mL of acetone. The hexane/CH₂Cl₂ and CH₂Cl₂ fractions were combined and reduced to 250 mL by rotary evaporator. A further 150 mL of hexanes was added and the solution reduced to 50 mL during which time the molybdenum metalla-crown-ether tetracarbonyl precipitated as a white crystalline product. The tungsten and chromium analogues were synthesized as described above except that the reagents $M(CO)_4(NBD)$ (M = W, Cr) and

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the α,ω -di-P-donor ligand were added over a period of 12 h to 3 L of refluxing benzene followed by a further period of reflux of 48 h. Yields and selected characterization data for complexes 6-16 are given in Tables I and II.

The isolation of acylate and benzoylate complexes 17-25 is illustrated by the synthesis of the 13C4[2.2.2] benzoylate complex 19a (eq 6). In a typical reaction 0.98 g of $Mo(CO)_4$ -MeNCH₂CH₂N(Me)POCH₂(CH₂OCH₂)₂CH₂OPN(Me)-CH₂CH₂NMe) (8a) was dissolved in 10 mL of dry benzene and 1.3 mL of 1.40 M phenyllithium in Et_2O (ca. 1.15 equiv) added. The pale yellow solution went immediately orange, and an orange precipitate formed. The orange precipitate was recrystallized from hot CH_2Cl_2 followed by rapid addition of hexanes to give the benzoylate $Mo(CO)_3(PhCOLi)P_2 \supset (19a)$ as an orange powder in 40% yield. Analytical and spectroscopic data for 17-25 are given in Table III. The determination of the equilibrium constants K(eq 6) and K' (eq 8) were determined by IR spectroscopy as previously described for "Ph2P" metalla-crown ether analogues.¹⁵ Studies of benzoylate stability in 0.044 M H₂O/THF solutions were also carried out as previously described.¹⁶

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Registry No. 2a (M = Mo), 78353-57-8; 3a (M = Mo, R = Ph), 78353-63-6; 5 (OO = $O(CH_2)_2O(CH_2)_3O$, XX = MeN- $(CH_2)_2NMe$), 123030-27-3; 5 (OO = $O(CH_2)_2O(CH_2)_3O$, XX = 1,2- $O_2C_6H_4$), 123030-28-4; 5 (OO = $O(CH_2)_2O(CH_2)_3O$, XX = OCH_2CH_2O), 123030-29-5; 5 (OO = $O(CH_2)_3O(CH_2)_3O$, XX = $MeN(CH_2)_2NMe$), 123030-30-8; 5 (OO = $O(CH_2)_3O(CH_2)_3O$, XX = $1,2-O_2C_6H_4$), 123030-31-9; 5 (OO = $O(CH_2)_3O(CH_2)_3O$, XX = OCH_2CH_2O), 123030-32-0; 5 (OO = $O(CH_2)_2O(CH_2)_2O$, XX = $MeN(CH_2)_2NMe$), 123030-33-1; 5 (OO = $O(CH_2)_2O(CH_2)_2O$, XX = $MeN(CH_2)_2NMe$), 123030-33-1; 5 (OO = $O(CH_2)_2O(CH_2)_2O(CH_2)_2O$, XX = $MeN(CH_2)_2O(CH_2)_2O$, XX = $MeN(CH_2)_3NMe$), 123030-34-2; 5 (OO = $O(CH_2)_2O(CH_2)_2O(CH_2)_2O$, XX = $MeN(CH_2)_2NMe$), 123030-33-1; 5 (OO = $O(CH_2)_2O(CH_2)_2O(CH_2)_2O$, XX = $MeN(CH_2)_2NMe$), 123030-34-2; 5 (OO = $O(CH_2)_2O(CH_2)_2O(CH_2)_2O$, XX = $MeN(CH_2)_2NMe$), 123030-34-2; 5 (OO = $O(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2O$, XX = $1,2-O_2C_6H_4$), 55330-62-6; 5 (OO = $O(CH_2)_2O(CH_2)$

 $= O(CH_2)_2O(CH_2)_2O(CH_2)_2O, XX = OCH_2CH_2O), 123030-35-3;$ 5 (OO = $O(CH_2)_2O(CH_2)_2O(CH_2)_3O$, XX = MeN(CH₂)₂NMe), 123030-38-6; 5 (OO = $O(CH_2)_2O(CH_2)_2O(CH_2)_3O$, XX = OCH_2CH_2O , 123030-39-7; 5 ($OO = O(CH_2)_2NMe(CH_2)_2NMe$ $(CH_2)_2O$, XX = MeN $(CH_2)_2NMe$), 123030-40-0; 5 (OO = O- $(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O, XX = OCH_2CH_2O), 123030-41-1;$ 5 $(OO = O(CH_2)_2 NMe(CH_2)_3 NMe(CH_2)_2 O$, XX = MeN- $(CH_2)_2NMe_2$, 123030-42-2; 5 (OO = MeN(CH₂)₃NMe(CH₂)₃NMe, $XX = 1,2-O_2C_6H_4$, 123030-43-3; 5 (OO = MeN(CH₂)₃NMe- $(CH_2)_3NMe$, XX = OCH_2CH_2O , 123030-44-4; 6a, 123051-70-7; 6b, 123051-77-4; 6b·PhLi, 123052-01-7; 6c, 123051-80-9; 6c·PhLi, 123051-94-5; 7a, 84537-76-8; 7b, 84537-75-7; 7b-PhLi, 123051-93-4; 7c, 84537-74-6; 7c.PhLi, 123051-95-6; 8a, 84558-17-8; 8b, 84537-73-5; 8c, 84558-16-7; 8c·PhLi, 123051-92-3; 9a, 123051-71-8; 10a, 123051-72-9; 11a, 123051-73-0; 11c, 123051-81-0; 12a, 123051-74-1; 12c, 123051-82-1; 12c.PhLi, 123051-96-7; 13a, 123051-75-2; 14a, 123051-76-3; 15b, 123051-78-5; 15c, 123051-83-2; 16, 123051-79-6; 17a, 123074-00-0; 17b, 123074-01-1; 18a, 123074-02-2; 18b, 123074-03-3; 19a, 123074-04-4; 19b, 123074-05-5; 20a, 123051-84-3; 20b, 123051-85-4; 21a, 123051-86-5; 22a, 123051-87-6; 23a, 123051-90-1; 24a, 123051-88-7; 24b, 123051-89-8; 25a, 123074-06-6; **25b**, 123051-91-2; **26** (OO = $O(CH_2)_3O(CH_2)_3O$, R = Ph), 123051-98-9; 26 (OO = $O(CH_2)_2O(CH_2)_2O(CH_2)_2O(R = Ph)$, 123051-99-0; 26 (OO = $MeN(CH_2)_3NMe(CH_2)_3NMe$, R = Ph), 123052-00-6; 27 (R = Ph), 123051-97-8; $HO(CH_2)_3O(CH_2)_2OH$, 929-28-2; HO(CH₂)₂O(CH₂)₂O(CH₂)₂OH, 112-27-6; (1,2-O₂C₆-OCH2CH2OPCI, H₄)PCl, 1641-40-3; 822-39-9; Me-NCH₂CH₂CH₂N(Me)PCl, 40201-85-2; MeNCH₂CH₂N(Me)PCl,

6069-36-9; $Mo(CO)_4(NBD)$, 12146-37-1; $W(CO)_4(NBD)$, 12129-25-8; $Cr(CO)_4(NBD)$, 12146-36-0; $HO(CH_2)_2O(CH_2)_2O(CH_2)_3OH$, 123030-36-4; $HO(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2OH$, 14037-83-3; $HO(CH_2)_2NMe(CH_2)_3NMe(CH_2)_2OH$, 10394-83-9; $MeNH-(CH_2)_2NMe(CH_2)_3NMe(CH_2)_2OH$, 10394-83-9; $MeNH-(CH_2)_2NMe(CH_2)_3NMe(CH_2)NMe$, 123030-37-5; PhLi, 591-51-5; MeLi, 917-54-4; $P(OMe)(1,2-O_2C_6H_4)$, 20570-25-6; 4-oxa-1,7-heptanediol, 2396-61-4.