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Preliminary communication

COMPLEXES OF A "MONO-P-DONOR CROWN ETHER" HYBRID LIGAND WITH POTENTIAL FOR THE ACTIVATION OF A COORDINATED CARBON MONOXIDE VIA SELECTIVE CATION BINDING

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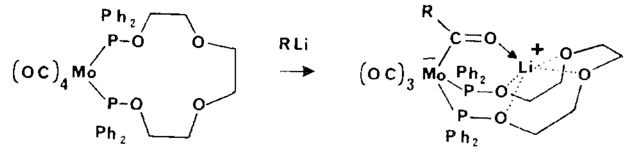
Summary

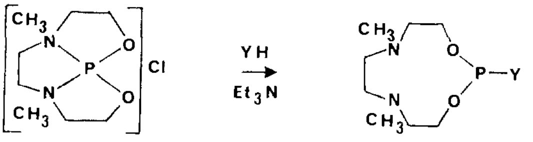
Derivatives of 1,10-dioxa-4,7-diaza-11-phosphacycloundecane are shown to function as mono-P-donor crown ether ligands. When complexed to molybdenum or tungsten in the form of $M(CO)_5P$ derivatives they provide an additional incentive for nucleophilic attack (RLi reagents) at the C-atom of a coordinated CO via selective Li^+ ion binding by the benzoylate/acylate product. The structure of one of these products, *cis*-$[(\overline{OCH_2CH_2N(Me)CH_2CH_2N(Me)CH_2CH_2O)P}(OEt)]-{}^{-}Mo(CO)_4(PhCO)\rightarrow Li^+$, has been determined by X-ray crystallography.

Selective cation binding by the "product molecule" may provide additional activation for nucleophilic addition to coordinated carbon monoxide [1]. For example the addition of a nucleophile to a coordinated CO of complex 1 is enhanced by a cooperativity effect, the reaction at the molybdenum carbonyl occurring because it leads to a product molecule 2 that is a good ligand for Li^+. However, whilst complexes containing *cis*-di-P-donor hybrid ligand derived from polyglycols may have the appropriate ring size and stereochemistry necessary to accommodate a bridging $M(RCO)Li^+$ unit, they are unlikely to be useful in a catalytic sense owing to (i) their need to maintain a *cis*-P-donor geometry (in order to be effective in stabilizing a bridging $M(RCO)—Li^+$), and (ii) the introduction of two P-donor groups on metal carbonyls frequently deactivates desired catalytic phenomena. In contrast mono-P-donor-crown ether ligands may have the potential to accommodate a $M(RCO)—Li^+$ interaction regardless of the coordination number/stereochemistry about the transition metal whilst introducing only one P donor group on the metal carbonyl. We here report the first example of a mono-P-donor-crown ether ligand capable of stabilising acylate/benzoylate products via selective cation binding effects.

Derivatives of 1,10-dioxa-4,7-diaza-11-phosphacycloundecane (4) may readily



1 **2**



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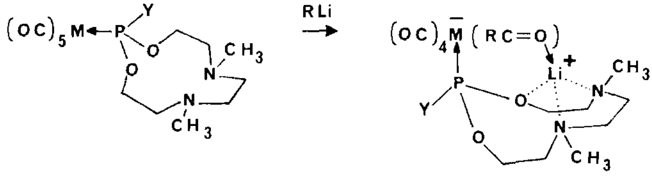
4a (Y = OEt)
4b ($Y = NEt_2$)



5 **6**

be prepared from the chloro salt 3, and the phosphite derivative 4a will give a 1/1 complexation with Li^+ [2,3]. Reaction of 4 with $M(CO)_5Cl^-$ (M = Mo, W) in the presence of a silver salt [4] yields the complexes $[M(CO)_5(4)]$ (i.e. 5) as colourless oils (30—49% yield; characterized by infrared, ν(CO) region, and ^1H and ^{31}P NMR spectroscopy). Reaction of the complexes 5 with RLi (R = Ph, Me) in THF or benzene solution results in the formation of the lithium benzoylate/acylate complexes, 6. Complexes 6, obtained in essentially quantitative yield, may be recrystallised from CH_2Cl_2/hexane and have been fully characterized by IR, NMR and microanalysis. The basic features of the molecular geometry of the benzoylate complex 6 (M = Mo; R = Ph), as determined by X-ray crystallography, are shown in Fig. 1. The lithium cation, which is in a distorted tetrahedral environment, is coordinated to the two nitrogens and one oxygen of the cyclic phosphite ring. However, instead of the expected intramolecular interaction between the Li^+ and the benzoylate oxygen (i.e. 6) the observed structural array is that of a dimer with two benzoylate complexes joined via two (PhCO)—Li^+ interactions. The structural features of the benzoylate ligand are very similar to those found for the bisphosphinite crown ether complex 2(M = Mo, R = Ph) [1]. However, the Li^+ ion is situated 0.7 Å out from the benzoylate OCCMo plane with the Li^+—O interaction (vector) being between the two lone-pair sp^2 (O) orbitals but closer to L P(2), see Fig. 2. A similar, but not identical, Li^+—benzoylate interaction has previously been observed for the complex $[Li(THF)_3]^+$-$[Fe_2(CO)_5(C(O)Ph)(\mu_2\text{-}PPh_2)_2]^-$ [5]. In contrast the Li^+—O(benzoylate) vector for complex 2(M = Mo) points directly at an oxygen lone-pair sp^2 orbital [1]. These observations suggest that a strong benzoylate—Li^+ interaction may be

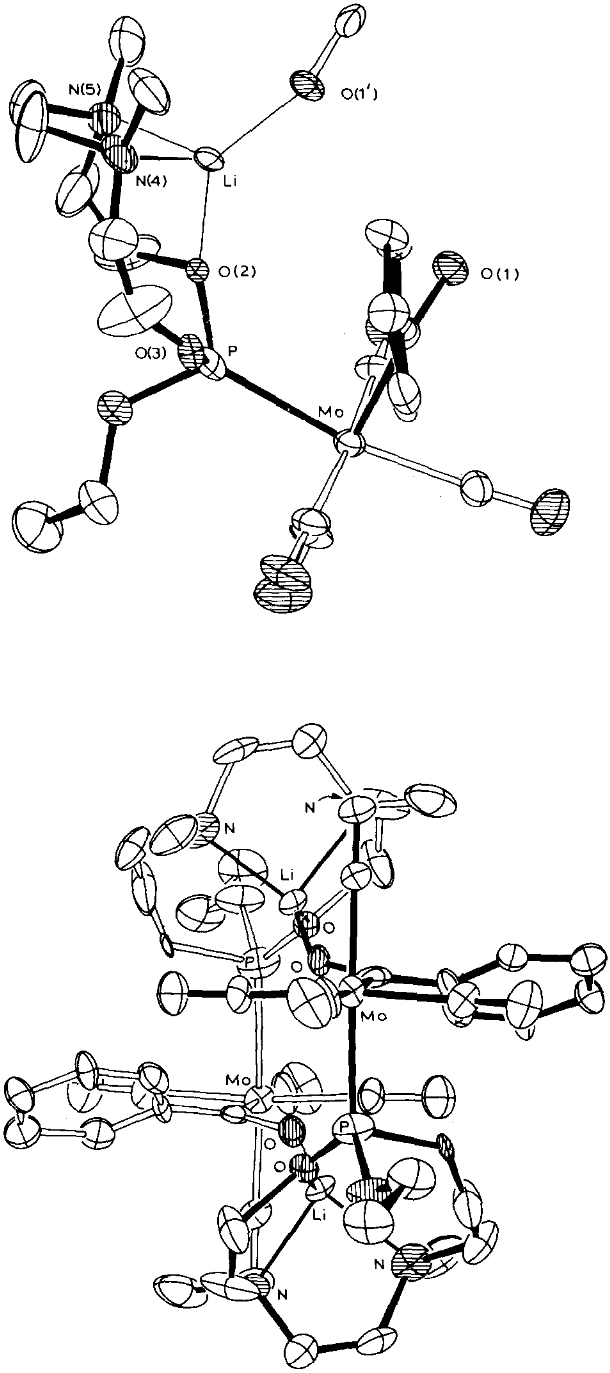


Fig. 1. The molecular geometry of the complex *cis*-(OC)$_4$Mo(PhCOLi)[EtOP$\{$OCH$_2$CH$_2$N(CH$_3$)CH$_2\}_2$] (**6**) as determined by X-ray crystallography. (A) The basic geometry about Mo and Li$^+$. (B) The dimeric structure found for **6** in the crystalline state. Selected bond lengths (Å) and angles (°) are: lengths: LiO(1′) 1.88; LiO(2) 1.93; LiN(4) 2.12; LiN(5) 2.10; (N.B. LiO(3) separation = 3.12); angles: O(1′) LiO(2) 131; O(1′) LiN(4) 112; O(1′)LiN(5) 118; O(2)LiN(4) 112; O(2)LiN(5) 84; N(4)LiN(5) 89.

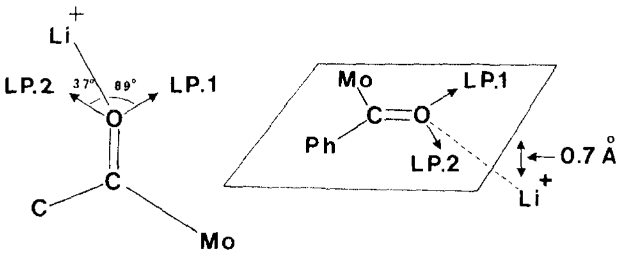
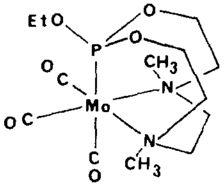


Fig. 2. Schematic representation of position of Li^+ relative to the sp^2 oxygen lone pairs, LP(1) and LP(2) of the benzoylate ligand. The Li^+ is positioned 0.7 Å; out of the MoCO plane.

maintained over a considerable range of benzoylate conformations and consequently this reduces the number of conformational restrictions that have to be considered when designing P-donor crown ether ligands.

Molecular weight studies indicate that in solution the monomeric form of complexes **6** (presumed to have the structure **6**) is the major solution species. Mol. wt. for **6**(M = Mo, R = Ph) determined osmometrically in benzene. Calcd. 570 Found: 633. The complexes **6** are reasonably stable. Dichloromethane solutions of **6**(M = Mo, R = Ph, Y = OEt) have been stored at −20°C for several months without any noticeable decomposition. However, on exposure to water, benzaldehyde is formed (via the hydroxy carbene) and **6**(M = Mo, R = Ph, Y = OEt) is converted into the tricarbonyl derivative **7** in which the ligand **4a** functions as a "PNN tridentate" ligand.



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In conclusion appropriately designed mono-P-donor crown ether systems offer the potential for the stabilization of benzoylate/acylate/formylate products or intermediates via selective cation binding effects. However, the presence of N donor functions, as in ligand **4** is not likely to be desirable with respect to the design of potential catalytic systems owing to their capacity to coordinate to the transition metal carbonyl centre (as in **7**). Efforts aimed at designing and synthesising suitable mono-P-donor "all oxygen" crown ether systems are currently in progress.

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