*Acta Cryst.* (1990). **B46**, 753–762

# Structures of Three Compounds Involving Lithium-Ion Encapsulation by Group 6 Carbonyl Phosphinite Crown Ether Complexes

By John Powell, Jeffery F. Sawyer, Patricia E. Meindl and Stuart J. Smith

*Lash Miller Chemical Laboratories, University of Toronto,* 80 *St George Street, Toronto, Ontario, Canada M5S* 1*A*1

(*Received* 9 *March* 1989; *accepted* 4 *July* 1990)

## Abstract

Lithium *fac*-benzoyl-*cis*-{1,11-bis[2-(1,3-dimethyl-1,3,2-diazaphospholidinyl)]-4,8-dimethyl-4,8-diaza-1,11-dioxaundecane-*P*,*P*′}tricarbonylmolybdenum, (I), $\mathrm{Li[Mo(C_7H_5O)\{(C_4H_{10}N_2P)_2C_9H_{20}N_2O_2\}(CO)_3]}$, $M_r = 714{\cdot}5$, monoclinic, $P2_1/c$, $a = 10{\cdot}996\,(2)$, $b = 17{\cdot}051\,(3)$, $c = 18{\cdot}437\,(4)$ Å, $\beta = 103{\cdot}90\,(1)^\circ$, $U = 3356$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}41\ \mathrm{g\,cm^{-3}}$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 5{\cdot}2\ \mathrm{cm^{-1}}$, $F(000) = 1488$, $T = 298$ K, $R = 0{\cdot}0345$ ($wR = 0{\cdot}0442$) for 3008 observed $[I > 3\sigma(I)]$ reflections. Lithium *fac*-benzoyl-*cis*-[1,7-bis(diphenylphosphinito)-4-methyl-4-azaheptane-*P*,*P*′]tricarbonylmolybdenum dichloromethane solvate, (II), $\mathrm{Li[Mo(C_7H_5O)\{(C_{12}H_{10}P)_2C_7H_{15}NO_2\}(CO)_3].\frac{3}{2}CH_2Cl_2}$, $M_r = 935{\cdot}0$, triclinic, $P\bar{1}$, $a = 13{\cdot}007\,(3)$, $b = 17{\cdot}257\,(3)$, $c = 20{\cdot}397\,(4)$ Å, $\alpha = 95{\cdot}13\,(2)$, $\beta = 102{\cdot}66\,(2)$, $\gamma = 95{\cdot}78\,(2)^\circ$, $U = 4415$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}41\ \mathrm{g\,cm^{-3}}$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 5{\cdot}9\ \mathrm{cm^{-1}}$, $F(000) = 1916$, $T = 298$ K, $R = 0{\cdot}0724$ ($wR = 0{\cdot}0787$) for 7605 observed $[I > 3\sigma(I)]$ reflections. Lithium *fac*-benzoyltricarbonyl-*cis*-[3-(diphenylphosphinitomethyl)-1-(3-diphenylphosphinitopropyl)piperidine-*P*,*P*′]molybdenum, (III), $\mathrm{Li[Mo(C_7H_5O)\{(C_{12}H_{10}P)_2C_9H_{17}NO_2\}(CO)_3]}$, $M_r = 833{\cdot}7$, monoclinic, $P2_1$, $a = 10{\cdot}811\,(2)$, $b = 16{\cdot}398\,(3)$, $c = 11{\cdot}432\,(2)$ Å, $\beta = 100{\cdot}99\,(2)^\circ$, $U = 1990$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}39\ \mathrm{g\,cm^{-3}}$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 4{\cdot}5\ \mathrm{cm^{-1}}$, $F(000) = 860$, $T = 298$ K, $R = 0{\cdot}0317$ ($wR = 0{\cdot}0374$) for 3145 observed $[I > 3\sigma(I)]$ reflections. All three compounds contain lithium encapsulated inside different bis(phosphinito)molybda crown ligands with the remaining vertex being the O atom of the benzoylate group on molybdenum. In (I) the molecule has approximate mirror symmetry while in both independent molecules in the asymmetric unit of compound (II) the mirror symmetry is broken by slight twists of the benzoylate phenyl ring away from the mirror plane and by some disorder in the $\mathrm{OCH_2CH_2O}$ linkages. In compound (III) the unsymmetrical crown ligand forces an approximately perpendicular arrangement in the ‘equatorial’ and ‘axial’ phenyl rings on the phosphinito P atoms. In (I) the resultant geometry about $\mathrm{Li^+}$ is a square pyramid with Li···O distances of 1·899 (8), 2·125 (9) and 2·137 (8) Å and Li···N distances of 2·205 (9) and 2·227 (9) Å. In (II) and (III) the $\mathrm{Li^+}$ geometries are distorted tetrahedra with Li···O = 1·88 (2), 1·93 (2) and 1·93 (2) Å and Li···N = 2·03 (2) Å in the ordered molecule of compound (II) and with the corresponding distances in compound (III) 1·854 (11), 1·909 (10), 1·942 (11) and 2·092 (11) Å respectively. In each case the shortest distance involves the benzoylato O atom and is reflected in small changes in the C═O distances. The geometries of the Mo atom in each complex are distorted octahedra and the Mo—P distances and PMoP bond angles [2·474 (1) and 2·477 (1) Å, 99·53 (4)° (I); 2·473 (3)–2·491 (3) Å, 96·31 (9) and 98·71 (8)° (II); and 2·492 (2) and 2·500 (2) Å and 96·28 (5)° (III)] are reasonably consistent with the estimated steric sizes of the phosphinito ligands.

## Introduction

A simple approach to the synthesis of heterodinuclear complexes containing low-oxidation-state transition metals and cations of groups 1A and 2A involves the synthesis of ditopic ligands which combine a subunit containing a ‘soft’ binding site with one bearing a ‘hard’ site (Powell, Gregg, Kuksis, May & Smith, 1989; Powell, Kuksis, May, Meindl & Smith, 1989; Powell, Gregg & Meindl, 1989; and references therein). Of particular relevance are hybrid P-donor crown ether ligands that combine a crown ether or cryptand functionality with one or more P-donor groups and 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. Recently we have described (Powell *et al.*, 1989) the synthesis of a range of ditopic $\alpha,\omega$-bis(diphenylphosphinito)polyether ligands and their amino analogs [*e.g.* $\mathrm{P_2}\supset = \mathrm{Ph_2POCH_2(CH_2}A\mathrm{CH_2)}_n\mathrm{CH_2OPPh_2}$ ($A$ = O, NMe; $n$ = 1–4); $\mathrm{Ph_2PO(CH_2)_3}A\mathrm{(CH_2)_3OPPh_2}$ ($A$ = O, NMe), *etc.*]. The *cis* chelation of these ligands to group 6 metal carbonyls gave complexes of the type *cis*-$M\mathrm{(CO)_4(P_2}\supset)$ ($M$ = Cr, Mo, W) in which $M$ is incorporated into the crown ether backbone. While

0108-7681/90/060753-10$03.00

$M(CO)_4(PR_3)_2$ complexes are unreactive toward *R*Li reagents (Darensbourg & Darensbourg, 1970; Darensbourg & Hankel, 1982), the addition of *R*Li to a coordinated carbonyl group in these metallacrown ether complexes gave acylate/benzolate *fac*-complexes $M(CO)_3(RCOLi)(P_2\supset)$ whose stabilities are determined by the ease of formation and degree of 'preferential $Li^+$ cation binding' observed. In the present paper we report structural studies of the compounds (I)–(III) obtained by reacting the complexes 14C4[2.3.2], 12C3[3.3] and 12C3[3.3.*β* ring],* containing the ligands 1,11-bis[2-(1,3-dimethyl-1,3,2-diazaphospholidinyl)]-4,8-dimethyl-4,8-diaza-1,11-dioxaundecane, 1,7-bis(diphenylphosphinito)-4-methyl-4-azaheptane and *N*-(3-diphenylphosphinitopropyl)-3-(diphenylphosphinitomethyl)-piperidine respectively, with phenyl lithium.

## Experimental

Yellow–orange crystals were prepared by published methods (Powell *et al.*, 1989; Smith, 1987). Crystals slowly decompose in air owing to solvent loss and oxidation and hence were sealed in 0·2–0·3 mm diameter Lindemann capillaries. Precession photographs were used to check crystal quality and to obtain preliminary cell and space-group information. Further work on the diffractometer gave the crystal data given in Table 1, which also summarizes the data-collection options used and the structure refinements undertaken. Lorentz, polarization and crystal decay corrections were applied to all collected data as indicated (Table 1). No absorption corrections were considered necessary in view of the magnitudes of $\mu$ and the regular crystal shapes used. In compounds (I) and (III), H atoms were included in calculated positions (C—H 0·95 Å, $B = 6$ Å$^2$) but were not refined. H atoms in compound (II) (representing 9% of the electron density) were not included in the refinements. Calculations were performed on PDP 11/23 and Gould 9705 computers using the *SHELX* (Sheldrick, 1976) and Enraf-Nonius *SDP* (Frenz, 1981) packages. Scattering factors stored in the programs were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The final atomic positional parameters and selected bond lengths and bond angles for each compound are given in Tables 2–5 and 7.† Various *ORTEP* views (Johnson, 1965) of the molecular structures of compounds (I)–(III) are given in Figs. 1–4.

Table 1. *Crystal data, data-collection and structure-refinement details*

| | (I) $C_{27}H_{45}MoN_6$-$O_6P_2^-.Li^+$ | (II) $C_{41}H_{40}MoNO_6P_2^-$.-$Li^+.\frac{3}{2}CH_2Cl_2$ | (III) $C_{43}H_{42}MoN$-$O_6P_2^-.Li^+$ |
|---|---|---|---|
| System | Monoclinic | Triclinic | Monoclinic |
| *a* (Å) | 10·996 (2) | 13·007 (3) | 10·814 (2) |
| *b* (Å) | 17·051 (3) | 17·257 (3) | 16·398 (3) |
| *c* (Å) | 18·437 (4) | 20·397 (4) | 11·432 (2) |
| $\alpha$ (°) | 90 | 95·13 (2) | 90 |
| $\beta$ (°) | 103·90 (1) | 102·66 (2) | 100·99 (2) |
| $\gamma$ (°) | 90 | 95·78 (2) | 90 |
| *U* (Å$^3$) | 3356 | 4415 | 1990 |
| *Z*, $D_x$ (g cm$^{-3}$) | 4, 1·41 | 4, 1·41 | 2, 1·39 |
| $M_r$ | 714·5 | 935·0 | 833·7 |
| $\mu$ (Mo $K\bar{\alpha}$) (cm$^{-1}$)$^a$ | 5·2 | 5·9 | 4·5 |
| Reflections used in cell determination, No., $\theta$ range (°) | 25, 6·9–11·7 | 25, 4·6–14·8 | 25, 5·6–15·3 |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1$ |
| Crystal shape | Block | Needle | Irregular |
| Crystal dimensions (mm) | {100}:0·15<br>{100}:0·095<br>{001}:0·13 | {100}:0·07<br>{010}:0·26<br>{001}:0·11 | *ca* 0·16 × 0·16 × 0·20 |
| Scan range$^c$ (°) | 0·90 + 0·35tan$\theta$ | 0·8 + 0·35tan$\theta$ | 0·90 + 0·35tan$\theta$ |
| Max. scan time$^b$ (s) | 60 | 75 | 90 |
| Standard reflections, No., interval (s) | 3, 7500 | 3, 1200 | 3, 8000 |
| Max 2$\theta$ (°) | 50 | 45 | 50 |
| No. of data collected | 4995 | 12619 | 5316 |
| Structure solution | Patterson for Mo, least squares, Fourier and $\Delta F$ Fourier for other atoms. H atoms in calculated positions | | |
| No. of non-zero data | 4398 | 9882 | 3707 |
| No. of data with $I > 3\sigma(I)$ | 3008 | 7605 | 3145 |
| *R* | 0·03 | 0·07 | 0·0317$^d$ |
| *wR* | 0·0442 | 0·0787 | 0·0374$^d$ |
| No. of parameters refined | 388 | 520 | 486 |
| Max. $\Delta/\sigma$ | 0·14 | 0·11 | 0·09 |
| Factor in weighting scheme,$^d$ *p* | 0·050 | 0·00135 | 0·045 |
| Final $\Delta F$ Fourier max. peak (e Å$^{-3}$) | 0·45 | 1·06 [near C(25)] | 0·37 |

Notes: (*a*) Enraf–Nonius CAD diffractometer; Mo $K\bar{\alpha}$ radiation ($\lambda$ = 0·71069 Å), graphite monochromator, $\omega$–2$\theta$ scans. (*b*) Scan speeds chosen to give $I/\sigma(I) \geq 25$ within maximum scan time specified (prescans at 10° min$^{-1}$). (*c*) Backgrounds by extending peak by 25% on either side were measured for half the time taken to collect the peak. (*d*) Weights *w* given by $4F^2[\sigma^2(I) + (pF^2)^2]^{-1}$ for compounds (I) and (III), $[\sigma^2(F) + pF_o^2]^{-1}$ for (II). Alternative 'hand' for (III) gave *R* (*wR*) = 0·0324 (0·0383).

## Discussion

There are two independent molecules in the asymmetric unit of compound (II) along with three molecules of dichloromethane solvent which are only weakly held in the lattice and have high temperature factors (Table 2). Disorder is apparent in the $OCH_2CH_2CH_2N$ backbones of one of the crown ether molecules as well as in the chlorine positions for one of the $CH_2Cl_2$ solvent molecules.

As envisaged in the synthesis of these compounds (Powell *et al.*, 1989) the molybda-phosphinito crown ligands have effectively encapsulated lithium *via* three or four $Li^+\cdots O$ or $Li^+\cdots N$ interactions and the remaining bond to each Li atom (which is the strongest) involves the O atom of the benzoylate group on molybdenum. Thus the geometry of $Li^+$ is square pyramidal in (I) and distorted tetrahedral in

---

* See Powell *et al.* (1989) for discussion of this notation.

† Lists of structure-factor amplitudes, additional bond lengths and bond angles in the crown ether and phosphorus ligands, and anisotropic thermal parameters for all three compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53394 (97 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters and their estimated standard deviations*

Compound (I)

| | $x$ | $y$ | $z$ | $B$(Å$^2$) |
|---|---|---|---|---|
| Mo | 0·11284 (4) | 0·24273 (2) | 0·23404 (2) | 2·582 (8) |
| P1 | −0·0051 (1) | 0·15956 (7) | 0·30360 (7) | 3·04 (3) |
| P2 | 0·1987 (1) | 0·13960 (7) | 0·16607 (7) | 3·30 (3) |
| O2 | 0·0556 (3) | 0·0716 (2) | 0·3225 (2) | 3·18 (7) |
| O14 | 0·2192 (3) | 0·0554 (2) | 0·2123 (2) | 3·56 (8) |
| O28 | 0·3154 (3) | 0·1544 (2) | 0·3548 (2) | 3·68 (8) |
| O36 | 0·2320 (4) | 0·3704 (2) | 0·1514 (2) | 6·5 (1) |
| O38 | 0·0055 (4) | 0·3853 (2) | 0·3039 (2) | 6·0 (1) |
| O40 | −0·1184 (4) | 0·2519 (2) | 0·0966 (2) | 6·1 (1) |
| N5 | 0·2195 (4) | −0·0145 (2) | 0·4294 (2) | 3·7 (1) |
| N10 | 0·3922 (4) | −0·0310 (2) | 0·3121 (2) | 3·9 (1) |
| N15 | 0·3317 (4) | 0·1517 (2) | 0·1398 (2) | 4·6 (1) |
| N19 | 0·1225 (4) | 0·1159 (2) | 0·0785 (2) | 4·3 (1) |
| N21 | −0·0273 (4) | 0·1903 (2) | 0·3865 (2) | 4·3 (1) |
| N25 | −0·1590 (4) | 0·1455 (3) | 0·2703 (2) | 4·7 (1) |
| C3 | 0·0012 (5) | 0·0156 (3) | 0·3644 (3) | 4·4 (1) |
| C4 | 0·0947 (5) | −0·0463 (3) | 0·3949 (3) | 4·8 (1) |
| C6 | 0·2175 (6) | 0·0410 (4) | 0·4890 (3) | 6·0 (2) |
| C7 | 0·3062 (6) | −0·0789 (3) | 0·4603 (3) | 5·7 (2) |
| C8 | 0·3534 (6) | −0·1284 (3) | 0·4040 (3) | 6·5 (2) |
| C9 | 0·4434 (5) | −0·0892 (3) | 0·3692 (3) | 5·3 (2) |
| C11 | 0·4984 (5) | 0·0129 (3) | 0·2974 (4) | 5·7 (2) |
| C12 | 0·3201 (5) | −0·0688 (3) | 0·2450 (3) | 4·8 (1) |
| C13 | 0·2710 (5) | −0·0115 (3) | 0·1822 (3) | 4·4 (1) |
| C16 | 0·4295 (5) | 0·2034 (4) | 0·1793 (4) | 6·2 (2) |
| C17 | 0·3192 (6) | 0·1441 (4) | 0·0590 (3) | 7·2 (2) |
| C18 | 0·2034 (7) | 0·0958 (4) | 0·0307 (3) | 6·4 (2) |
| C20 | 0·0013 (6) | 0·0801 (3) | 0·0619 (3) | 6·1 (2) |
| C22 | 0·0658 (6) | 0·2365 (3) | 0·4390 (3) | 5·9 (2) |
| C23 | −0·1564 (6) | 0·2062 (4) | 0·3840 (3) | 6·2 (2) |
| C24 | −0·2311 (6) | 0·1553 (4) | 0·3256 (4) | 7·2 (2) |
| C26 | −0·2092 (6) | 0·0992 (4) | 0·2054 (4) | 7·0 (2) |
| C27 | 0·2848 (4) | 0·2210 (2) | 0·3292 (2) | 2·9 (1) |
| C29 | 0·3798 (4) | 0·2834 (3) | 0·3683 (2) | 3·0 (1) |
| C30 | 0·4924 (5) | 0·2608 (3) | 0·4133 (3) | 4·2 (1) |
| C31 | 0·5786 (5) | 0·3157 (3) | 0·4502 (3) | 4·8 (1) |
| C32 | 0·5502 (5) | 0·3941 (3) | 0·4419 (3) | 4·4 (1) |
| C33 | 0·4410 (5) | 0·4179 (3) | 0·3971 (3) | 4·7 (1) |
| C34 | 0·3537 (5) | 0·3633 (3) | 0·3596 (3) | 4·0 (1) |
| C35 | 0·1928 (5) | 0·3209 (3) | 0·1829 (3) | 3·9 (1) |
| C37 | 0·0469 (5) | 0·3315 (3) | 0·2808 (3) | 3·7 (1) |
| C39 | −0·0328 (5) | 0·2480 (3) | 0·1485 (3) | 3·8 (1) |
| Li | 0·2495 (8) | 0·0521 (4) | 0·3313 (5) | 3·6 (2) |

Compound (II)

| | $x$ | $y$ | $z$ | $U/U_{eq}$ (Å$^2$ × 10$^3$) |
|---|---|---|---|---|
| Mo1 | 30496 (6) | 66409 (4) | 71131 (4) | 31·6 (3) |
| P11 | 4032 (2) | 5483 (1) | 7022 (1) | 34·9 (8) |
| P12 | 1489 (2) | 5932 (1) | 7413 (1) | 35·0 (8) |
| O1A | 4147 (7) | 6959 (5) | 8647 (4) | 82 (3)* |
| O1B | 2067 (7) | 8170 (5) | 7401 (4) | 79 (2)* |
| O1C | 4865 (7) | 7762 (5) | 6794 (4) | 83 (3)* |
| C1A | 3723 (8) | 6829 (6) | 8064 (5) | 54 (3)* |
| C1B | 2395 (8) | 7580 (6) | 7260 (5) | 54 (3)* |
| C1C | 4178 (9) | 7314 (7) | 6910 (5) | 58 (3)* |
| O11 | 3250 (5) | 4675 (3) | 6654 (3) | 39 (2)* |
| O12 | 1137 (5) | 5035 (4) | 7030 (3) | 42 (2)* |
| N11 | 1103 (6) | 3796 (4) | 5818 (4) | 41 (2)* |
| C11 | 3676 (8) | 3935 (6) | 6463 (5) | 53 (3)* |
| C12 | 2770 (8) | 3257 (6) | 6357 (5) | 54 (3)* |
| C13 | 1887 (8) | 3253 (6) | 5722 (5) | 51 (3)* |
| C14 | 513 (9) | 3911 (7) | 5122 (6) | 62 (3)* |
| C15 | 354 (8) | 3438 (6) | 6196 (5) | 53 (3)* |
| C16 | −311 (9) | 4013 (6) | 6450 (5) | 58 (3)* |
| C17 | 237 (8) | 4503 (6) | 7128 (5) | 55 (3)* |
| O13 | 1880 (5) | 5669 (4) | 5725 (3) | 50 (2)* |
| C18 | 2322 (7) | 6337 (5) | 5992 (4) | 38 (2)* |
| C111 | 2429 (7) | 6895 (5) | 5478 (5) | 43 (2) |
| C112 | 2634 (8) | 6607 (6) | 4858 (5) | 56 (3) |
| C113 | 2750 (10) | 7106 (7) | 4379 (6) | 71 (3)* |
| C114 | 2616 (11) | 7889 (8) | 4504 (7) | 88 (4)* |
| C115 | 2379 (11) | 8184 (8) | 5093 (7) | 81 (4)* |
| C116 | 2302 (9) | 7678 (7) | 5600 (6) | 62 (3)* |
| C121 | 4686 (7) | 5189 (6) | 7827 (5) | 44 (2) |
| C122 | 4204 (9) | 4567 (6) | 8093 (5) | 58 (3) |
| C123 | 4642 (11) | 4412 (8) | 8760 (7) | 84 (4)* |
| C124 | 5556 (11) | 4873 (8) | 9146 (7) | 90 (4)* |
| C125 | 6030 (11) | 5489 (8) | 8885 (7) | 80 (4)* |
| C126 | 5619 (9) | 5660 (7) | 8206 (6) | 63 (3)* |
| C131 | 5072 (7) | 5499 (5) | 6548 (5) | 41 (2) |
| C132 | 5928 (9) | 5081 (7) | 6716 (6) | 60 (3)* |
| C133 | 6681 (10) | 5067 (7) | 6292 (6) | 70 (3)* |
| C134 | 6518 (10) | 5446 (7) | 5715 (6) | 73 (3)* |
| | $x$ | $y$ | $z$ | U/U$_{eq}$ (Å$^2$ × 10$^3$) |
| C135 | 5666 (10) | 5857 (7) | 5547 (7) | 76 (4)* |
| C136 | 4936 (9) | 5890 (6) | 5982 (5) | 58 (3)* |
| C141 | 203 (8) | 6341 (6) | 7251 (5) | 45 (2)* |
| C142 | −516 (8) | 6238 (6) | 7661 (5) | 54 (3)* |
| C143 | −1489 (9) | 6518 (7) | 7479 (6) | 64 (3)* |
| C144 | −1731 (10) | 6918 (7) | 6913 (6) | 74 (4)* |
| C145 | −1020 (9) | 7036 (7) | 6519 (6) | 66 (3)* |
| C146 | −19 (9) | 6745 (6) | 6680 (5) | 57 (3)* |
| C151 | 1677 (7) | 5812 (5) | 8310 (5) | 41 (2)* |
| C152 | 1659 (8) | 6455 (6) | 8766 (5) | 49 (3)* |
| C153 | 1868 (9) | 6409 (7) | 9447 (6) | 59 (3)* |
| C154 | 2103 (10) | 5690 (7) | 9695 (6) | 76 (4)* |
| C155 | 2151 (10) | 5062 (7) | 9242 (6) | 72 (4)* |
| C156 | 1947 (8) | 5105 (6) | 8544 (5) | 56 (3)* |
| Li1 | 1812 (13) | 4865 (10) | 6284 (8) | 48 (4)* |
| Mo2 | −9167 (6) | −15939 (4) | 21843 (4) | 30·5 (3) |
| P21 | 251 (2) | −323 (1) | 2459 (1) | 34·9 (8) |
| P22 | −2640 (2) | −1090 (1) | 1814 (1) | 33·5 (8) |
| O2A | −1222 (6) | −1465 (4) | 3663 (4) | 70 (2)* |
| O2B | −2168 (7) | −3265 (5) | 1932 (4) | 77 (2)* |
| O2C | 1074 (7) | −2396 (5) | 2772 (4) | 79 (2)* |
| C2A | −1118 (8) | −1503 (6) | 3109 (5) | 44 (2)* |
| C2B | −1701 (8) | −2628 (6) | 2011 (5) | 45 (2)* |
| C2C | 342 (8) | −2089 (6) | 2536 (5) | 49 (3)* |
| O21 | −159 (5) | 351 (4) | 1975 (3) | 41 (2)* |
| O22 | −2588 (5) | −304 (4) | 1410 (3) | 42 (2)* |
| N21 | −1465 (6) | 817 (5) | 623 (4) | 47 (2)* |
| C21 | 474 (9) | 1118 (7) | 2009 (6) | 64 (3)* |
| C22A | 319 (17) | 1420 (12) | 1324 (11) | 45 (5)* |
| C22B | −34 (22) | 1611 (16) | 1566 (15) | 77 (8)* |
| C23 | −721 (11) | 1508 (8) | 958 (7) | 88 (4)* |
| C24 | −1265 (12) | 639 (9) | −52 (7) | 94 (4)* |
| C25 | −2539 (12) | 1031 (9) | 519 (7) | 95 (4)* |
| C26A | −3225 (16) | 899 (13) | 968 (11) | 49 (5)* |
| C26B | −3379 (19) | 538 (14) | 589 (12) | 64 (6)* |
| C27 | −3551 (10) | 50 (7) | 1126 (6) | 69 (3)* |
| O23 | −871 (5) | −1037 (4) | 767 (3) | 49 (2)* |
| C28 | −776 (7) | −1618 (5) | 1096 (5) | 41 (2)* |
| C211 | −676 (8) | −2351 (6) | 668 (5) | 46 (2)* |
| C212 | −154 (9) | −2955 (7) | 941 (6) | 64 (3)* |
| C213 | −121 (10) | −3645 (8) | 508 (7) | 77 (4)* |
| C214 | −620 (10) | −3731 (8) | −170 (7) | 75 (4)* |
| C215 | −1138 (10) | −3139 (7) | −437 (6) | 73 (3)* |
| C216 | −1170 (8) | −2431 (6) | −24 (5) | 55 (3)* |
| C221 | 1636 (8) | −319 (6) | 2409 (5) | 48 (3)* |
| C222 | 2463 (10) | 205 (7) | 2834 (6) | 74 (4)* |
| C223 | 3515 (11) | 185 (8) | 2757 (7) | 84 (4)* |
| C224 | 3722 (11) | −353 (8) | 2269 (7) | 85 (4)* |
| C225 | 2918 (11) | −847 (8) | 1850 (7) | 82 (4) |
| C226 | 1866 (8) | −840 (6) | 1908 (5) | 56 (3)* |
| C231 | 394 (7) | 159 (5) | 3305 (5) | 41 (2)* |
| C232 | −217 (9) | 753 (7) | 3416 (6) | 65 (3)* |
| C233 | −126 (11) | 1097 (8) | 4101 (7) | 81 (4)* |
| C234 | 530 (11) | 839 (8) | 4621 (7) | 90 (4)* |
| C235 | 1125 (11) | 228 (8) | 4525 (7) | 85 (4)* |
| C236 | 1054 (10) | −122 (7) | 3845 (6) | 69 (3)* |
| C241 | −3729 (7) | −1730 (5) | 1225 (5) | 43 (2)* |
| C242 | −3487 (8) | −2204 (6) | 703 (5) | 52 (3)* |
| C243 | −4279 (10) | −2675 (7) | 220 (6) | 68 (3)* |
| C244 | −5329 (9) | −2681 (7) | 252 (6) | 66 (3)* |
| C245 | −5581 (10) | −2216 (7) | 766 (6) | 70 (3)* |
| C246 | −4787 (9) | −1741 (7) | 1258 (6) | 63 (3)* |
| C251 | −3220 (7) | −785 (5) | 2509 (5) | 41 (2)* |
| C252 | −3060 (9) | 14 (7) | 2771 (6) | 61 (3)* |
| C253 | −3412 (11) | 222 (8) | 3368 (7) | 82 (4)* |
| C254 | −3866 (11) | −337 (8) | 3684 (7) | 85 (4)* |
| C255 | −4020 (10) | −1098 (8) | 3443 (7) | 78 (4)* |
| C256 | −3691 (9) | −1336 (7) | 2839 (6) | 60 (3)* |
| Li2 | −1224 (13) | 110 (10) | 1170 (8) | 49 (4)* |
| Cl11 | 3691 (6) | 997 (4) | 874 (3) | 190 (4)* |
| Cl12 | 3070 (4) | 2153 (3) | 1743 (3) | 151 (3)* |
| Cl21 | 2071 (5) | 5801 (4) | 2001 (4) | 194 (4)* |
| Cl22 | 3828 (6) | 7019 (4) | 2589 (5) | 222 (5)* |
| Cl31 | 4559 (7) | 887 (4) | 4681 (4) | 216 (5)* |
| Cl3A | 3284 (8) | 2043 (6) | 4676 (5) | 188 (3)* |
| Cl3B | 4095 (21) | 2336 (15) | 5184 (13) | 165 (9)* |
| C1 | 4078 (15) | 1651 (11) | 1565 (9) | 129 (6)* |
| C2 | 2766 (21) | 6601 (15) | 1830 (13) | 182 (9)* |
| C3 | 4574 (18) | 1863 (14) | 4594 (11) | 163 (8)* |

Compound (III)

| | $x$ | $y$ | $z$ | $B$(Å$^2$) |
|---|---|---|---|---|
| Mo1 | 0·26226 (4) | 0·250 | 0·16986 (3) | 2·141 (6) |
| P1 | 0·3931 (1) | 0·37613 (9) | 0·1875 (1) | 2·51 (3) |

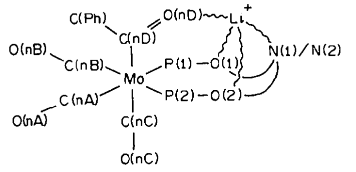
Table 2 (*cont.*)

| | $x$ | $y$ | $z$ | $B$(Å$^2$) |
|---|---|---|---|---|
| P2 | 0·0621 (1) | 0·31537 (9) | 0·0667 (1) | 2·58 (3) |
| O1 | 0·5003 (5) | 0·1552 (3) | 0·3000 (4) | 5·3 (1) |
| O2 | 0·3542 (5) | 0·1927 (3) | −0·0590 (4) | 5·5 (1) |
| O3 | 0·1422 (5) | 0·0764 (3) | 0·1469 (5) | 5·9 (1) |
| O4 | 0·3231 (3) | 0·4565 (2) | 0·2349 (3) | 2·83 (8) |
| O5 | 0·0337 (4) | 0·4048 (2) | 0·1255 (3) | 3·34 (8) |
| O6 | 0·1645 (4) | 0·3475 (3) | 0·3758 (4) | 4·5 (1) |
| N1 | 0·1054 (5) | 0·5426 (3) | 0·3116 (4) | 3·2 (1) |
| C1 | 0·4133 (6) | 0·1921 (4) | 0·2558 (4) | 3·0 (1) |
| C2 | 0·3174 (5) | 0·2188 (3) | 0·0220 (5) | 3·0 (1) |
| C3 | 0·1808 (6) | 0·1421 (3) | 0·1583 (5) | 3·3 (1) |
| C4 | 0·3792 (6) | 0·5371 (3) | 0·2384 (5) | 3·5 (1) |
| C5 | 0·3174 (6) | 0·5990 (4) | 0·3072 (5) | 3·7 (1) |
| C6 | 0·1761 (6) | 0·6070 (4) | 0·2650 (5) | 3·7 (1) |
| C7 | −0·0321 (6) | 0·5511 (4) | 0·2646 (6) | 4·1 (1) |
| C8 | −0·0757 (6) | 0·5347 (4) | 0·1362 (6) | 4·5 (2) |
| C9 | −0·0895 (6) | 0·4434 (4) | 0·1040 (6) | 4·3 (1) |
| C10 | 0·1293 (7) | 0·5501 (4) | 0·4431 (5) | 4·6 (2) |
| C11 | 0·2656 (8) | 0·5339 (4) | 0·4932 (5) | 5·2 (2) |
| C12 | 0·3498 (7) | 0·5935 (4) | 0·4429 (6) | 4·9 (2) |
| C13 | 0·2128 (5) | 0·2821 (4) | 0·3483 (5) | 3·2 (1) |
| C14 | 0·2520 (6) | 0·2281 (3) | 0·4576 (5) | 3·6 (1) |
| C15 | 0·2311 (8) | 0·1439 (4) | 0·4541 (6) | 5·6 (2) |
| C16 | 0·2670 (8) | 0·0986 (5) | 0·5584 (7) | 6·6 (2) |
| C17 | 0·3259 (7) | 0·1360 (5) | 0·6610 (6) | 6·6 (2) |
| C18 | 0·3483 (9) | 0·2168 (6) | 0·6647 (6) | 6·8 (2) |
| C19 | 0·3117 (6) | 0·2619 (5) | 0·5627 (5) | 5·2 (2) |
| C111 | 0·5366 (6) | 0·3697 (4) | 0·3025 (5) | 3·4 (1) |
| C112 | 0·5286 (6) | 0·3866 (5) | 0·4185 (6) | 4·8 (2) |
| C113 | 0·6311 (8) | 0·3735 (6) | 0·5102 (6) | 6·3 (2) |
| C114 | 0·7407 (7) | 0·3435 (5) | 0·4852 (7) | 6·4 (2) |
| C115 | 0·7506 (6) | 0·3270 (5) | 0·3704 (7) | 6·2 (2) |
| C116 | 0·6505 (6) | 0·3400 (4) | 0·2792 (6) | 4·7 (2) |
| C121 | 0·4482 (5) | 0·4158 (3) | 0·0559 (5) | 2·8 (1) |
| C122 | 0·5556 (6) | 0·4629 (4) | 0·0600 (6) | 3·9 (1) |
| C123 | 0·5877 (6) | 0·4934 (4) | −0·0420 (6) | 4·6 (1) |
| C124 | 0·5145 (7) | 0·4749 (4) | −0·1522 (6) | 5·1 (2) |
| C125 | 0·4091 (7) | 0·4278 (5) | −0·1575 (6) | 5·1 (2) |
| C126 | 0·3774 (6) | 0·3982 (4) | −0·0552 (5) | 3·7 (1) |
| C211 | 0·0524 (5) | 0·3424 (3) | −0·0901 (5) | 2·8 (1) |
| C212 | 0·0611 (5) | 0·2801 (3) | −0·1701 (5) | 3·2 (1) |
| C213 | 0·0654 (6) | 0·2970 (4) | −0·2869 (5) | 4·0 (1) |
| C214 | 0·0620 (7) | 0·3755 (5) | −0·3261 (5) | 4·8 (2) |
| C215 | 0·0540 (7) | 0·4375 (4) | −0·2506 (6) | 5·2 (2) |
| C216 | 0·0497 (6) | 0·4220 (4) | −0·1312 (6) | 4·2 (1) |
| C221 | −0·0877 (5) | 0·2603 (4) | 0·0602 (4) | 3·3 (1) |
| C222 | −0·0979 (6) | 0·2090 (5) | 0·1532 (6) | 4·8 (2) |
| C223 | −0·2123 (7) | 0·1660 (5) | 0·1522 (7) | 6·0 (2) |
| C224 | −0·3118 (7) | 0·1783 (5) | 0·0615 (7) | 6·1 (2) |
| C225 | −0·3021 (6) | −0·2306 (5) | −0·0295 (6) | 5·7 (2) |
| C226 | −0·1909 (6) | 0·2713 (4) | −0·0327 (5) | 4·3 (2) |
| Li | 0·1564 (9) | 0·4302 (6) | 0·2640 (8) | 3·2 (2) |

* Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. *Selected bond lengths* (Å) *and bond angles* (°)

See Table 4 for lithium coordination geometries in compounds (I)–(III).



| | (I) | (II) | | (III) |
|---|---|---|---|---|
| | | $n$ = 1 | $n$ = 2 | |
| Mo—P(1) | 2·477 (1) | 2·491 (3) | 2·485 (2) | 2·492 (2) |
| —P(2) | 2·474 (1) | 2·484 (3) | 2·473 (3) | 2·500 (2) |
| —C(*nA*) | 1·958 (5) | 1·934 (11) | 1·928 (9) | 1·970 (6) |
| —C(*nB*) | 1·965 (5) | 1·919 (12) | 1·950 (11) | 1·980 (6) |
| —C(*nC*) | 1·961 (6) | 1·930 (10) | 1·955 (11) | 1·965 (6) |
| —C(*nD*) | 2·278 (5) | 2·267 (8) | 2·264 (10) | 2·268 (6) |
| C(*nA*)—O(*nA*) | 1·165 (5) | 1·180 (15) | 1·182 (13) | 1·153 (7) |
| C(*nB*)—O(*nB*) | 1·150 (5) | 1·201 (15) | 1·168 (14) | 1·151 (7) |
| C(*nC*)—O(*nC*) | 1·171 (6) | 1·187 (13) | 1·165 (14) | 1·156 (7) |
| C(*nD*)—O(*nD*) | 1·246 (5) | 1·255 (10) | 1·256 (12) | 1·258 (7) |
| C(*nD*)—C(Ph) | 1·543 (6) | 1·504 (14) | 1·506 (14) | 1·524 (8) |
| P(1)—Mo—P(2) | 99·53 (4) | 96·31 (9) | 98·71 (8) | 96·28 (5) |
| —C(*nA*) | 171·9 (2) | 174·5 (3) | 174·3 (3) | 172·1 (2) |
| —C(*nB*) | 85·4 (1) | 91·2 (4) | 87·1 (3) | 87·5 (2) |
| —C(*nC*) | 90·8 (2) | 89·0 (3) | 89·2 (3) | 91·4 (2) |
| —C(*nD*) | 87·1 (1) | 86·6 (2) | 89·4 (2) | 87·8 (2) |
| P(2)—Mo—C(*nA*) | 88·3 (2) | 85·9 (3) | 86·9 (3) | 91·0 (2) |
| —C(*nB*) | 174·7 (1) | 172·4 (4) | 172·4 (3) | 175·9 (2) |
| —C(*nC*) | 87·9 (1) | 88·5 (3) | 88·7 (3) | 94·8 (2) |
| —C(*nD*) | 85·8 (1) | 91·7 (2) | 86·8 (3) | 89·6 (2) |
| C(*nA*)—Mo—C(*nB*) | 86·7 (2) | 86·5 (5) | 87·3 (4) | 85·3 (3) |
| —C(*nC*) | 87·5 (2) | 85·9 (4) | 90·1 (4) | 85·0 (3) |
| —C(*nD*) | 95·5 (2) | 98·4 (4) | 91·7 (4) | 95·2 (2) |
| C(*nB*)—Mo—C(*nC*) | 90·1 (2) | 90·3 (5) | 86·4 (4) | 86·8 (2) |
| —C(*nD*) | 96·5 (2) | 90·0 (4) | 98·2 (4) | 88·8 (2) |
| C(*nC*)—Mo—C(*nD*) | 172·9 (2) | 175·6 (4) | 175·0 (4) | 175·6 (3) |
| Mo—C(*nA*)—O(*nA*) | 174·9 (5) | 174·0 (8) | 177·3 (8) | 173·7 (6) |
| Mo—C(*nB*)—O(*nB*) | 175·8 (4) | 177·2 (10) | 176·7 (10) | 175·9 (5) |
| Mo—C(*nC*)—O(*nC*) | 178·7 (5) | 178·6 (9) | 178·1 (9) | 172·7 (5) |
| Mo—C(*nD*)—O(*nD*) | 122·6 (3) | 124·1 (7) | 123·5 (7) | 127·0 (5) |
| —C(Ph) | 126·2 (3) | 123·0 (7) | 123·6 (7) | 121·8 (4) |
| O(*nD*)—C(*nD*)—C(Ph) | 111·1 (4) | 112·5 (8) | 112·6 (8) | 110·8 (5) |
| P(*n*1)—O(*n*1)—Li | 120·5 (2) | 112·7 (6) | 111·3 (6) | 112·0 (4) |
| C—O(*n*1)—Li | 113·1 (3) | 123·3 (7) | 122·5 (8) | 126·5 (5) |
| P(*n*2)—O(*n*2)—Li | 121·3 (2) | 110·9 (6) | 110·9 (6) | 112·0 (4) |
| C—O(*n*2)—Li | 113·2 (3) | 123·3 (7) | 125·5 (8) | 121·0 (5) |
| C—O(*n*3)—Li | 134·3 (4) | 118·4 (7) | 119·1 (8) | 114·8 (5) |
| C—N(1)—Li | 98·2 (3) | 112·2 (7) | 110·0 (8) | 111·8 (5) |
| C′—N(1)—Li | 108·3 (4) | 107·3 (8) | 110·5 (9) | 107·0 (5) |
| C″—N(1)—Li | 119·0 (4) | 111·2 (8) | 114·1 (9) | 110·1 (5) |
| C—N(2)—Li | 119·2 (4) | – | – | |
| C′—N(2)—Li | 109·2 (4) | – | – | – |
| C″—N(2)—Li | 99·2 (4) | – | – | – |

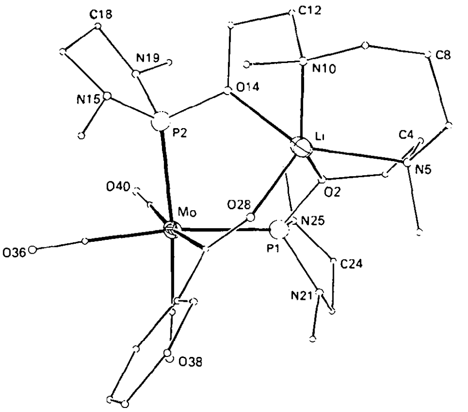


Fig. 1. View of compound (I) containing the 14C4[2.3.2] ligand. Thermal ellipsoids for P, Li and Mo atoms are drawn at the 20% probability level. C, N and O atoms have been assigned radii of arbitrary size.

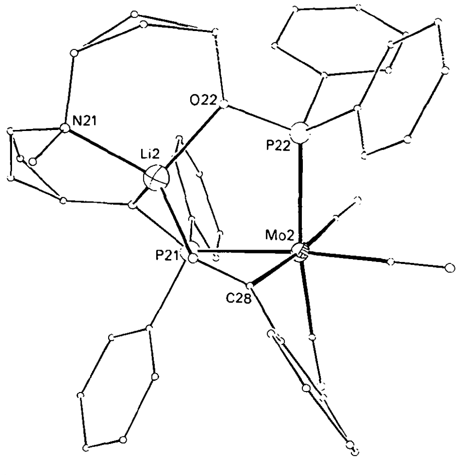


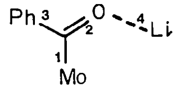
Fig. 2. View of one of the independent molecules in compound (II) containing the disordered example of the 12C3[3.3] ligand.

Table 4. *Lithium coordination geometries* (Å, °)

| | (I) | (II) | | (III) | (IV) | (V) | (VIII) |
|---|---|---|---|---|---|---|---|
| Li—O(*n*1) | 2·125 (9) | 1·930 (17) | 1·948 (16) | 1·942 (11) | 2·09 | 2·01 (1) | 1·93 |
| —O(*n*2) | 2·137 (8) | 1·931 (20) | 1·946 (19) | 1·909 (10) | 2·00 | 2·09 (1) | [3·12] |
| —O(*n*3) | 1·899 (8) | 1·879 (19) | 1·880 (19) | 1·854 (11) | 1·84 | 1·92 (1) | 1·88$^a$ |
| —N(1) | 2·227 (9) | 2·030 (17) | 2·041 (19) | 2·029 (11) | 2·20 [0] | 2·23 (1) | 2·12 |
| —N(2) | 2·205 (9) | | | | 2·05 [0] | 2·02 (1) [0] | 2·10 |
| O(*n*1)—Li—O(*n*2) | 90·7 (3) | 107·6 (8) | 108·9 (9) | 115·3 (5) | 103 | 96·6 (5) | |
| —O(*n*3) | 101·2 (4) | 107·3 (9) | 112·9 (9) | 111·0 (5) | 104 | 102·7 (5) | 131 |
| —N(1) | 78·5 (3) | 103·0 (8) | 103·0 (8) | 98·8 (5) | 79 | 80·0 (4) | 112 |
| —N(2) | 145·9 (4) | | | | | 120·2 (6) | 84 |
| O(*n*2)—Li—O(*n*3) | 99·6 (4) | 117·8 (9) | 110·5 (8) | 110·3 (6) | 103 | 100·6 (6) | |
| —N(1) | 146·1 (4) | 103·5 (8) | 101·0 (8) | 103·8 (5) | 78 | 78·0 (4) | |
| —N(2) | 78·1 (3) | | | | | 132·1 (6) | |
| O(*n*3)—Li—N(1) | 114·0 (4) | 116·4 (8) | 119·6 (10) | 117·4 (5) | 118 | 177·1 (7) | 112 |
| —N(2) | 112·3 (4) | | | | 111 | 99·8 (6) | 118 |
| N(1)—Li—N(2) | 93·0 (3) | | | | 76 | 79·4 (5) | 89 |
| $\theta^b$ | 97·2 | 110·9 | 110·8 | 112·2 | 103 | 100·0 | NA |
| C(*D*)—Mo—P(*n*) | 87·1 | 86·6 | 89·4 | 87·8 | 91·2 | | NA |
| | 85·8 | 91·7 | 86·8 | 89·6 | 86·8 | | |
| Mean | 86·4 | 89·2 | 88·1 | 88·7 | 89·0 | | |
| $Li^+$ diameters$^c$ | 1·389 | 1·066 (average) | | 1·037 | 1·272 | 1·284 | 1·155 |
| CN | 5 | 4 | 4 | 4 | 5 | 5 | 4 |

Notes: (*a*) Intermolecular distance. (*b*) $\theta$ is the average of the O(*D*)—Li—O(*n*l), O(*D*)—Li—O(*n*2) and O(*n*l)—Li—O(*n*2) bond angles. (*c*) Ionic radii of $O^{2-}$(1·40 Å) and $N^{3-}$ [1·46 Å; Greenwood & Earnshaw (1984)] subtracted from above Li···O and Li···N distances and averaged to give $Li^+$ radius for each coordination number.

Table 5. *Geometrical parameters* (Å, °) *for the benzoylate–lithium interactions*



Bond distances

| Compound | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| (I) | 2·278 (5) | 1·246 (5) | 1·543 (6) | 1·899 (8) |
| (II) | 2·267 (8) | 1·255 (10) | 1·504 (14) | 1·879 (19) |
| | 2·264 (10) | 1·256 (12) | 1·506 (14) | 1·880 (19) |
| (III) | 2·268 (6) | 1·258 (7) | 1·524 (8) | 1·854 (11) |
| (IV) | 2·255 | 1·26 | 1·53 | 1·84 |
| (V) | 2·239 (6) | 1·236 (7) | 1·53 (1) | 1·92 (1) |
| (VI) | 2·172 (6) | 1·333 (7) | 1·497 (8) | - |

Angles between bonds

| Compound | 1–2 | 1–2 | 2–3 | 2–4 |
|---|---|---|---|---|
| (I) | 122·6 (3) | 126·2 (3) | 111·1 (4) | 134·3 (4) |
| (II) | 124·1 (7) | 123·0 (6) | 112·5 (8) | 118·4 (7) |
| | 123·5 (7) | 123·6 (7) | 112·6 (8) | 119·1 (8) |
| (III) | 127·0 (5) | 121·8 (4) | 110·8 (5) | 114·8 (5) |
| (IV) | 124·6 | 123·4 | 111·5 | 126·0 |
| (V) | 125·1 (4) | 122·8 (4) | 111·5 (5) | 131·1 (5) |
| (VI) | 124·0 (4) | 128·1 (5) | 107·8 (5) | - |

(II) and (III), while in the previously published complexes (IV) (Powell, Kuksis, May, Nyburg & Smith, 1981) and the lariat system (V) (Powell, Nyburg & Smith, 1983) the environments of the $Li^+$ ions are distorted square pyramidal and trigonal bipyramidal respectively (Table 4). In each case the cavity formed by the oxa and aza crown ethers has a radius of *ca* 2 Å, close to the sum of the Pauling hard-sphere ionic radii for $Li^+$ (0·60 Å) and $O^{2-}$ (1·40 Å). Equivalently, the bond-valence sums for each $Li^+$ environment calculated using the expression $S = 0{\cdot}25(R/1{\cdot}954)^{-3{\cdot}9}$ (Brown & Shannon, 1973) for both the Li—O and Li—N interactions are reasonably close to 1·0 as expected. For comparison, the standard Li—O and Li—N bond lengths have been calcu-

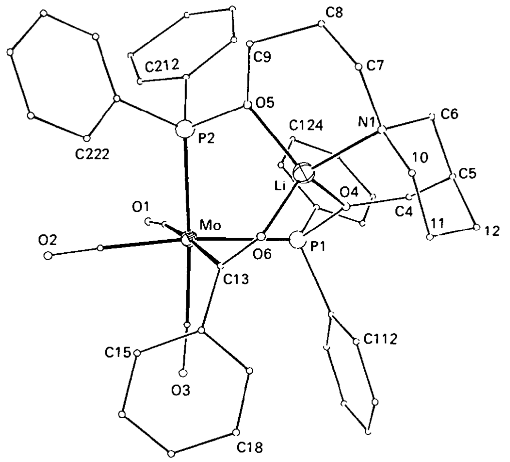


Fig. 3. View of compound (III) containing the 12C3[3.3.$\beta$ ring] ligand.

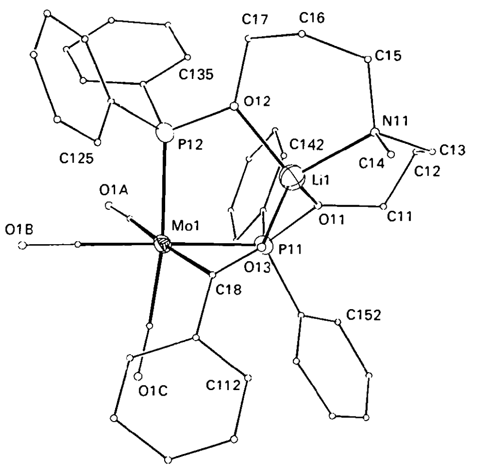
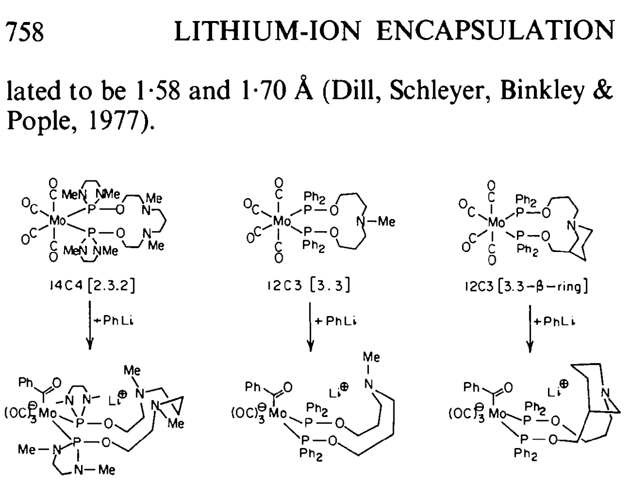
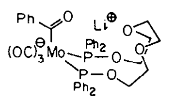


Fig. 4. View of the second molecule in compound (II) with the ordered example of the 12C3[3.3] ligand.

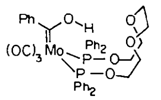
lated to be 1·58 and 1·70 Å (Dill, Schleyer, Binkley & Pople, 1977).



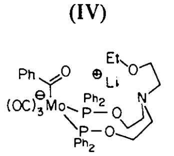
(I) (II) (III)



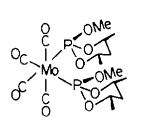
(IV)



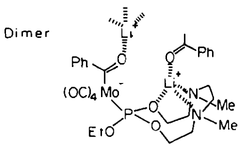
(V)



(VI)



(VII)



(VIII)

In a series of spherand host–guest complexes with lithium chloride or LiFeCl$_4$ salts the average Li$^+$ diameters [estimated by subtracting the radius of oxygen (1·40 Å) from the short Li$^+\cdots$O distances] were found to vary with the number of ligating atoms. Thus with five-, six- and seven-coordinating O atoms, diameters of 1·27, 1·48, and 1·71 Å were obtained (Cram, Kaneda, Helgeson, Brown, Knobler, Maverick & Trueblood, 1985; and references therein). As noted in the same paper, the O atoms in these spherands are preorganized rather than being organized by the guest on complexation. As such, their values were slightly less than average Li$^+$ diameters calculated from other Li$^+$ crystal structures, where values for four-coordinate tetrahedral, five-coordinate and six-coordinate octahedral Li$^+$ diameters of 1·12, 1·36 and 1·50 Å were referenced (Hermansson, Thomas & Olovsson, 1977). In the present series of compounds the Li$^+$ diameters calculated for compounds (II), (III), (IV) and (V) are significantly smaller than the above values (Table 4) while the Li$^+$ diameters for the five-coordinate ion in compound (I) (1·39 Å) and for the four-coordinate ion in (VIII) (Powell, Ng, Ng & Nyburg, 1983), where one of the interactions is intermolecular (Li$^+$ diameter = 1·16 Å), are slightly larger.

In each system, the shortest interaction is to the benzoylate O atom and although the measured e.s.d.'s are somewhat high, it does seem that there is a gradual lengthening of the C=O bond length as the Li—O distance shortens (Table 5, Fig. 5). The present C=O distances are all longer than that observed in the acyl Mo complex (Cp)(CO)$_2$(PPh$_3$)MoC(O)CH$_3$ [1·211 (16) Å] (Churchill & Fennessey, 1968) and most of the distances observed in weak Lewis acid acyl complexes [C=O = 1·211 (6)–1·236 (7) Å] (Chevrier & Weiss, 1974) but are significantly shorter than the C—O distance in the carbene complex (VI) [1·333 (7) Å] (Powell, Farrar & Smith, 1984). Presumably the lithium$\cdots$oxygen interaction prevents any possible $\eta^2$-acyl bonding. The direction of approach of the Li$\cdots$benzoylate O interactions varies from a COLi angle of 114·8 (5)° in (III) to 134·3 (4)° in (I) (Table 5), that is, close to one of the lone-pair directions on the $sp^2$-hybridized O atom. However, in the lariat ether system (VIII) the crown ligand can only provide three interactions (two Li$\cdots$N and one Li$\cdots$O) and the distorted tetrahedral geometry at Li is completed by an intermolecular Li$^+\cdots$benzoylate interaction (Li$\cdots$O = 1·88 Å) resulting in dimers. Notably, the C—O—Li bond angle in this arrangement is *ca* 157°, similar to the bonding situation in the complex Li(THF)$_3$.OC(Ph)Fe$_2$(CO)$_5$($\mu$-PPh$_2$) where the COLi bond angle is 149° (Ginsberg, Berg, Rothrock, Collman, Hodgson & Dahl, 1979) and in Li(THF)$_3$.OC(Ph)Fe(CO)[C$_6$H$_4$S(SMe)]$_2$.THF where the LiOC angle is 153·7 (14)° with Li$\cdots$O = 1·86 (3) Å and C=O = 1·25 (2) Å (Sellmann, Lanzrath, Huttner, Zsolnai, Kruger & Claus, 1983).

The very symmetrical arrangement of the 14C4[2.3.2] ligand in (I) can also be contrasted with the Li coordination geometry in the 13C4[2.2.2] alloxa system in (IV). In both complexes the Li geometry is distorted square pyramidal but the extra C

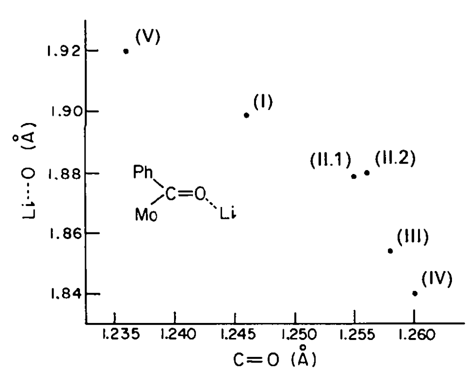


Fig. 5. Correlation between lithium$\cdots$oxygen and benzoylate C=O distances in the molybda-phosphinito crown ether and aza ether complexes (I)–(V).

atom in (I) allows the NLiN angle to increase to 93·0° from the corresponding OLiO angle of 76° in (VI). Furthermore, there is some asymmetry in the two Li···O distances (2·05 and 2·20 Å) in the latter complex as well as disorder in the atoms of the —$CH_2$—O—$CH_2$— chain forming the longer of these two interactions, and this section of the crown ether in (IV) is much flatter than that in (I). Additionally, this has resulted in the equatorial plane of the Mo atom in (IV) being inclined at a much larger angle than that in (I). This can be seen in the PMoPO torsion angles which are 29·1 (1) and −28·7 (1)° in (I) and 44·4 and −45·3° in (IV). A similar large inclination of the Mo equatorial plane is seen in molecule (III) where the PMoPO torsion angles are 45·7 (1) and −43·6 (2)° (Fig. 6). Significantly this forces the axial C═O *trans* to the benzoylate away from the 'axial' phenyl rings on the phosphinito P atoms, thus allowing one of these rings to rotate away from a face-on-face situation and into a face-edge conformation (*cf.* Figs. 1 and 3). In both molecules of (II) these PMoPO torsion angles are variable ($|\tau|$ = 32·8–40·00°), but are closer to the situation in (III) and (IV) than (I). These conformational differences are also reflected in several other parameters of molecule (I) including smaller PMoC(*D*) bond angles [85·8 and 87·1 (1)°] and significantly smaller OLiO bond angles between the benzoylate and phosphinato O atoms which average 97° in (I) and 111, 112 and 103° in compounds (II), (III) and (IV), respectively.

The observed Mo—C(*D*) distances in the Ph(Mo)C═O—Li systems also vary in length but do not display any correlation with the Li···O(*D*) distance. All of these values are, however, longer than the Mo—C≡O distances and the Mo—carbene distances in (VI) [2·172 (6) Å], $Mo(CO)_5[C(OEt)(SiPh_3)]$ [2·15 (2) Å] (Fischer, Hollfelder, Friedrich, Kreissl & Huttner, 1977), $(Cp)(CO)_2MoC(O)CHPhCHMe$-NHMe [2·17 (1) Å] (Liu, Beck, Huttner & Lorentz, 1977) and $Cp(CO)_2MoC(OH)C(CO_2Et)NNH$ [2·092 (12) Å] (Knox & Prout, 1969), but are comparable to the Mo—C distance in $Cp(CO)_2(PPh_3)Mo$ $C(O)CH_3$ [2·264 (14) Å] (Churchill & Fennessey, 1968). All these distances are, however, significantly shorter than typical Mo—C($sp^3$) distances, *e.g.* 2·40 (3) Å in $\eta^5$-$C_5H_5(OC)_3MoC_2H_5$ and 2·38 Å in $C_{10}H_8(OC)_3MoEt$ (Churchill & Fennessey, 1968).

The coordination geometry of the Mo atom in each complex is distorted octahedral. Selected bond distances and bond angles are given in Table 6, where they are compared with the structural data for a series of *cis*-phosphine $Mo(CO)_4(PR_3)_2$ complexes. As has been reported elsewhere (Cotton, Darensbourg, Klein & Kolthammer, 1982) there are some trends between the PMoP bond angle and the Tolman cone angle for the phosphine ligands involved, although they note that deviations from this trend are apparent for unsymmetrical phosphines where conformational effects can reduce the effective (average) cone angle of the ligand involved. Similar comments can be applied to the present crown ether ligands so that the cone angles given in Table 6 for these ligands should be regarded as upper estimates. Furthermore, as can be seen from the 2·4° difference in the PMoP angles for the two independent molecules in compound (II) other steric and

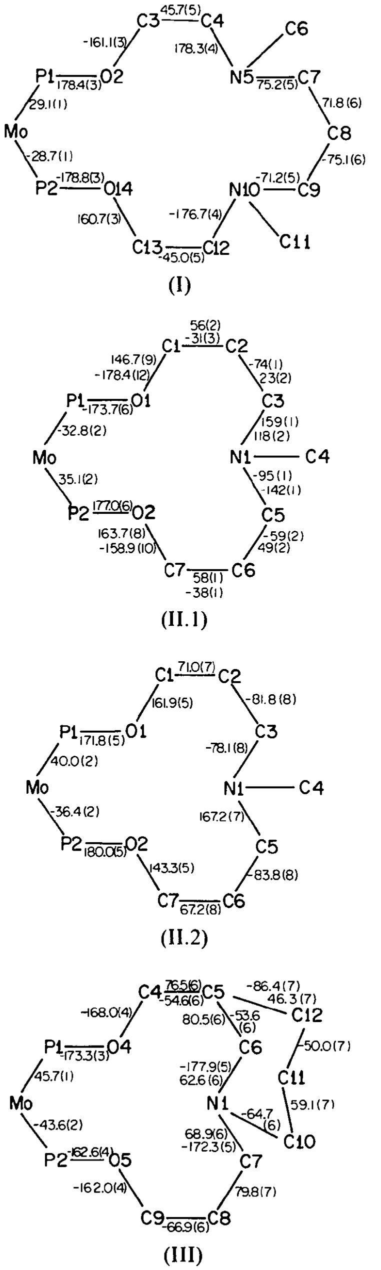


Fig. 6. Endocyclic torsion angles (°) for the molybda-aza/oxa crown ether ligands.

Table 6. *Selected bond lengths* (Å) *and bond angles* (°) *in some cis-phosphine tetracarbonyl molybdenum and molybda-phosphinito crown complexes*

| $(OC)_4Mo(L)_2$ | $\theta$ | Mo—P | Mo—$C_{trans}$ | PMoP | Mo—$C_{cis}$ |
|---|---|---|---|---|---|
| $L = PMe_3$ | 118 | 2·522 (1) | 1·971 (6) | 97·54 (4) | 2·032 (14) |
| $PEt_3$ | 132 | 2·544 (4) | 1·977 (4) | 100·27 (3) | 2·032 (5) |
| $P^nBu_3$ | 132 | 2·552 (8) | 1·96 (1) | 99·29 (9) | 1·99 (1) |
| $PMe_2Ph$ | 122 | 2·529 (5) | 1·982 (3) | 94·78 (5) | 2·016 (18) |
| $PMePh_2$ | 136 | 2·555 (14) | 1·978 (4) | 92·52 (5) | 2·027 (7) |
| $PPh_3$ | 145 | 2·577 (2) | 1·972 (2) | 104·62 (7) | 2·040 (19) |
| $PMe_2Ph/PPh_3$ | 122/145 | 2·562 (1)/2·538 (1) | 1·977 (3) | 97·73 (2) | 2·034 (3) |
| Compound | | | | | |
| (I) | 141[a] | 2·474 (1)/2·477 (1) | 1·958 (5)/1·965 (5) | 99·53 (4) | 1·961 (6) |
| (II) | 133[b] | 2·491 (3)/2·484 (3) | 1·934 (11)/1·919 (12) | 96·31 (9) | 1·930 (10) |
| | | 2·485 (2)/2·473 (3) | 1·928 (9)/1·950 (11) | 98·71 (8) | 1·955 (11) |
| (III) | 133[b] | 2·492 (2)/2·500 (2) | 1·970 (6)/1·980 (6) | 96·28 (5) | 1·965 (6) |
| (IV) | | 2·486/2·485 | 2·001/2·001 | 95·44 | 2·024 |
| (V) | | 2·506 (2)/2·528 (1) | 1·964 (8)/1·966 (6) | 97·06 (5) | 1·980 (7) |
| (VI) | 133[b] | 2·496 (2)/2·485 (2) | 1·968 (7) × 2 | 90·85 (5) | 2·000 (7) |
| (VII) | 108 | 2·459/2·468 | 2·021/2·061 | 90·1 | 1·996/2·053 |

Notes: (*a*) Estimated from $\frac{2}{3}[\theta P(NMe_2)_3] + \frac{1}{3}[\theta P(OEt)_3] = \frac{2}{3}(157) + \frac{1}{3}(109)$. (*b*) Estimated from $\frac{2}{3}(\theta PPh_3) + \frac{1}{3}[\theta P(OEt)_3] = \frac{2}{3}(145) + \frac{1}{3}(109)$. Note, however, that $\theta_{\text{diphos}} = 125°$ whereas a calculation using $\frac{2}{3}\theta PPh_3 + \frac{1}{3}\theta PMe_3$ gives a value of 136°.

electronic effects are also significant.* The observed angles in (I)–(III) are qualitatively compatible with the above correlation, especially if the tabulated values are assumed to be over-estimated by *ca* 10%. Interestingly, extrapolation of the above data indicated a PMoP bond angle of 90° for phosphines with $\theta \simeq 99·5°$. Such an angle (90·1°) is observable for compound (VII) with an estimated $\theta$ of *ca* 108° (Jacobson, Karcher, Montag, Socol, Vande Griend & Verkade, 1981). In the hydroxycarbene system (VI), intramolecular hydrogen bonding might help to explain the small observed PMoP angle [90·85 (5)°] (Powell *et al.*, 1984).

The Mo—P distances to the present phosphinito ligands are, however, all significantly shorter than those to the phosphine ligands in the $Mo(CO)_4P_2$ compounds. This shortening is especially true for compound (I) where the average Mo—P distance of 2·476 Å is shorter than most of the other distances, despite the larger estimated cone angle, and the Mo—C(*D*) distance is the longest. Only the Mo—P distances in (VII) are shorter. Similarly, in the tetracarbonyl diphenylphosphinite complexes $Et_4N^+.(OC)_4Mo(PPh_2O)_2H^-$ (IX) and $(OC)_4Mo(PPh_2OH)(PPh_2OCH_2CH_2NMe_2).H_2O$ (X) the Mo—P distances are again longer than those in (I) at 2·487 (2)–2·563 (2) Å (Cotton, Falvello, Thomas, Gray & Kraihanzel, 1984). Furthermore, in the second compound, the distance to the $PPh_2OH$ ligand [2·563 (2) Å] is 0·07 Å longer than that to the dimethylaminoethoxy ligand. These long bonds as well as intramolecular hydrogen bonding result in small PMoP bond angles of 88·06 (4) and 86·36 (7)° in the two compounds. Presumably in (I) the possibility of back-bonding interactions involving the O and N atoms of the dimethyldiazaphospholidine ligand can stabilize more multiple-bond character in the Mo—P bonds. This is consistent with the class (III) (good $\sigma$ donor and $\pi$ acceptor) behavior of phosphite-type ligands compared to the class (I) or (II) ($\sigma$ donor $\sigma$ donor/$\pi$ donor) behavior of other phosphines (Golovin, Rahmin, Belmonte & Giering, 1985).

Table 7. *Bond angles at the phosphinito* O *atoms* (°)

| Compound | | Mo—P—O | P—O—C (*a*) | P—O—Li (*b*) | C—O—Li (*c*) | *a* + *b* + *c* |
|---|---|---|---|---|---|---|
| (I) | P(1) | 113·3 (1) | 121·2 (3) | 120·5 (2) | 113·1 (3) | 354·8 |
| | P(2) | 112·1 (1) | 120·3 (3) | 121·3 (2) | 113·2 (3) | 354·8 |
| (II) | P(11) | 113·1 (2) | 122·5 (5) | 112·7 (6) | 123·3 (7) | 358·5 |
| | P(12) | 114·4 (3) | 124·1 (6) | 110·9 (6) | 123·3 (7) | 358·3 |
| | P(21) | 113·8 (2) | 122·4 (6) | 111·3 (6) | 122·5 (8) | 356·2 |
| | P(22) | 114·7 (2) | 121·8 (6) | 110·9 (6) | 125·5 (8) | 358·2 |
| (III) | P(1) | 113·5 (2) | 121·1 (4) | 112·0 (4) | 126·5 (5) | 359·6 |
| | P(2) | 113·4 (2) | 123·3 (4) | 112·0 (4) | 121·0 (5) | 356·3 |

The reduced *trans* effect of the phosphinito ligands and the increased electron density on Mo caused by the acyl group also leads to shorter Mo—C≡O distances in (I), (II) and (III) [average 1·961, 1·936 and 1·972 Å respectively] than in compound (X) above [1·994–2·018 (10) Å] and than the 1·96 (1)–1·982 (3) Å [Mo—C≡$O_{trans}$] and 1·99 (1)–2·040 (19) Å [Mo—C≡$O_{cis}$] in the *cis*-$Mo(CO)_4(PR_3)_2$ compounds determined by Cotton *et al.* (1982). The differences in the ⟨Mo—C≡O⟩ distances are also correlated with the average lengths of the carbonyl bonds [1·162, 1·181 and 1·153 Å in (I)–(III) respectively].

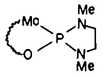
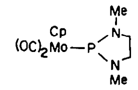
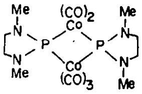
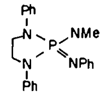
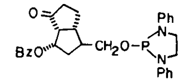
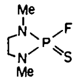
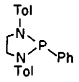
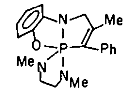
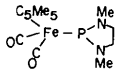
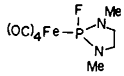
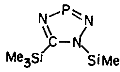
Endocyclic torsion angles in each ring are indicated in Fig. 6 and bond distances and angles for the crown ligands have been deposited.* However, the observed P—O distances do not vary significantly from the average of 1·650 Å. Similarly the MoPO bond angles display only small but nonethe-

---

* The Mo—P distances in the second molecule (larger PMoP angle) are, however, shorter than those in the first.

* See deposition footnote.

Table 8. P—N *distances* (Å) *and* NPN *bond angles* (°) *in some* 1,3,2-*diazaphospholidine structures*

| Compound | P—N | NPN | $\langle \mathrm{NCH_2} \rangle$ | $\langle \mathrm{NMe} \rangle$ | References |
|---|---|---|---|---|---|
|  | 1·688 (4)<br>1·673 (4)<br>1·660 (5)<br>1·679 (4) | 91·4 (2)<br>91·2 (2) | 1·440 | 1·446 | This work |
|  | 1·641 (5)<br>1·650 (5) | 92·1 (3) | 1·429 | 1·449 | (1) |
|  | 1·659 (4)<br>1·664 (4)<br>1·658 (4)<br>1·637 (4) | 91·9 (2)<br>93·1 (3) | 1·449 | 1·437 | (2) |
|  | 1·663 (6)<br>1·669 (7) | 91·8 (3) | 1·440 | | (3) |
|  | 1·717 (11)<br>1·702 (12) | 89·5 (6) | 1·451 | [P—O = 1·614 (10)] | (4) |
|  | 1·613 (5)<br>1·603 (6) | 95·0 (3) | 1·428 | 1·438 | (5) |
|  | 1·700 (5) [ × 2] | 90·20 (5) | 1·464 (7) | | (6) |
|  | 1·662 (3)<br>1·737 (3) (Axial distance in trigonal bipyramid) | 88·9 (1) | | | (7) |
|  | 1·701 (6)<br>[Fe—P = 2·340 (2)] | 89·3 (3) | 1·450 | 1·456 | (8) |
|  | 1·635 (5)<br>1·642 (5)<br>[Fe—P = 2·174 (1)] | 93·7 (3) | | | (9) |
|  | 1·637 | 97·0 | | | (10) |

References: (1) Hutchings, Paine & Campana (1980); (2) Hutchings, Light & Paine (1982); (3) Marre *et al.* (1984); (4) Ferrier, Tyler & Gainsford (1985); (5) Light, Campana, Paine & Morosin (1978); (6) Clardy, Kolpa, Verkade & Zuckerman (1974); (7) Sheldrick, Schomburg & Schmidpeter (1980); (8) Hutchings, Duesler & Paine (1982); (9) Bennett, Neustadt, Parry & Cagle (1978); (10) Pohl (1979).

less significant variations, from 112·7 (1) to 114·7 (2)°, owing to steric interactions involving the Ph groups. Notably, the Li···phosphinito oxygen interactions complete approximately planar $sp^2$-type environments at each O atom as can be seen from the sums of the bond angles POC + POLi + COLi at each atom with the most distortion occurring in (I) (angle sum = 354·8°) (Table 7). Apart from the bond angle at the 'hinge' atoms in each crown ligand [those C atoms adjacent to the phosphinito O atoms with the exception of C(4) in (III)], which remain close to tetrahedral values, the remaining CCN, CCC and CNC bond angles in the ordered ligands are all greater than 109·5° with average values of 113·4 (I), 113·1 (II) and 113·7° (III). These latter values should be compared with average OCC and COC bond angles of 109·5 and 112·6° in various structure determinations of large crown ethers such as 18-crown-6 (Uiterwijk, Harkema, van de Waal, Gobel & Nibbeling, 1983). In the hydroxycarbene (VI), intramolecular hydrogen bonding is the only interaction constraining the crown ether conformation, and endocyclic bond angles are more variable with an average OCC bond angle of 109·5° and COC bond angles of 115·8 (5) and 116·3 (7)°. In the corresponding Li$^+$ salt with the same ligand, disorder in two of the $\mathrm{OCH_2CH_2O}$ linkages leads to some uncertainty in some of the angles: ⟨OCC⟩ = 110·6° and the COC angles are 115·6° and an average value of 123·8° for the ordered and disordered parts of the ligand.

Compound (I) contains 1,3-dimethyl-1,3,2-diazaphospholidine ligands. Several examples of this ligand with 1,3-dimethyl, 1,3-diphenyl or 1,3-ditolyl substituents have been recently characterized. These structures indicate that a significant shortening of the P—N bond lengths from *ca* 1·70–1·72 Å to values in the range 1·60–1·69 Å occurs when the number of ligands bonded to P increases from three to four. Similarly, the NPN angle increases from 89·3–89·5 to 91·2–93·7°. It is apparent that the present structure contains some of the longer P—N distances* and some of the smaller NPN bond angles (Table 8). Furthermore, ⟨MoPN⟩ and ⟨OPN⟩ bond angles (120·4 and 104·5° respectively) are very similar at both P atoms, again confirming the near *m* symmetry of the overall molecule.

In both molecules of compound (II), the arrangements of the phenyl rings are very similar and the overall *m* symmetry is broken by the disorder in the O—$CH_2CH_2CH_2N$ linkages and by the twist of the benzoylate phenyl ring away from a perpendicular or parallel disposition with respect to this mirror plane (Figs. 2 and 4). However, in (III) the unsymmetrical crown ligand results in the planes of the 'equatorial' and 'axial' phenyl rings on the two phosphinito P atoms being rotated *ca* 90° with respect to each other (Fig. 3). Average ⟨MoPPh⟩, ⟨OPPh⟩ and ⟨PhPPh⟩ bond angles in compound (II) (116·7, 102·5 and 102·7° respectively) are, however, very similar to the values in (III) (117·2, 102·0 and 102·7° respectively). Distortions in PCC bond angles at the $\alpha$-C atoms result in differences in P—C(1)—C(2) and P—C(1)—C(6) bond angles as large as 6·7°. At the benzoylate phenyl $\alpha$-C atoms, these differences are as large as 4·2° [molecule 2 in compound (III)].

We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work and Dr Alan Lough for technical assistance.

---

* The P—N distances have an average bond valence of 1·06 using an expression given by Marre, Sanchez, Wolf, Jaud & Galy (1984).

## References

Bennett, D. W., Neustadt, R. J., Parry, R. W. & Cagle, F. W. Jr (1978). *Acta Cryst.* **B34**, 3362–3364.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* **A29**, 266–282.

Chevrier, B. & Weiss, R. (1974). *Angew. Chem. Int. Ed. Engl.* **13**, 1–9.

Churchill, M. R. & Fennessey, J. P. (1968). *Inorg. Chem.* **7**, 953–959.

Clardy, J. C., Kopla, R. L., Verkade, J. G. & Zuckerman, J. J. (1974). *Phosphorus*, **4**, 145–149.

Cotton, F. A., Darensbourg, D. J., Klein, S. & Kolthammer, B. W. S. (1982). *Inorg. Chem.* **21**, 2661–2666.

Cotton, F. A., Falvello, L. R., Thomas, M., Gray, G. M. & Kraihanzel, C. S. (1984). *Inorg. Chim. Acta*, **82**, 129–139.

Cram, D. J., Kaneda, T., Helgeson, R. C., Brown, S. B., Knobler, C. B., Maverick, E. & Trueblood, K. N. (1985). *J. Am. Chem. Soc.* **107**, 3645–3657.

Darensbourg, D. J. & Darensbourg, M. Y. (1970). *Inorg. Chem.* **9**, 1691–1694.

Darensbourg, D. J. & Hankle, J. M. (1982). *Organometallics*, **1**, 82–87.

Dill, J. D., Schleyer, P. V. R., Binkley, J. S. & Pople, J. A. (1977). *J. Am. Chem. Soc.* **99**, 6159–6173.

Ferrier, R. J., Tyler, P. C. & Gainsford, C. J. (1985). *J. Chem. Soc. Perkin Trans.* 1, pp. 295–300.

Fischer, E. O., Hollfender, H., Friedrich, P., Kreissl, F. R. & Huttner, G. (1977). *Chem. Ber.* **110**, 3467–3480.

Frenz, B. A. (1981). *Enraf–Nonius Structure Determination Package*. College Station, Texas, USA.

Ginsberg, R. E., Berg, J. M., Rothrock, R. K., Collman, J. P., Hodgson, K. O. & Dahl, L. F. (1979). *J. Am. Chem. Soc.* **101**, 7218–7231.

Golovin, M. N., Rahman, M., Belmonte, J. E. & Giering, W. P. (1985). *Organometallics*, **4**, 1981–1991.

Greenwood, N. N. & Earnshaw, A. (1984). *Chemistry of the Elements*. Oxford: Pergamon Press.

Hermansson, K., Thomas, J. O. & Olovsson, I. (1977). *Acta Cryst.* **B33**, 2857–2861.

Hutchings, L. D., Duesler, E. N. & Paine, R. T. (1982). *Organometallics*, **1**, 1254–1256.

Hutchings, L. D., Light, R. W. & Paine, R. T. (1982). *Inorg. Chem.* **21**, 226–272.

Hutchings, L. D., Paine, R. T. & Campana, C. F. (1980). *J. Am. Chem. Soc.* **102**, 4521–4523.

Jacobson, R. A., Karcher, B. A., Montag, R. A., Socol, S. M., Vande Griend, L. J. & Verkade, J. G. (1981). *Phosphorus Sulfur*, **11**, 27–32.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Knox, J. R. & Prout, C. K. (1969). *Acta Cryst.* **B25**, 1952–1958.

Light, R. W., Campana, C. F., Paine, R. T. & Morosin, B. (1978). *Acta Cryst.* **B34**, 3671–3674.

Liu, A. T., Beck, W., Huttner, G. & Lorentz, H. (1977). *J. Organomet. Chem.* **129**, 91–96.

Marre, M.-R., Sanchez, M., Wolf, R., Jaud, J. & Galy, J. (1984). *Can. J. Chem.* **62**, 2186–2191.

Pohl, S. (1979). *Chem. Ber.* **112**, 3159–3165.

Powell, J., Farrar, D. H. & Smith, S. J. (1984). *Inorg. Chim. Acta*, **85**, L23–L25.

Powell, J., Gregg, M. R., Kuksis, A., May, C. J. & Smith, S. J. (1989). *Organometallics*, **8**, 2918–2932.

Powell, J., Gregg, M. R. & Meindl, P. E. (1989). *Organometallics*, **8**, 2942–2947.

Powell, J., Kuksis, A., May, C. J., Meindl, P. E. & Smith, S. J. (1989). *Organometallics*, **8**, 2933–2941.

Powell, J., Kuksis, A., May, C. J., Nyburg, S. C. & Smith, S. J. (1981). *J. Am. Chem. Soc.* **103**, 5941–5943.

Powell, J., Ng, K. S., Ng, W. W. & Nyburg, S. C. (1983). *J. Organomet. Chem.* **243**, C1–C4.

Powell, J., Nyburg, S. C. & Smith, S. J. (1983). *Inorg. Chim. Acta*, **76**, L75–L76.

Sellman, D., Lanzrath, G., Huttner, G., Zsolnai, L., Kruger, C. & Claus, K. H. (1983). *Z. Naturforsch. Teil B*, **38**, 961–981.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, W. S., Schomburg, D. & Schmidpeter, A. (1980). *Acta Cryst.* **B36**, 2316–2323.

Smith, S. J. (1987). PhD Thesis. Univ. of Toronto, Canada.

Uiterwijk, J. W. H. M., Harkema, S., van de Waal, B. W., Gobel, F. & Nibbeling, H. T. M. (1983). *J. Chem. Soc. Perkin Trans.* 2, pp. 1843–1855.