Stereochemical Studies of a Multifunctional P-Donor Ligand Capable of Selective Lithium Ion Binding for CO Activation via a 'Tripodal O_3N Unit'

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There is considerable current interest in the synthesis of hybrid ligands that are capable of holding two different metal centers in close proximity in a single complex [1]. Of particular interest is the potential for cooperativity effects between the two metal centers of such a complex with regard to the chemistry of a coordinated substrate. For example, it is well established that the susceptibility of a coordinated CO group with respect to nucleophilic addition (a reduction process) may be enhanced by the addition of Lewis acids [2, 3]. The presence of a strong '$MCO \rightarrow Li^+$' interaction can be particularly significant [3] and recently we have utilized hybrid P-donor crown ether ligands derived from ethylene glycols as a means of providing *significant additional activation* of coordinated CO towards nucleophilic addition via selective Li^+ binding by the product molecule [4]. However, activation of a coordinated CO in this way imposes considerable restrictions/limitations with regard to the cavity (ring) size, and the electronic and stereochemical features of the hybrid ligand. The ligand *must be capable of three synchronous functions*:

(i) complexing the transition metal in a *cis* fashion;

(ii) providing Li^+ with all but one donor atom of a complete coordination sphere in a desirable configurational array; and

(iii) coordinating the transition metal and the Li^+ such that their *preferred separation and orientation* are appropriate for a $M-(RCO) \rightarrow Li^+$ bridge. In this communication we report that the readily synthesized ligand $(Ph_2POCH_2CH_2)_2NCH_2CH_2OMe$ (*1*),

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which contains an unusual 'tripodal O_3N' unit for complexing Li^+, meets all of these criteria.

The bisdiphenylphosphinite ligand *1* is readily prepared from the reaction of N-(2-methoxyethyl)-diethanolamine with two equivalents of Ph_2PCl in the presence of base (*e.g.* Et_3N)[**]. Reaction of *1* with $Mo(CO)_4$(norbornadiene) using high dilution techniques gives complex *2* in 70% yield[†].

Complex *2* can be thought of as a 'mono-aza-10-crown-3' with the 'dangling' N-(2-methoxyethyl) 'arm' being capable of providing a fourth donor atom.

Reaction of *2* with MeLi and PhLi in benzene solution gives the acylate and benzoylate products *3* which can be recrystallized from CH_2Cl_2/pentane mixtures[≠].

The extent of RLi addition to *2*, as measured by the equilibrium constant K = [*3*]/[*2*] [RLi], may be determined by solution infrared studies. Equilibrium

TABLE I. Equilibrium Constant Data [$K = [Mo(CO)_3(RCOLi)P_2]/([Mo(CO)_4P_2] \times [RLi])$] Determined by Infrared Spectroscopy (νCO region) in THF and Benzene Solutions (7.25×10^{-3} *M* in Mo) at 25 °C.

Complex	Equilibrium Constants L mol^{-1}		
	$K(MeLi)_{THF}$	$K(PhLi)_{THF}$	$K(PhLi)_{C_6H_6}$
2	22	20	1500
cis-$Mo(CO)_4[Ph_2PO(CH_2CH_2O)_2PPh_2]$	<7	<7	<45

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[**] Obtained in 85% yield. Satisfactory ^1H and ^{13}C-NMR were obtained. $\delta\, ^{31}P$ 113.9 ppm (external $H_3PO_4/CDCl_3$).

[†] *Anal.* Calc. for *2*, $C_{35}H_{35}NO_7P_2Mo$: C, 56.8; H, 4.8; N, 1.9; P, 8.4. Found: C, 56.5; H, 4.8; N, 1.9; P, 8.6%. Spectroscopic data: $\delta^{31}P$ 140.5 ppm (external H_3PO_4/CD_2Cl_2); νCO 2023(s), 1908(s, broad).

[≠] *Anal.* Calc. for $C_{41}H_{40}NO_7P_2MoLi \cdot CH_2Cl_2$ (*3*, R = Ph): C, 55.5; H, 4.7; N, 1.5; P, 6.8. Found: C, 55.8; H, 4.7; N, 1.7; P, 6.7%. Spectroscopic data: $\delta^{31}P$ 152.7 ppm (external H_3PO_4/CD_2Cl_2); νCO 1931 (s), 1830 (s, broad).

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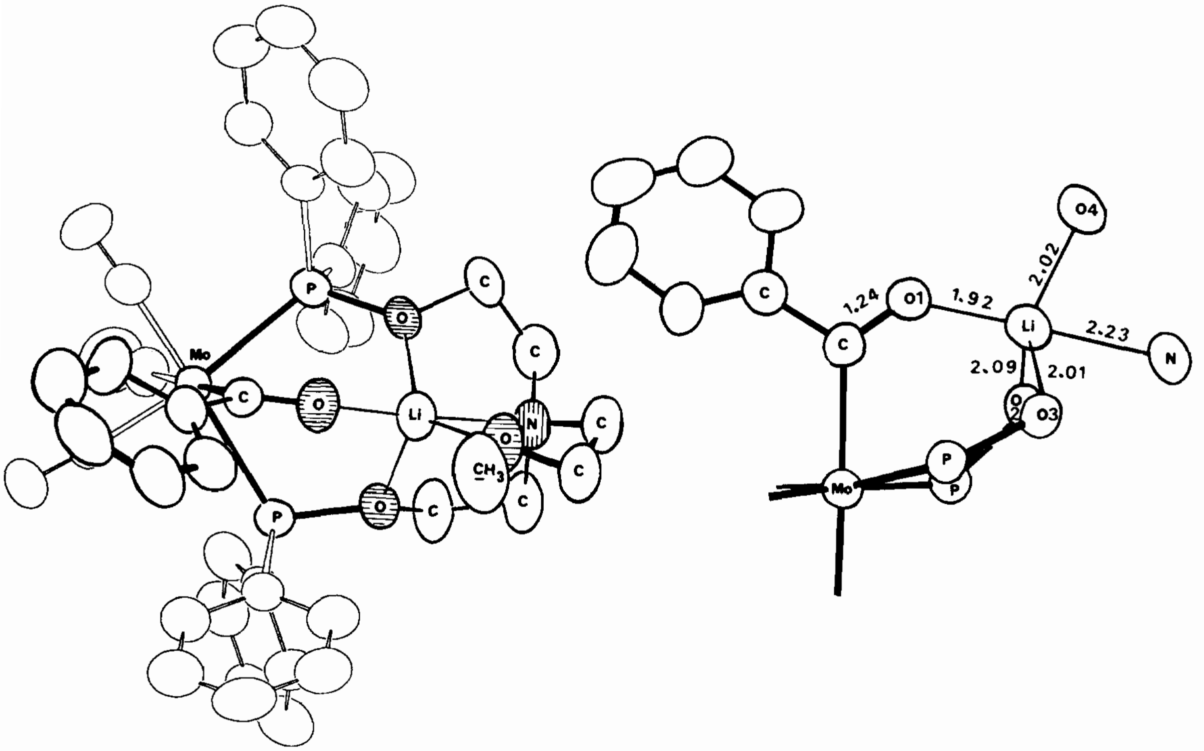
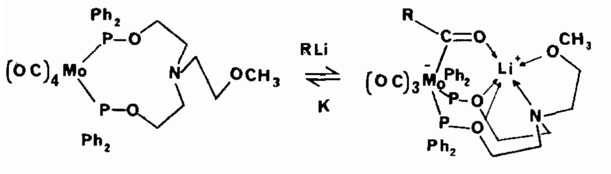


Fig. 1. Molecular geometry of $Mo(CO)_3(PhCOLi)$ [$(Ph_2POCH_2CH_2)_2NCH_2CH_2OCH_3$], complex *3* as determined by X-ray crystallography. Selected bond lengths (Å) and angles (deg) are shown. Bond angles (deg) about the Li^+ are: $\angle O_1LiO_2$, 103; $\angle O_1LiO_3$, 101; $\angle O_1LiO_4$, 100; $\angle O_1LiN$, 177; $\angle O_2LiO_3$, 97; $\angle O_2LiO_4$, 120; $\angle O_2LiN$, 80; $\angle O_3LiO_4$, 132, $\angle O_3LiN$, 77; $\angle O_4LiN$, 79.



2 *3*

constant data for *2* and RLi including analogous data for *cis*-$Mo(CO)_4[Ph_2PO(CH_2CH_2O)_2PPh_2]$ [4] (*i.e.* an example of a 10-crown-3 system without the 2-methoxyethyl 'dangling arm') are given in Table I. The data suggest that *selective* Li^+ binding as in *3* is rather poor in THF but is markedly increased in the non-polar solvent benzene, the value of K being comparable to that for the reaction of PhLi with the 12-crown-3 complex *cis*-$Mo(CO)_4[Ph_2PO(CH_2CH_2CH_2O)_2PPh_2]$ (K in C_6H_6 = 1100) [4].

The molecular structure of the benzoylate *3* has been determined by X-Ray crystallography and the basic features are given in Fig. 1. The molybdenum and the lithium ion are both bound by the multifunctional ligand and bridged by the 'CO unit' of the benzoyl group, the Mo(PhCOLi) unit being approximately planar. The Li^+ ion has an uncommon trigonal bipyramidal environment in which there is a 'tripodal' interaction with the O_3N unit of the bisphosphinite ligand. The benzoylate oxygen, O_1, which occupies an apical position *trans* to the ligand nitrogen atom, exhibits the strongest interaction with the lithium ion (O_1–Li^+ = 1.92 Å) whilst the N–Li^+ interaction appears to be the weakest. Complex *3* represents only the second example of a trigonal bipyramidally coordinated lithium ion [5].

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