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The Crystal and Molecular Structures of Cyclotetra-μ-lithio-tetra[hydrido{bis-(π-cyclopentadienyl)}molybdenum] and its Tungsten Analogue

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The structures of the crystalline products of the reactions of $(\pi\text{-}C_5H_5)_2MH_2$ (M = Mo and W) with n-butyllithium have been determined from diffractometer data and refined by least-squares methods. The two compounds are isomorphous, crystallizing in space group $C2/c$ with $Z=4$. $C_{40}H_{44}Li_4Mo_4$ has $a=26{\cdot}39$, $b=7{\cdot}72$, $c=22{\cdot}43$ Å, $\beta=124{\cdot}8°$, and was refined to $R=0{\cdot}071$ for 1624 reflexions; $C_{40}H_{44}Li_4W_4$ has $a=26{\cdot}24$, $b=7{\cdot}76$, $c=22{\cdot}35$ Å, $\beta=124{\cdot}6°$, and was refined to $R=0{\cdot}035$ for 2744 reflexions. The molecules consist of eight-membered rings of alternate lithium and transition-metal atoms, each of the latter retaining its two π-cyclopentadienyl rings. In addition, it is postulated that an extra hydrogen atom is associated with each transition metal atom.

Treatment of the dihydrides $(\pi\text{-}C_5H_5)_2MH_2$ (M = Mo or W) in toluene at 50° with n-butyllithium gives yellow-orange crystalline products, now formulated as $[(\pi\text{-}C_5H_5)_2M(H)Li]_4$. They are highly reactive, pyrophoric compounds; some of their unusual chemistry has already been communicated (Francis, Green & Roberts, 1971). Their characterization required full X-ray diffraction studies which are here reported. A preliminary account has appeared (Benfield, Forder, Green, Moser & Prout, 1973).

Experimental

Samples of the Mo (orange-red needles) and W (orange-yellow needles) compounds were kindly provided by Drs G. A. Moser and M. L. H. Green. The compounds are very sensitive to air and moisture, and were mounted under dry nitrogen in glass capillaries. It was not possible to measure their densities. Survey photography was carried out by oscillation and Weissenberg techniques.

(1) *Molybdenum compound*

The crystal was mounted, with *b* as rotation axis, on a Hilger and Watts linear diffractometer and the cell dimensions were determined by careful measurement of the setting angles of reflexions on the three reciprocal axes.

Crystal data

$C_{40}H_{44}Li_4Mo_4$, $M=936{\cdot}3$. Monoclinic: $a=26{\cdot}39$ (2), $b=7{\cdot}72$ (1), $c=22{\cdot}43$ (2) Å, $\beta=124{\cdot}8$ (5)°, $U=3752{\cdot}4$ Å^3. Systematic extinctions hkl, $h+k=2n+1$; $h0l$, $l=2n+1$. Space group $C2/c$ (C^6_{2h}, No. 15). $d_{\text{calc}}=1{\cdot}66$ g cm^{-3} for $Z=4$. $F(000)=1856$, Mo $K\alpha$, $\lambda=0{\cdot}71069$ Å.

The linear diffractometer had been modified so that, in the automatic mode, the moving-crystal stationary-counter method was used, for both peak and background. Total scan width was 3°, the middle $1\frac{1}{2}$° being treated as peak. Mo $K\alpha$ radiation was used, with balanced filters. Reflexions with very unequal backgrounds or whose intensities were less than 3σ, where σ is the standard deviation based on simple counting statistics, were not included in subsequent calculations, which were based on the remaining 1624 independent reflexions. No corrections for absorption were applied.

The crystal used for data collection, like all those examined, was twinned, but systematic overlap of reflexions occurred only in the $hk0$ zone. Measurements of selected reflexions from both components of the twin permitted corrections to be applied.

(2) *Tungsten compound*

The crystal was set up on a Hilger and Watts PDP8-controlled four-circle diffractometer and accurate cell dimensions and orientation matrix obtained by a least-squares fit to the setting angles of 20 reflexions.

Crystal data

$C_{40}H_{44}Li_4W_4$, $M=1288{\cdot}7$. Monoclinic: $a=26{\cdot}24$ (1), $b=7{\cdot}759$ (5), $c=22{\cdot}35$ (1) Å, $\beta=124{\cdot}6$ (4)°, $U=3747{\cdot}3$ Å^3. Systematic extinctions hkl, $h+k=2n+1$; $h0l$, $l=2n+1$. Space group $C2/c$ (C^6_{2h}, No. 15). $d_{\text{calc}}=2{\cdot}28$ g cm^{-3} for $Z=4$. $F(000)=2368$. Mo $K\alpha$, $\lambda=0{\cdot}71069$ Å.

The intensities of at least two equivalents of every independent reflexion with $\theta<25°$ were measured with an $\omega/2\theta$ scan and the ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970) with 60 steps of 0·02°. The 30 consecutive steps giving the highest total count were treated as peak, and the remaining 30 as background. Counting time at each step was 1 s for $\theta<15°$ and 2 s for $\theta>15°$. Mo $K\alpha$ radiation was used with a graphite monochromator (Bragg angle 6·05°). Reflexions with intensity less than 4σ, where σ is the standard deviation based on simple counting statistics, or whose apparent centre was more than 0·14° from the predicted position were not included in the subsequent calculations, which were based on the remaining 2744 independent reflexions. An empirical absorption correction was applied by the method of North, Phillips & Mathews (1968).

Structure solution and refinement

The Mo compound was solved by Patterson and Fourier techniques. Full-matrix least-squares refinement converged to an R of 0·103 with isotropic temperature factors, and 0·071 when anisotropic variation was permitted for all atoms except Li. H atoms were not located. The retention of unit weights throughout was found to give the minimum variation of mean $w(|F_o|-|F_c|)^2$ with F_o. All calculations were performed with the program system written by Sheldrick (1972) and implemented on the Oxford ICL 1906A computer. The complex neutral atom scattering factors of Cromer (1965) and Cromer & Waber (1965) were used.

Since the Mo and W compounds were clearly isomorphous, the coordinates of the former were used as the trial structure for the latter. In this case a large block approximation to the least-squares normal matrix was used, with one block calculated from the derivatives of the space parameters and a second block

Table 1. $C_{40}H_{44}Li_4Mo_4$: *fractional atomic coordinates and temperature factors*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	0·0817 (1)	0·6207 (2)	0·4486 (1)	0·042 (1)	0·045 (1)	0·033 (1)	0·002 (1)	0·020 (1)	−0·001 (1)
Mo(2)	0·1445 (1)	0·4269 (2)	0·2689 (1)	0·033 (1)	0·045 (1)	0·042 (1)	−0·001 (1)	0·023 (1)	−0·002 (1)
C(11)	0·0949 (9)	0·3262 (24)	0·4676 (10)	0·08 (1)	0·03 (1)	0·07 (1)	0·01 (1)	0·05 (1)	0·02 (1)
C(12)	0·0660 (10)	0·3962 (33)	0·5059 (12)	0·08 (1)	0·06 (2)	0·06 (1)	0·01 (1)	0·02 (1)	−0·01 (1)
C(13)	0·1107 (10)	0·5116 (35)	0·5573 (11)	0·08 (1)	0·09 (2)	0·05 (1)	0·00 (1)	0·05 (1)	0·00 (1)
C(14)	0·1626 (10)	0·5225 (32)	0·5515 (10)	0·07 (1)	0·07 (2)	0·04 (1)	0·01 (1)	0·01 (1)	0·00 (1)
C(15)	0·1539 (10)	0·4089 (39)	0·4976 (13)	0·06 (2)	0·11 (2)	0·08 (2)	0·01 (1)	0·04 (1)	0·02 (1)
C(21)	0·1194 (13)	0·8943 (33)	0·4688 (20)	0·09 (2)	0·03 (1)	0·15 (3)	−0·01 (1)	0·03 (2)	−0·02 (1)
C(22)	0·0657 (14)	0·8801 (42)	0·4782 (15)	0·10 (2)	0·08 (2)	0·10 (2)	0·00 (2)	0·04 (2)	0·02 (2)
C(23)	0·0103 (11)	0·8419 (35)	0·4038 (17)	0·09 (2)	0·06 (2)	0 13 (2)	0·03 (2)	0·07 (2)	0·00 (1)
C(24)	0·0317 (11)	0·8353 (39)	0·3603 (13)	0·07 (1)	0·09 (2)	0·07 (1)	0·05 (1)	0·02 (1)	0·00 (1)
C(25)	0·0972 (15)	0·8571 (37)	0·3995 (17)	0·14 (2)	0·06 (2)	0·11 (2)	0·01 (1)	0·10 (2)	−0·01 (2)
C(31)	0·1740 (12)	0·1492 (39)	0·2996 (14)	0·08 (2)	0·08 (2)	0·07 (2)	0·01 (1)	0·01 (1)	0·02 (1)
C(32)	0·1453 (9)	0·1643 (33)	0·2260 (14)	0·05 (1)	0·07 (2)	0·12 (2)	−0·03 (1)	0·05 (1)	0·01 (1)
C(33)	0·0827 (10)	0·2243 (35)	0·1916 (12)	0·07 (1)	0·08 (2)	0·07 (1)	−0·02 (1)	0·05 (1)	−0·02 (1)
C(34)	0·0699 (13)	0·2238 (42)	0·2438 (19)	0·10 (2)	0·09 (2)	0·11 (2)	−0·01 (2)	0·06 (2)	−0·04 (2)
C(35)	0·1254 (22)	0·1934 (38)	0·3111 (19)	0·24 (4)	0·05 (2)	0·12 (2)	0·00 (2)	0·14 (3)	−0·04 (2)
C(41)	0·2157 (11)	0·6218 (33)	0·3517 (12)	0·08 (1)	0·07 (2)	0·06 (1)	−0·02 (1)	0·04 (1)	−0·03 (1)
C(42)	0·2445 (9)	0·5088 (41)	0·3325 (14)	0·04 (1)	0·11 (2)	0·09 (2)	−0·03 (2)	0·02 (1)	−0·03 (1)
C(43)	0·2169 (12)	0·5198 (46)	0·2548 (17)	0·07 (2)	0·13 (3)	0·12 (2)	−0·02 (2)	0·06 (2)	−0·05 (2)
C(44)	0·1740 (13)	0·6511 (38)	0·2264 (12)	0·10 (2)	0·08 (2)	0·07 (1)	−0·01 (1)	0·06 (1)	−0·02 (1)
C(45)	0·1700 (14)	0·7167 (38)	0·2828 (15)	0·13 (2)	0·10 (2)	0·11 (2)	−0·05 (2)	0·10 (2)	−0·07 (2)
Li(1)	0·0387 (19)	0·5343 (64)	0·1438 (23)	0·08 (1)	(U_{iso})				
Li(2)	0·1216 (16)	0·5198 (53)	0·3631 (20)	0·07 (1)	(U_{iso})				

Table 2. $C_{40}H_{44}Li_4W_4$: *fractional atomic coordinates and temperature factors*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W(1)	0·08196 (2)	0·62070 (5)	0·44865 (2)	0·0460 (3)	0·0365 (2)	0·0399 (2)	0·0007 (2)	0·0231 (2)	−0·0013 (2)
W(2)	0·14437 (2)	0·42776 (5)	0·26791 (2)	0·0381 (2)	0·0376 (2)	0·0470 (3)	−0·0005 (2)	0·0256 (2)	−0·0012 (2)
C(11)	0·0950 (7)	0·3282 (15)	0·4704 (7)	0·09 (1)	0·04 (1)	0·08 (1)	0·02 (1)	0·05 (1)	0·01 (1)
C(12)	0·0664 (7)	0·3992 (17)	0·5050 (7)	0·10 (1)	0·06 (1)	0·07 (1)	0·02 (1)	0·05 (1)	−0·01 (1)
C(13)	0·1100 (7)	0·5197 (21)	0·5577 (7)	0·10 (1)	0·09 (1)	0·05 (1)	0·01 (1)	0·04 (1)	−0·01 (1)
C(14)	0·1637 (6)	0·5286 (18)	0·5552 (7)	0·07 (1)	0·07 (1)	0·06 (1)	0·02 (1)	0·02 (1)	0·01 (1)
C(15)	0·1550 (7)	0·4089 (16)	0·5012 (9)	0·07 (1)	0·05 (1)	0·10 (1)	0·01 (1)	0·03 (1)	0·01 (1)
C(21)	0·1188 (8)	0·8922 (18)	0·4779 (10)	0·09 (1)	0·05 (1)	0·12 (1)	0·02 (1)	0·03 (1)	−0·01 (1)
C(22)	0·0640 (8)	0·8806 (17)	0·4775 (10)	0·11 (1)	0·05 (1)	0·11 (1)	0·01 (1)	0·07 (1)	0·01 (1)
C(23)	0·0128 (8)	0·8431 (19)	0·4053 (10)	0·10 (1)	0·05 (1)	0·12 (1)	0·03 (1)	0·05 (1)	0·03 (1)
C(24)	0·0345 (8)	0·8338 (19)	0·3620 (9)	0·11 (1)	0·06 (1)	0·08 (1)	0·04 (1)	0·04 (1)	0·02 (1)
C(25)	0·0983 (9)	0·8581 (20)	0·4016 (10)	0·12 (1)	0·08 (1)	0·11 (1)	0·04 (1)	0·08 (1)	0·01 (1)
C(31)	0·1753 (8)	0·1540 (16)	0·3044 (9)	0·11 (1)	0·04 (1)	0·09 (1)	0·02 (1)	0·03 (1)	0·03 (1)
C(32)	0·1473 (6)	0·1662 (16)	0·2253 (8)	0·08 (1)	0·05 (1)	0·09 (1)	−0·01 (1)	0·05 (1)	0·01 (1)
C(33)	0·0813 (6)	0·2173 (17)	0·1876 (8)	0·08 (1)	0·06 (1)	0·09 (1)	−0·03 (1)	0·05 (1)	−0·03 (1)
C(34)	0·0677 (8)	0·2288 (21)	0·2397 (10)	0·12 (2)	0·08 (1)	0·13 (1)	−0·03 (1)	0·09 (1)	−0·06 (1)
C(35)	0·1248 (11)	0·1945 (18)	0·3130 (11)	0·23 (1)	0·04 (1)	0·16 (2)	0·00 (1)	0·16 (1)	−0·02 (1)
C(41)	0·2125 (7)	0·6252 (22)	0·3483 (8)	0·08 (1)	0·11 (1)	0·07 (1)	−0·03 (1)	0·04 (1)	−0·03 (1)
C(42)	0·2437 (5)	0·4977 (19)	0·3312 (8)	0·04 (1)	0·08 (1)	0·08 (1)	−0·02 (1)	0·02 (1)	−0·01 (1)
C(43)	0·2189 (6)	0·5137 (21)	0·2541 (8)	0·06 (1)	0·11 (1)	0·10 (1)	−0·02 (1)	0·05 (1)	−0·04 (1)
C(44)	0·1734 (7)	0·6497 (18)	0·2256 (8)	0·10 (1)	0·07 (1)	0·09 (1)	−0·02 (1)	0·06 (1)	−0·03 (1)
C(45)	0·1713 (7)	0·7119 (18)	0·2848 (9)	0·10 (1)	0·06 (1)	0·09 (1)	−0·02 (1)	0·06 (1)	−0·03 (1)
Li(1)	0·0368 (9)	0·5350 (30)	0·1428 (11)	0·05 (1)	0·08 (1)	0·05 (1)	0·01 (1)	0·02 (1)	0·03 (1)
Li(2)	0·1199 (10)	0·5212 (34)	0·3633 (11)	0·07 (1)	0·10 (2)	0·06 (1)	−0·01 (1)	0·04 (1)	0·00 (1)

from those of the scale and temperature factors. Refinement converged to $R=0{\cdot}072$ with isotropic temperature factors, and then to $R=0{\cdot}035$ with all atoms anisotropic; in this case, anisotropic variations of the Li temperature factors resulted in a significantly better fit. In the final stages each reflexion was assigned a weight according to $w=[1+[(|F_o|-171)/68]^2]^{-1}$, chosen to minimize the variation of mean $w(|F_o|-|F_c|)^2$ with F_o. All calculations were performed with the Oxford package of crystallographic programs (Carruthers & Rollett, 1973) on the Oxford University ICL 1906A computer. Complex neutral atom scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Results

The final atomic parameters are given in Tables 1 (Mo compound) and 2 (W compound). A view of the latter projected onto the *xz* plane is shown in Fig. 1. Important intramolecular distances and angles are compared for the two compounds in Table 3, whilst other details of the molecular geometry are given in Tables 4 and 5. All estimated standard deviations were calculated from the full variance–covariance matrix.*

Table 3. *Principal molecular dimensions*

M is Mo or W; $C_5H_5(1)$ denotes the cyclopentadienyl ring consisting of atoms C(11) to C(15), and similarly for the other rings. The values given for $M\text{–}C_5H_5$ are the perpendicular distances of the metal atoms from the mean plane of the rings, while $C_5H_5\text{–}M\text{–}C_5H_5$ denotes angles between ring normals.

	$C_{40}H_{44}Li_4Mo_4$	$C_{40}H_{44}Li_4W_4$
M(1)–Li(1)	2·71 (4) Å	2·66 (2) Å
M(1)–Li(2)	2·77 (4)	2·72 (2)
M(2)–Li(1)	2·72 (4)	2·75 (2)
M(2)–Li(2)	2·61 (4)	2·65 (2)
Mean M–Li	2·70	2·69
Li(1)–M(1)–Li(2)	98 (1)°	97 (2)°
Li(1)–M(2)–Li(2)	100 (1)	99 (2)
M(1)–Li(1)–M(2)	158 (2)	159 (1)
M(1)–Li(2)–M(2)	173 (2)	174 (1)
M(1)–C_5H_5(1)	1·91 Å	1·91 Å
M(1)–C_5H_5(2)	1·92	1·92
M(2)–C_5H_5(3)	1·90	1·91
M(2)–C_5H_5(4)	1·93	1·90
C_5H_5(1)–M(1)–C_5H_5(2)	149°	147°
C_5H_5(3)–M(2)–C_5H_5(4)	148	146

Discussion

The molecules represent a new type of metal cluster compound, based on eight-membered rings of alternate Mo (W) and Li atoms. The heavy metal is part of a bent $(\pi\text{-}C_5H_5)_2M$ group.

Table 4. $C_{40}H_{44}Li_4Mo_4$: *further bond lengths and angles*

Mo(1)–C(11)	2·30 (2) Å	Mo(1)–C(21)	2·27 (2) Å
Mo(1)–C(12)	2·33 (2)	Mo(1)–C(22)	2·23 (3)
Mo(1)–C(13)	2·26 (2)	Mo(1)–C(23)	2·31 (3)
Mo(1)–C(14)	2·20 (2)	Mo(1)–C(24)	2·33 (2)
Mo(1)–C(15)	2·26 (2)	Mo(1)–C(25)	2·29 (2)
Mo(2)–C(31)	2·25 (3)	Mo(2)–C(41)	2·29 (2)
Mo(2)–C(32)	2·25 (2)	Mo(2)–C(42)	2·26 (2)
Mo(2)–C(33)	2·21 (2)	Mo(2)–C(43)	2·22 (2)
Mo(2)–C(34)	2·32 (3)	Mo(2)–C(44)	2·31 (3)
Mo(2)–C(35)	2·22 (2)	Mo(2)–C(45)	2·31 (3)
C(11)–C(12)	1·53 (3)	C(15)–C(11)–C(12)	109 (2)°
C(12)–C(13)	1·40 (3)	C(11)–C(12)–C(13)	103 (2)
C(13)–C(14)	1·45 (3)	C(12)–C(13)–C(14)	111 (2)
C(14)–C(15)	1·40 (3)	C(13)–C(14)–C(15)	110 (2)
C(15)–C(11)	1·45 (3)	C(14)–C(15)–C(11)	106 (2)
C(21)–C(22)	1·55 (4)	C(25)–C(21)–C(22)	108 (2)
C(22)–C(23)	1·49 (4)	C(21)–C(22)–C(23)	105 (2)
C(23)–C(24)	1·38 (3)	C(22)–C(23)–C(24)	105 (2)
C(24)–C(25)	1·43 (4)	C(23)–C(24)–C(25)	114 (2)
C(25)–C(21)	1·34 (4)	C(24)–C(25)–C(21)	108 (2)
C(31)–C(32)	1·37 (3)	C(35)–C(31)–C(32)	105 (2)
C(32)–C(33)	1·44 (3)	C(31)–C(32)–C(33)	110 (2)
C(33)–C(34)	1·39 (3)	C(32)–C(33)–C(34)	108 (2)
C(34)–C(35)	1·40 (4)	C(33)–C(34)–C(35)	108 (2)
C(35)–C(31)	1·49 (4)	C(34)–C(35)–C(31)	109 (2)
C(41)–C(42)	1·38 (3)	C(45)–C(41)–C(42)	104 (2)
C(42)–C(43)	1·46 (4)	C(41)–C(42)–C(43)	110 (3)
C(43)–C(44)	1·38 (4)	C(42)–C(43)–C(44)	108 (3)
C(44)–C(45)	1·42 (3)	C(43)–C(44)–C(45)	108 (3)
C(45)–C(41)	1·50 (4)	C(44)–C(45)–C(41)	109 (3)

Table 5. $C_{40}H_{44}Li_4W_4$: *further bond lengths and angles*

W(1)–C(11)	2·31 (1) Å	W(1)–C(21)	2·26 (1) Å
W(1)–C(12)	2·30 (1)	W(1)–C(22)	2·25 (1)
W(1)–C(13)	2·25 (1)	W(1)–C(23)	2·29 (1)
W(1)–C(14)	2·23 (1)	W(1)–C(24)	2·30 (1)
W(1)–C(15)	2·28 (1)	W(1)–C(25)	2·28 (1)
W(2)–C(31)	2·26 (1)	W(2)–C(41)	2·26 (1)
W(2)–C(32)	2·26 (1)	W(2)–C(42)	2·22 (1)
W(2)–C(33)	2·29 (1)	W(2)–C(43)	2·25 (1)
W(2)–C(34)	2·32 (1)	W(2)–C(44)	2·29 (1)
W(2)–C(35)	2·27 (1)	W(2)–C(45)	2·28 (1)
C(11)–C(12)	1·46 (2)	C(15)–C(11)–C(12)	109 (3)°
C(12)–C(13)	1·43 (2)	C(11)–C(12)–C(13)	106 (3)
C(13)–C(14)	1·44 (2)	C(12)–C(13)–C(14)	110 (3)
C(14)–C(15)	1·44 (2)	C(13)–C(14)–C(15)	108 (3)
C(15)–C(11)	1·46 (2)	C(14)–C(15)–C(11)	107 (3)
C(21)–C(22)	1·43 (2)	C(25)–C(21)–C(22)	106 (4)
C(22)–C(23)	1·43 (2)	C(21)–C(22)–C(23)	109 (3)
C(23)–C(24)	1·38 (2)	C(22)–C(23)–C(24)	108 (4)
C(24)–C(25)	1·39 (2)	C(23)–C(24)–C(25)	112 (3)
C(25)–C(21)	1·50 (3)	C(24)–C(25)–C(21)	106 (4)
C(31)–C(32)	1·49 (2)	C(35)–C(31)–C(32)	105 (4)
C(32)–C(33)	1·49 (2)	C(31)–C(32)–C(33)	109 (3)
C(33)–C(34)	1·40 (2)	C(32)–C(33)–C(34)	108 (3)
C(34)–C(35)	1·49 (3)	C(33)–C(34)–C(35)	100 (4)
C(35)–C(31)	1·48 (2)	C(34)–C(35)–C(31)	108 (3)
C(41)–C(42)	1·47 (2)	C(45)–C(41)–C(42)	107 (3)
C(42)–C(43)	1·46 (2)	C(41)–C(42)–C(43)	108 (3)
C(43)–C(44)	1·44 (2)	C(42)–C(43)–C(44)	107 (3)
C(44)–C(45)	1·44 (2)	C(43)–C(44)–C(45)	107 (3)
C(45)–C(41)	1·38 (2)	C(44)–C(45)–C(41)	112 (3)

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* Observed structure amplitudes and structure factors calculated from the final atomic parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30474 (33 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The size and shape of the metal atom ring does not differ significantly between the two compounds (Table 3). Its crystallographic symmetry is C_2, but the molecules are not much distorted from an idealized structure with D_{2d} symmetry. The angle of fold between the M(1)–M(2)–M(1′) and M(1)–M(2′)–M(1′) planes is 135° in both cases. The long Mo–Li and W–Li bonds, which do not vary significantly around the rings, are a reflexion of the large covalent radius of Li. The bond length in Li_2 is 2·673 Å (Herzberg, 1950) and the resulting radius of 1·34 Å is consistent also with the structures of the tetrameric alkyllithiums (Dietrich, 1963; Weiss & Hencken, 1970). The covalent radius of Mo is usually put at 1·6 Å, derived by halving the length of the Mo–Mo bond in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (Wilson & Shoemaker, 1957). The radius of W is closely similar on account of the lanthanide contraction. It can therefore be seen that, allowing for a rather indeterminate 'electronegativity correction', the transition-metal–lithium bond lengths observed here are within the expected range.

The coordination around Li would be expected to be linear, and to a first approximation this is observed. Nevertheless, in both compounds, the two independent angles at Li are significantly different, with one deviating by about 20° from the idealized configuration. Since, however, these angles are probably quite sensitive to intermolecular packing forces, it would be unwise to attach much chemical significance to these observations.

The Li–Mo(W)–Li angles, on the other hand, are closely similar and rather higher (mean 99°) than would be expected in a bent bis-π-cyclopentadienyl metal system (Green, Green & Prout, 1972) or required by the ring geometry. The observed values are thought to result from the existence of an extra hydrogen atom bonded to each transition metal atom, and probably occupying a position within this angle. Independent evidence for the existence of this hydrogen atom arises from the reactions of the compounds (Francis, Green & Roberts, 1971) where hydrides often result [for example, treatment of the W compound with bromobenzene yields $(C_5H_5)_2W(H)(C_6H_5)$], and from infrared spectroscopy, including measurements on deuterated specimens (Green & Moser, 1973). The stoichiometry of the synthesis is also compatible with this formulation:

$$4(C_5H_5)_2MH_2+4LiBu \rightarrow [(C_5H_5)_2M(H)Li]_4+4C_4H_{10}.$$

The perpendicular cyclopentadienyl–transition metal distances lie in the range 1·90–1·93 Å for both compounds, with angles of 148–149° between the ring normals. These are outside the normal range of 1·96–1·99 Å and 130–133° for bent $(\pi C_5H_5)_2Mo$ compounds (Green, Green & Prout, 1972; Prout, Allison, Delbaere & Gore, 1972), but are comparable to the values observed in bis-(π-cyclopentadienyl)molybdenumdihydride (Gerloch & Mason, 1965) and in two cyclopentadienyl–molybdenum–aluminum compounds (Forder, Green, MacKenzie, Poland & Prout, 1973). The correlation between short metal–ring distances and wide inter-ring angles is probably steric in origin, resulting from the need to restrict non-bonded interactions between cyclopentadienyl ring hydrogen atoms.

The carbon–carbon bond lengths within the cyclopentadienyl rings do not differ significantly from their overall mean, which is 1·43 Å for the Mo compound and 1·44 Å for its W analogue. These values are larger than normally observed, and it is interesting that a similar effect is noticeable in a molybdenum–magnesium complex obtained from bis-(π-cyclopentadienyl)-molybdenumdihydride and a Grignard reagent (Forder, Green & Prout, 1974). It is not yet clear whether this can be correlated with the electron-deficient nature of these compounds.

The shortest contacts between Li and ring C atoms are in the range 2·6–2·8 Å, but the directions are not consistent with any rational coordination sphere for the lithium atom.

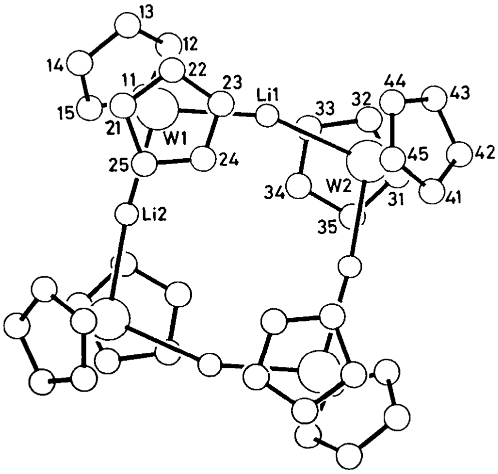

Fig. 1. The molecule of $C_{40}H_{44}Li_4W_4$ in projection down the *b* axis. For clarity, carbon atoms are denoted by their serial numbers only.

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Carbohydrate Orthoesters. III.* The Crystal and Molecular Structure of 3,4,6-Tri-*O*-acetyl-1,2-*O*-[1-(*exo*-ethoxy)ethylidene]-α-D-glucopyranose†

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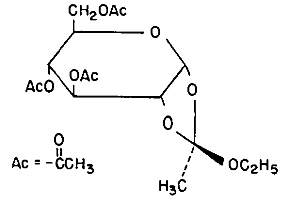
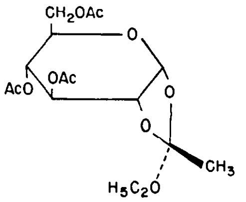
3,4,6-Tri-*O*-acetyl-1,2-*O*-[1-(*exo*-ethoxy)ethylidene]-α-D-glucopyranose ($C_{16}H_{24}O_{10}$) crystallizes in the monoclinic space group, $P2_1$, with $Z=2$ and cell parameters $a=7\cdot649$ (4), $b=14\cdot465$ (5), $c=8\cdot213$ (3) Å, and $\beta=96\cdot26$ (7)° at the experimental temperature of about −193°C. The structure was solved using Patterson search and tangent formula methods. Block-diagonal least-squares refinement, with fixed hydrogen parameters, resulted in a final R index of 0·068 for 1680 observed reflections. The diastereoisomer investigated, which exhibits a p.m.r. methyl singlet at δ 1·71 p.p.m. ($CDCl_3$), has the (S)-configuration at the dioxolane-2-carbon atom, *i.e.*, the ethoxy substituent is *trans* or *exo* to the pyranoid ring. The dioxolane ring has an envelope conformation, with O(2) deviating 0·46 Å from the plane of the other four atoms toward the glucose-ring side of the plane. There are considerable structural differences in the O(1) and O(2) sides of the dioxolane ring. The pyranoid ring approximates a skew ($^3S_5$) conformation with some additional flattening in the vicinity of C(1) and C(2) due to the presence of the dioxolane ring. The solution p.m.r. data are consistent with the pyranoid-ring conformation found in the crystal structure.

Introduction

During the formation of 3,4,6-tri-*O*-acetyl-1,2-(1-ethoxyethylidene)-α-D-glucopyranose and similar orthoacylates, an asymmetric center evolves at the dioxolane-2-carbon atom, resulting in the possibility of two diastereoisomers, the *exo*- (I) and *endo*-alkoxy (II) isomers. In proton magnetic resonance (p.m.r.) spectra, the singlets attributable to the methyl groups attached to the dioxolane-2-carbon atoms of the isomeric orthoacetates appear at high field and are well resolved (Lemieux & Morgan, 1965). This crystal structure investigation was to determine the configuration at the dioxolane-2-carbon atom of one of the two diastereomers, and also aid in interpreting the p.m.r. data related to the conformation of the pyranoid ring. Coxon & Hall (1964) predicted skew conformations for related 1,2-*O*-alkylidene-α-D-glucopyranose derivatives which have similar ring structures and p.m.r. coupling constants. Lemieux & Morgan (1965) subsequently predicted flattened-chair conformations for the pyranoid rings of several acetylated 1,2-*O*-(1-alkoxyethylidene)-α-D-glucopyranoses, including (I). Trotter & Fawcett (1966) showed such a flattened-chair conformation in the crystal structure of the hydroiodide derivative of 1,2-*O*-(2-amino-1-methylethylidene)-α-D-glucopyranose and indicated that the p.m.r. data of Coxon & Hall (1964) for the parent amine could be reinterpreted reasonably well in terms of a flattened-chair conformation. Thus, since the p.m.r. data for many of the 1,2-*O*-alkylidene and 1,2-*O*-(1-alkoxy-alkylidene) derivatives of α-D-glucopyranose are similar, later workers (Rees, Tatchell & Wells,



(I)



(II)

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* Part II: Hultman, Schroeder & Haigh (1972).

† A portion of a thesis submitted by J. A. Heitmann in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence University, Appleton, Wisconsin, June 1972. A preliminary account of portions of this work has appeared (Heitmann & Richards, 1973).