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Crystal and Molecular Structure of (*pentahapto*-Cyclopentadienyl)hydridomolybdenum-μ-dimethylaluminum-μ-[methylaluminum-di-(μ-*pentahapto*(*monohapto*)-cyclopentadienyl)dimethylaluminum]-(*pentahapto*-cyclopentadienyl)hydridomolybdenum, $[(C_5H_5)(C_5H_4)MoH]_2Al_3(CH_3)_5$

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Crystals of the title compound are orthorhombic, $a=19{\cdot}398$ (4), $b=14{\cdot}438$ (9), $c=9{\cdot}035$ (2) Å, $Z=4$, space group $P2_12_12_1$. The structure was determined by Patterson and Fourier syntheses, and refined by full-matrix least-squares procedures to $R=0{\cdot}066$ and $R_w=0{\cdot}063$ for 1213 observed reflexions. The molecular structure exhibits several unusual features: C_5H_4 groups which are *pentahapto* to the molybdenum atoms and are involved *via* the unique carbon atom in multicentre bonding to two aluminum atoms, one of which occurs as an $AlMe_2$ unit and the other an AlMe unit which also bridges the two molybdenum atoms. The third aluminum atom is probably involved in a Mo–H–Al(Me_2)–H–Mo linkage. Mean bond distances are: Mo–Al, 2·659 and 2·974, Al–C(terminal), 2·00, Al–C(bridge), 2·05 and 2·33, Mo–C(cyclopentadienyl), 2·285, and C–C(cyclopentadienyl), 1·389 Å.

Introduction

An earlier report (Storr & Thomas, 1971) indicated that slow decomposition of the adduct $Cp_2MoH_2.AlMe_3$ occurs in benzene solution at room temperature. Methane is liberated and eventually a solid is deposited from solution. From one such solution a small amount of crystalline material was produced suitable for X-ray analysis and an investigation was carried out to determine the extent of the expected Mo–Al network in the crystals. The novel† structure which resulted (shown in Fig. 1) contained two molybdenum and three aluminum atoms per molecular unit.

Experimental

The small amount of crystalline material deposited as a result of the slow methane elimination from benzene solutions of the parent compound, $Cp_2MoH_2.AlMe_3$, was sufficient only for the crystal structure investigation and consequently no chemical analyses are reported. The molecular formula given in the title was derived from the experimental X-ray data collected on the sample.

The air-sensitive crystals were mounted in glass capillary tubes under a nitrogen atmosphere and subsequently sealed off. An irregularly shaped crystal with dimensions of *ca.* 0·15 × 0·15 × 0·15 mm was mounted with the [011] vector parallel to the goniostat axis. Unit-cell and space-group data were obtained from film and diffractometer measurements. The unit-cell parameters were refined by a least-squares treatment of $\sin^2\theta$ values for 30 reflexions measured on a diffractometer with Mo $K\alpha$ radiation. Crystal data are: $C_{25}H_{35}Al_3Mo_2$, F.W. = 608·4.

Orthorhombic, $a=19{\cdot}398$ (4), $b=14{\cdot}438$ (9), $c=9{\cdot}035$ (2) Å, $V=2531$ (2) Å^3, $Z=4$, $D_x=1{\cdot}597$ (1) g cm^{-3}, $F(000)=1232$ (20°C, Mo $K\alpha$, $\lambda=0{\cdot}71069$ Å, $\mu=10{\cdot}9$ cm^{-1}). Absent spectra: $h00$, $h\neq 2n$, $0k0$, $k\neq 2n$, and $00l$, $l\neq 2n$ define uniquely the space group $P2_12_12_1$ (D_2^4, No. 19).

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Mo $K\alpha$ radiation (zirconium filter and pulse-height analyser), and a θ–2θ scan at 2° min^{-1} over a range of $(1{\cdot}80+0{\cdot}86\tan\theta)$ degrees in 2θ, with 20s background counts being measured at each end of the scan. Data were measured to $2\theta=45°$ (minimum interplanar spacing 0·93 Å) initially and later data for $l=0$ to 7 were collected between $2\theta=45$ and $2\theta=50°$ (minimum interplanar spacing 0·84 Å). Data collection in the $2\theta=45$–$50°$ shell was discontinued at $l=7$ owing to a very low percentage of observed reflexions. A check reflexion was monitored every 40 reflexions throughout the data collection. The intensity of the check reflexion remained within 10% of its original value during the data collection, the final measurement of the check reflexion gave 95% of the original count. Lorentz and polarization corrections and check reflexion scaling were applied in deriving the structure-factor amplitudes. No absorption correction was made

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† During the preparation of this manuscript a preliminary report of this structure by Dr C. K. Prout and coworkers appeared in *J. Chem. Soc. Chem. Commun.* (1973), p. 426. The authors acknowledge correspondence with Dr Prout who will in the future publish an account on both the $[(C_5H_5)(C_5H_4)MoH]_2Al_3Me_5$ and $[(C_5H_4)_2MoH]_2Al_4Me_6$ structures contained in his preliminary report.

in view of the relatively small value of μ. Of the 2352 independent reflexions measured, 1113 had intensities less than $3\sigma(I)$ above background where $\sigma^2(I)=S+B+(0{\cdot}03\ S)^2$ with S = scan count and B = time-averaged background count. These reflexions were classified as unobserved.

Structure analysis

The positions of the two molybdenum atoms were determined from the three-dimensional Patterson function. One cycle of isotropic full-matrix least-squares refinement gave $R=0{\cdot}25$. A subsequent difference map revealed three large peaks, two of which were clearly the bridging aluminum atoms. The third peak was thought to be anomalous at the time and was left out of the calculations. The molybdenum and two aluminum atoms were refined isotropically for one cycle and a second difference Fourier map was calculated. The R factor at this point was 0·200. The difference map showed the same large peak as the previous one, which was deduced to be a third aluminum atom, as well as probable positions for 16 carbon atoms. The molybdenum atoms were then refined anisotropically and the 3 aluminum and 16 carbon atoms isotropically for one cycle, giving $R=0{\cdot}130$. After one additional cycle of refinement and difference Fourier synthesis all 25 carbon atoms had been located. Refinement with anisotropic carbon atoms gave an R value of 0·051 but 3 carbon atoms had non-positive definite temperature factors. Since the number of observed reflexions was relatively low it was decided to refine the structure with isotropic thermal parameters for the carbon atoms. Hydrogen-atom positions were calculated with C–H = 0·97 Å for the methyl and cyclopentadienyl groups. The hydrogen atoms were assigned isotropic temperature factors approximately 1·5 Å^2 larger than the mean B for the carbon atom type to which they are

Table 1. *Final positional (fractional,* × 10^4*) and thermal parameters with standard deviations in parentheses*

	x	y	z	B (Å^2)
Mo(1)	4031 (1)	9007 (1)	5698 (2)	*
Mo(2)	2971 (1)	6488 (1)	3182 (2)	*
Al(1)	3720 (2)	8025 (4)	3296 (7)	*
Al(2)	3440 (3)	7152 (4)	6166 (6)	*
Al(3)	5033 (3)	7308 (4)	2544 (8)	*
C(1)	3610 (8)	8777 (11)	1476 (20)	3·3 (4)
C(2)	2652 (9)	7175 (12)	7586 (21)	3·3 (4)
C(3)	4111 (9)	6284 (11)	7097 (19)	3·4 (4)
C(4)	5311 (12)	7847 (17)	585 (30)	7·1 (6)
C(5)	5728 (10)	6463 (15)	3457 (24)	5·5 (5)
C(11)	4825 (8)	8301 (12)	4091 (20)	2·6 (4)
C(12)	4980 (10)	8119 (14)	5585 (26)	4·5 (5)
C(13)	5159 (10)	8891 (15)	6371 (22)	4·4 (5)
C(14)	5093 (11)	9578 (15)	5439 (27)	4·9 (5)
C(15)	4895 (9)	9309 (12)	4061 (22)	3·4 (4)
C(21)	4121 (8)	6588 (12)	2430 (18)	2·7 (4)
C(22)	3675 (9)	6443 (14)	1167 (20)	3·9 (4)
C(23)	3358 (11)	5571 (15)	1344 (24)	5·0 (5)
C(24)	3548 (10)	5133 (13)	2729 (24)	4·2 (5)
C(25)	4013 (9)	5804 (11)	3290 (20)	3·1 (4)
C(31)	2859 (10)	9264 (12)	6137 (20)	3·4 (4)
C(32)	3082 (12)	9808 (15)	4941 (25)	5·4 (6)
C(33)	3592 (12)	10424 (17)	5446 (30)	6·5 (6)
C(34)	3646 (12)	10331 (17)	6871 (31)	6·8 (6)
C(35)	3220 (11)	9617 (15)	7415 (25)	5·0 (5)
C(41)	1845 (11)	6082 (16)	3250 (30)	5·8 (6)
C(42)	1906 (10)	6793 (14)	4219 (25)	4·6 (5)
C(43)	2123 (12)	7557 (15)	3564 (26)	5·8 (6)
C(44)	2152 (10)	7337 (13)	2022 (25)	4·5 (5)
C(45)	1967 (11)	6402 (15)	1954 (26)	5·1 (5)

* Anisotropic temperature factors.

Table 1 (*cont.*)

Anisotropic temperature factors (U_{ij}, Å^2 × 10^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	2·65 (8)	2·79 (9)	3·46 (10)	0·30 (8)	0·25 (9)	−0·54 (10)
Mo(2)	2·35 (8)	3·24 (9)	3·87 (10)	−0·37 (8)	−0·12 (9)	−0·22 (10)
Al(1)	3·08 (31)	2·58 (29)	3·36 (35)	−0·10 (24)	−0·03 (31)	0·26 (33)
Al(2)	3·94 (35)	4·98 (40)	2·37 (35)	0·71 (30)	0·26 (28)	1·13 (32)
Al(3)	3·22 (33)	5·58 (42)	6·49 (44)	−0·38 (31)	1·61 (32)	−1·95 (37)

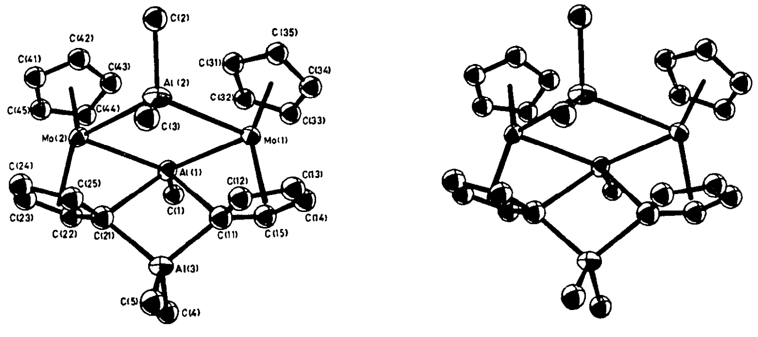

Fig. 1. A stereoscopic view of the $C_{25}H_{35}Al_3Mo_2$ molecule. 50% probability ellipsoids are shown for Mo and Al atoms. Carbon atoms are represented by equivalent spheres.

bonded. Difference maps did not unambiguously reveal the position of the molybdenum hydrogen atom. With the 33 methyl and cyclopentadienyl hydrogen atoms fixed, the remainder of the structure was refined to convergence with the carbon atoms isotropic, Mo and Al atoms anisotropic. The final agreement factors were R 0·066 and R_w 0·063 for 1213 observed reflexions.

Table 2. *Hydrogen atom and cyclopentadienyl ring centroid parameters*

(*a*) Calculated hydrogen atom positions* (fractional, $\times 10^4$) and assigned isotropic temperature factors.

	x	y	z	B (Å^2)
H(1*A*)	3164	9078	1488	5·0
H(1*B*)	3971	9244	1440	5·0
H(1*C*)	3646	8379	616	5·0
H(2*A*)	2290	7572	7195	5·0
H(2*B*)	2475	6554	7715	5·0
H(2*C*)	2808	7417	8529	5·0
H(3*A*)	4507	6213	6454	5·0
H(3*B*)	4256	6531	8044	5·0
H(3*C*)	3892	5687	7242	5·0
H(4*A*)	5718	8229	720	7·5
H(4*B*)	5413	7349	−98	7·5
H(4*C*)	4938	8221	201	7·5
H(5*A*)	6135	6817	3719	7·5
H(5*B*)	5533	6179	4328	7·5
H(5*C*)	5852	5987	2743	7·5
H(12)	4965	7499	6012	5·5
H(13)	5300	8922	7400	5·5
H(14)	5177	10220	5704	5·5
H(15)	4817	9712	3216	5·5
H(22)	3605	6870	349	5·5
H(23)	3051	5296	617	5·5
H(24)	3399	4547	3149	5·5
H(25)	4243	5719	4232	5·5
H(31)	2527	8758	6110	6·5
H(32)	2917	9764	3930	6·5
H(33)	3856	10854	4843	6·5
H(34)	3945	10705	7501	6·5
H(35)	3175	9405	8432	6·5
H(41)	1723	5446	3483	6·5
H(42)	1808	6742	5264	6·5
H(43)	2233	8144	4034	6·5
H(44)	2277	7747	1212	6·5
H(45)	1935	6046	1038	6·5

(*b*) Cyclopentadienyl ring centroid coordinates (fractional, $\times 10^4$).

Ring	x	y	z
R(1)	4990	8840	5109
R(2)	3743	5908	2192
R(3)	3280	9889	6162
R(4)	1999	6834	3002

* The hydrogen atoms are labelled as follows: a cyclopentadienyl hydrogen has the same number as the carbon to which it is bonded, *e.g.* H(12) is bonded to C(12); a methyl hydrogen is denoted by a numeral referring to the carbon atom to which it is bonded and by *A*, *B*, or C to distinguish between the three different hydrogens associated with each carbon.

The absolute configuration of the complex has been determined through the anomalous scattering of the molybdenum and aluminum atoms. Enantiomorph (*A*) is represented by the coordinates in Tables 1 and 2. Enantiomorph (*B*) was generated by changing the x coordinates of (*A*) to $1-x$. (*B*) was then refined to convergence and Hamilton's (1965) test was applied to the resulting R factor ratios. The results, summarized in Table 3, indicate that enantiomorph (*A*) is most probably the correct absolute configuration, assuming the data to be free of systematic error.

The least-squares refinement was based on the minimization of $\sum w(F_o-F_c)^2$. The scattering factors in *International Tables for X-ray Crystallography* were used for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the hydrogen atoms. Corrections for anomalous scattering have been made for the molybdenum and aluminum atoms. The anisotropic temperature factors employed in the refinement are U_{ij} in the expression:

$$f=f^\circ \exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\right]$$

where f° is the tabulated scattering factor and f is that corrected for thermal motion. A standard errors weighting scheme: $w=1/\sigma^2(F)$, where $\sigma^2(F)$ is derived from the previously defined $\sigma^2(I)$, gave constant average values of $w(F_o-F_c)^2$ over ranges of $|F_o|$ and was employed in the final stages of refinement.

On the final cycle of refinement the largest parameter was 0·31 σ. Final positional and thermal parameters appear in Table 1. The calculated positions of the hydrogen atoms and assigned temperature factor appear in Table 2. Observed and calculated structure factor amplitudes are available.* In the final stages of refinement 26 reflexions believed to be suffering from counter errors or which had ratios of greater than 10:1 between the two background counts were given zero weight.

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30251 (23 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Results of Hamilton's test*

Parameter compared	Value for enantiomorph (*A*)	(*B*)	Ratio (*B*)/(*A*)	Significance level*
Conventional R (all F)	0·1434	0·1439	1·0035	99·5
Conventional R (F_{obs} only)	0·0656	0·0658	1·0030	97·5
Weighted R (all F)	0·0651	0·0652	1·0021	99·5
Weighted R (F_{obs} only)	0·0631	0·0632	1·0022	95·0

* This is the % probability that enantiomorph (*A*) is the correct absolute configuration.

Table 4. *Bond distances with standard deviations in parentheses*

Mo(1)–Al(1)	2·662 (6) Å	Al(1) –C(1)	1·98 (2) Å
Mo(2)–Al(1)	2·655 (5)	Al(1) –C(11)	2·30 (2)
Mo(1)–Al(2)	2·944 (6)	Al(1) –C(21)	2·35 (2)
Mo(2)–Al(2)	3·003 (6)	Al(2) –C(2)	2·00 (2)
Mo(1)–C(11)	2·35 (2)	Al(2) –C(3)	1·99 (2)
Mo(1)–C(12)	2·25 (2)	Al(3) –C(4)	2·01 (3)
Mo(1)–C(13)	2·28 (2)	Al(3) –C(5)	2·00 (2)
Mo(1)–C(14)	2·23 (2)	Al(3) –C(11)	2·04 (2)
Mo(1)–C(15)	2·28 (2)	Al(3) –C(21)	2·05 (2)
Mo(1)–C(31)	2·34 (2)	C(11)–C(12)	1·41 (3)
Mo(1)–C(32)	2·28 (2)	C(12)–C(13)	1·37 (3)
Mo(1)–C(33)	2·23 (2)	C(13)–C(14)	1·31 (3)
Mo(1)–C(34)	2·31 (2)	C(14)–C(15)	1·36 (3)
Mo(1)–C(35)	2·38 (2)	C(15)–C(11)	1·46 (2)
Mo(2)–C(21)	2·34 (2)	C(21)–C(22)	1·45 (2)
Mo(2)–C(22)	2·28 (2)	C(22)–C(23)	1·41 (3)
Mo(2)–C(23)	2·25 (2)	C(23)–C(24)	1·45 (3)
Mo(2)–C(24)	2·29 (2)	C(24)–C(25)	1·42 (2)
Mo(2)–C(25)	2·25 (2)	C(25)–C(21)	1·39 (2)
Mo(2)–C(41)	2·26 (2)	C(31)–C(32)	1·40 (2)
Mo(2)–C(42)	2·31 (2)	C(32)–C(33)	1·41 (3)
Mo(2)–C(43)	2·28 (2)	C(33)–C(34)	1·30 (3)
Mo(2)–C(44)	2·26 (2)	C(34)–C(35)	1·41 (3)
Mo(2)–C(45)	2·25 (2)	C(35)–C(31)	1·44 (3)
Mo(1)–R(1)	1·95	C(41)–C(42)	1·35 (3)
Mo(2)–R(2)	1·94	C(42)–C(43)	1·32 (3)
Mo(1)–R(3)	1·98	C(43)–C(44)	1·43 (3)
Mo(2)–R(4)	1·96	C(44)–C(45)	1·40 (2)
		C(45)–C(41)	1·28 (3)

Table 5. *Bond angles with standard deviations in parentheses*

Al(1)—Mo(1)–Al(2)	62·9 (2)°	C(15)–C(11)–C(12)	101 (2)°
Al(1)—Mo(1)–R(1)	85·9	C(15)–C(11)–Al(1)	105 (1)
Al(1)—Mo(1)–R(3)	110·4	C(15)–C(11)–Al(3)	132 (1)
Al(2)—Mo(1)–R(1)	107·3	C(12)–C(11)–Al(1)	118 (1)
Al(2)—Mo(1)–R(3)	105·5	C(12)–C(11)–Al(3)	119 (1)
R(1) —Mo(1)–R(3)	147·1	Al(1) –C(11)–Al(3)	81·3 (6)
Al(1)—Mo(2)–Al(2)	62·1 (2)	C(25)–C(21)–C(22)	104 (2)
Al(1)—Mo(2)–R(2)	87·5	C(25)–C(21)–Al(1)	119 (1)
Al(1)—Mo(2)–R(4)	108·5	C(25)–C(21)–Al(3)	121 (1)
Al(2)—Mo(2)–R(2)	108·6	C(22)–C(21)–Al(1)	101 (1)
Al(2)—Mo(2)–R(4)	106·6	C(22)–C(21)–Al(3)	129 (1)
R(2) —Mo(2)–R(4)	144·8	Al(1) –C(21)–Al(3)	79·7 (6)
C(1)—Al(1)—Mo(1)	114·2 (5)	C(11)–C(12)–C(13)	114 (2)
C(1)—Al(1)—Mo(2)	111·5 (5)	C(12)–C(13)–C(14)	105 (2)
C(1)—Al(1)—C(11)	105·4 (7)	C(13)–C(14)–C(15)	114 (2)
C(1)—Al(1)—C(21)	104·1 (7)	C(14)–C(15)–C(11)	107 (2)
Mo(1)–Al(1)—Mo(2)	126·9 (2)	C(21)–C(22)–C(23)	107 (2)
Mo(1)–Al(1)—C(11)	56·0 (4)	C(22)–C(23)–C(24)	112 (2)
Mo(1)–Al(1)—C(21)	131·8 (5)	C(23)–C(24)–C(25)	100 (2)
Mo(2)–Al(1)—C(11)	131·9 (5)	C(24)–C(25)–C(21)	117 (2)
Mo(2)–Al(1)—C(21)	55·2 (4)	C(35)–C(31)–C(32)	106 (2)
C(11) –Al(1)—C(21)	87·1 (6)	C(31)–C(32)–C(33)	109 (2)
Mo(1)–Al(2)—Mo(2)	106·2 (2)	C(32)–C(33)–C(34)	108 (2)
Mo(1)–Al(2)—C(2)	112·0 (6)	C(33)–C(34)–C(35)	112 (2)
Mo(1)–Al(2)—C(3)	112·3 (5)	C(34)–C(35)–C(31)	105 (2)
Mo(2)–Al(2)—C(2)	110·5 (6)	C(45)–C(41)–C(42)	108 (2)
Mo(2)–Al(2)—C(3)	112·1 (6)	C(41)–C(42)–C(43)	112 (2)
C(2)—Al(2)—C(3)	103·9 (7)	C(42)–C(43)–C(44)	105 (2)
C(4)—Al(3)—C(5)	114·8 (10)	C(43)–C(44)–C(45)	104 (2)
C(4)—Al(3)—C(11)	112·6 (9)	C(44)–C(45)–C(41)	111 (2)
C(4)—Al(3)—C(21)	112·6 (9)		
C(5)—Al(3)—C(11)	106·2 (8)		
C(5)—Al(3)—C(21)	107·1 (8)		
C(11) –Al(3)—C(21)	102·7 (7)		

Results and discussion

Bond distances and angles appear in Tables 4 and 5 respectively. Weighted least-squares mean planes are given in Table 6 and some important non-bonded contacts in Table 7. Table 8 gives structural data for related molybdenum cyclopentadienyl complexes. Stereoscopic views of the structure viewed along the *c* and *b* axes are shown in Figs. 2 and 3.

Table 6. *Least-squares planes*

(*a*) Distances (Å) of relevant atoms from mean planes through the molecule

	d	d/σ
Plane 1: Ring(1), C(11)–C(15)		
C(11)	0·011	0·7
C(12)	−0·019	1·0
C(13)	0·011	0·6
C(14)	0·000	0·0
C(15)	−0·008	0·4
Mo(1)	−1·951	1296·3
Plane (2): Ring(2), C(21)–C(25)		
C(21)	0·008	0·5
C(22)	−0·014	0·8
C(23)	0·016	0·8
C(24)	−0·006	0·3
C(25)	−0·003	0·2
Mo(2)	−1·934	1278·7
Plane (3): Ring(3), C(31)–C(35)		
C(31)	0·012	0·6
C(32)	−0·024	1·1
C(33)	0·028	1·1
C(34)	−0·013	0·6
C(35)	−0·005	0·2
Mo(1)	1·976	1304·8

	d	d/σ
Plane 4: Ring(4), C(41)–C(45)		
C(41)	−0·024	1·2
C(42)	0·024	1·2
C(43)	−0·023	1·0
C(44)	0·007	0·3
C(45)	0·008	0·4
Mo(2)	−1·956	1339·1
Plane (5): Mo(1), Mo(2) Al(1), Al(2)		
Mo(1)	−0·017	11·5
Mo(2)	−0·017	11·3
Al(1)	0·240	49·4
Al(2)	0·176	30·8
Plane (6): Al(1), Al(3) C(11), C(12)		
Al(1)	0·033	5·7
Al(3)	0·064	9·4
C(11)	−0·390	22·2
C(21)	−0·375	22·3

(*b*) Equations of planes: $lX+mY+nZ=p$, where X, Y, and Z are orthogonal ångstrom coordinates derived as follows:

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Plane	l	m	n	p
(1)	0·9605	−0·1070	−0·2570	6·7463
(2)	0·7566	−0·4539	−0·4707	0·6892
(3)	0·7270	−0·6674	−0·1612	−5·8012
(4)	−0·9584	0·2596	−0·1189	−1·4746
(5)	0·8852	−0·4608	−0·0635	0·6188
(6)	−0·0060	0·5164	−0·8563	−3·3572

(*c*) Angles between normals to planes

Planes		Planes	
(1)–(2)	154°	(2)–(6)	81°
(1)–(3)	144	(3)–(4)	148
(1)–(4)	157	(3)–(5)	164
(1)–(5)	156	(3)–(6)	102
(1)–(6)	81	(4)–(5)	164
(2)–(3)	158	(4)–(6)	104
(2)–(4)	142	(5)–(6)	101
(2)–(5)	155		

The crystal structure consists of discrete molecular units with normal van der Waals contacts between units. The closest intermolecular contacts, including those for hydrogen atoms in calculated positions, are listed in Table 7.

The molecular structure exhibits several unusual and novel features. The three aluminum atoms in the molecule are of different structural types. One of them, Al(2), was of the predictable dimethylaluminum type, bridging the two molybdenum atoms. The distances Mo(1)–Al(2) and Mo(2)–Al(2) are 2·944 (6) and 3·003 (6). The Mo(1)–Al(2)–Mo(2) angle is 106·2 (2)° while the opposite angle C(2)–Al(2)–C(3) is 103·9 (7)°. Thus the coordination about Al(2) is that of a distorted tetrahedron. Other angles at Al(2) range from 110·5 to 112·3°, the mean angle at Al(2) being 109·5°.

The two remaining aluminum atoms are involved in the unique structural feature of this system. Instead of a second bridging $AlMe_2$ unit an AlMe group bridges the two molybdenum atoms and at the same time is involved in a novel multicentre bonding arrangement with the two unique carbon atoms of the C_5H_4 groups, C(11) and C(21), and the remaining aluminum atom, Al(3), which occurs as an $AlMe_2$ unit. The two Al(1)–Mo distances, 2·662 (6) and 2·657 (5) Å, are equal to within experimental error. The fact that these distances are more than 0·3 Å shorter than the corresponding Al(2)–Mo bond has interesting structural implications which will be discussed. The Al_2Mo_2 bridging system is significantly non-planar (see Table 6). The angle between the normals to the two AlAlMo planes is 168·9°. The Al(1)–Al(3) and Mo(1)–Mo(2) distances are 2·935 (8) and 4·757 (2) Å respectively, neither of which represents any direct interaction. The remaining angles in this system are Mo(1)–Al(1)–Mo(2), 129·9 (2)°, Al(1)–Mo(1)–Al(2), 62·9 (2)°, and Al(1)–Mo(2)–Al(2), 62·1 (2)°.

Bond angles at Al(1) involving the two molybdenum atoms, C(1), and Al(3) have a mean value of 108·2°. This is indicative that Al(1) is sp^3 hybridized with three hybrids nearly parallel to the two Al(1)–Mo and

Table 7. *Selected non-bonded contacts*

				Symmetry operation*		
Mo(1)–Mo(2)	4·757 (2) Å	C(13)—C(41)	3·29 (3) Å	$\frac{1}{2}+x$	$\frac{3}{2}-y$	$1-z$
Al(1)—Al(2)	2·935 (8)	C(1)—H(35)	3·02	x	y	$z-1$
Al(1)—Al(3)	2·831 (8)	C(2)—H(22)	3·14	x	y	$z+1$
C(11)—C(21)	3·20 (2)	C(3)—H(14)	2·87	$1-x$	$y-\frac{1}{2}$	$\frac{3}{2}-z$
C(15)—C(33)	3·25 (3)	C(23)—H(41)	2·98	$\frac{1}{2}-x$	$1-y$	$z-\frac{1}{2}$
C(23)—C(45)	3·00 (3)	C(41)—H(23)	2·93	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
C(33)—C(14)	3·16 (3)	H(2*B*)–H(24)	2·36	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
C(34)—C(14)	3·28 (3)	H(2*C*)–H(22)	2·39	x	y	$z+1$
C(2)—H(31)	2·66	H(3*C*)–H(41)	2·31	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
C(2)—H(42)	2·73					
C(3)—H(12)	2·60					
C(3)—H(25)	2·73					
C(31)—H(43)	2·77					
H(1*B*)–H(15)	2·39					
H(1*C*)–H(22)	2·19					
H(2*A*)–H(31)	2·07					
H(2*A*)–H(42)	2·31					
H(3*A*)–H(12)	2·10					
H(3*A*)–H(25)	2·19					
H(31) –H(43)	2·15					

* Coordinates of first atom are those listed in Tables 1 and 2, those of the second atom are related to those in Tables 1 and 2 by this operation.

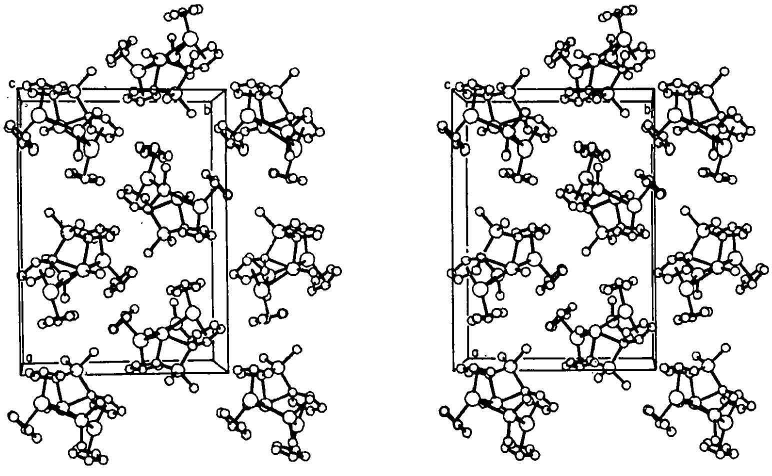

Fig. 2. The structure of $C_{25}H_{35}Al_3Mo_2$ viewed down **c**.

Al(1)–C(1) bonds, and the remaining hybrid, which is involved in the multicentre bonding, directed toward Al(3). The Al(1), C(11), C(21), Al(3) multicentre bonding arrangement resembles that in the trimethylaluminum dimer (Huffman & Streib, 1971), although closer examination reveals unique differences. The

Table 8. *Structural data for some molybdenum–cyclopentadienyl complexes*

Compound	Mean or range of Mo–C(Cp) (Å)	Mean or range of C–C(Cp) (Å)	Mean Mo–ring centroid distance (Å)
$C_{25}H_{35}Al_3Mo_2$ (this work)	2·285	1·389	1·96
$(C_5H_4)(C_5H_5)(CO)MoMn(CO)_4$[a]	—	1·40–1·44	—
$(C_5H_5)Mo(CO)(PPh_3)_2(NCO)$[b]	2·333	1·413	—
$(C_5H_5)Mo(CO)_2(PPh_3)I$[c]	2·333	1·412	—
$(C_5H_5)Mo(CO)(Ph_2PCH_2CH_2PPh_2)Cl$[c]	2·310	1·378	—
$(C_5H_5)_3Mo(NO)$[d]	2·32–2·68	1·347–1·427	—
$Mo(C_5H_5)(CO)_2(CH_2SCH_3)$[e]	2·34	1·41	2·08
$[Mo(C_5H_5)(SCH_3)_2]_2$[f]	2·30	—	1·97
$(C_5H_5)Mo(CO)_3CH_2COOH$[g]	2·35	1·42	2·01
$[PPh_4]^+[(C_5H_5)Mo\{S_2C_2(CN)_2\}_2]^-$[h]	2·338	1·418	2·00
$(C_5H_5)Mo(CO)(Ph_2PCH_2)_2Cl$[i]	2·324	1·421	—
$(C_5H_5)_2MoS_2C_6H_4$[j]	—	1·39	2·02
$(C_5H_5)_2MoH_2$[k]	2·289	1·425	1·94
$[(C_5H_5)Mo(CO)_3]_2$[l]	2·345	1·416	—
$(C_5H_5)Mo(CO)_3C_2H_5$[m]	2·38	1·43	2·04
$[(C_5H_5)Mo(CO)_2]_2(H)[P(CH_3)_2]$[n]	2·329	1·391	2·00
$(C_5H_5)_2MoS_2C_6H_3CH_3$[o]	2·253–2·368	1·385	1·999, 1·993
$C_5H_5(CO)_2MoN(H)NC(CO_2C_2H_5)COH$[p]	2·32–2·39	1·405	—
$(C_5H_5)_2MoS(CH_2)_2NH_2I$[q]	2·229–2·388	1·396	1·976, 2·002
$(C_5H_5(CO)_2MoN.N(CH_3).C(CO_2C_2H_5)COH)PF_6$[r]	—	1·41	—
$H[(C_5H_5)_2MoNH_2CH(CH_2S)COO]Cl$[s]	2·244–2·396	1·394	1·980, 1·981
$H[(C_5H_5)_2MoNH_2CH(CH_2S)COO]PF_6$[s]	2·21–2·42	1·40	1·96–2·01
$[(C_5H_5)_2MoNH_2CH_2COO]Cl.H_2O$[s]	2·27–2·36	1·27–1·42	1·986, 1·993
$[(C_5H_5)_2MoHN(CH_3)CH_2COO]Cl.CH_3OH$[s]	2·26–2·40	1·40	1·962, 1·991

[a] R. Hoxmeier, B. Deubzer & H. D. Kaesz (1971). *J. Amer. Chem. Soc.* **93**, 536.
[b] A. T. McPhail, G. R. Knox, C. G. Robertson & G. A. Sim (1971). *J. Chem. Soc.* (*A*), p. 205.
[c] M. A. Bush, A. D. U. Hardy, Lj. Manojlovic-Muir & G. A. Sim (1971). *J. Chem. Soc.* (*A*), p. 1003.
[d] J. L. Calderon, F. A. Cotton & P. Legzdins (1969). *J. Amer. Chem. Soc.* **91**, 2528.
[e] E. Rodulfo de Gil & L. F. Dahl (1969). *J. Amer. Chem. Soc.* **91**, 3751.
[f] N. G. Connelly & L. F. Dahl (1970). *J. Amer. Chem. Soc.* **92**, 7472.
[g] J. K. P. Ariyaratno, A. M. Bierrum, M. L. H. Green, M. Ishag, C. K. Prout & M. G. Swanwick (1969). *J. Chem. Soc.* (*A*), p. 1309.
[h] M. R. Churchill & J. Cooke (1970). *J. Chem. Soc.* (*A*), p. 2046.
[i] J. H. Cross & R. H. Fenn (1970). *J. Chem. Soc.* (*A*), p. 3019.
[j] A. Kutoglu & H. Köpf (1970). *J. Organometal. Chem.* **25**, 455.
[k] M. Gerloch & R. Mason (1965). *J. Chem. Soc.* p. 296.
[l] F. C. Wilson & D. P. Shoemaker (1957). *J. Chem. Phys.* **27**, 809.
[m] M. J. Bennett & R. Mason (1963). *Proc. Chem. Soc.* p. 273.
[n] R. J. Doedens & L. F. Dahl (1965). *J. Amer. Chem. Soc.* **87**, 2576.
[o] J. R. Knox & C. K. Prout (1969). *Acta Cryst.* B**25**, 2013.
[p] J. R. Knox & C. K. Prout (1969). *Acta Cryst.* B**25**, 1952.
[q] J. R. Knox & C. K. Prout (1969). *Acta Cryst.* B**25**, 2482.
[r] C. K. Prout, T. S. Cameron & A. R. Gent (1972). *Acta Cryst.* B**28**, 32.
[s] C. K. Prout, G. B. Allison, L. T. J. Delbaere & E. Gore (1972). *Acta Cryst.* B**28**, 3043.

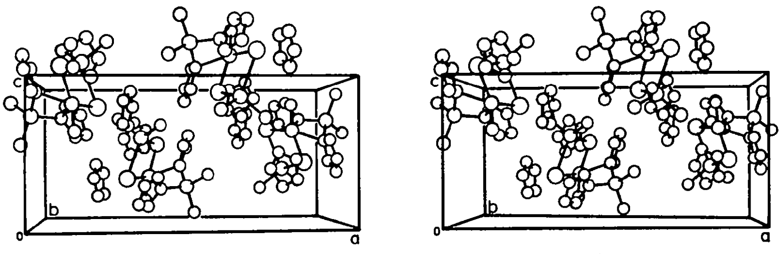

Fig. 3. The structure of $C_{25}H_{35}Al_3Mo_2$ viewed along **b**.

$[(CH_3)_3Al]_2$ structure is centrosymmetric with a planar bridging arrangement; the two independent Al–C (bridge) distances are 2·125 and 2·123 Å, and Al–C (terminal) are 1·949 and 1·956 Å. The angles in the bridge portion are 75·7° at C and 104·3° at Al. The bridge system in the present structure is non-planar (see Table 6), the angle between the two AlAlC planes is 149·7°, and also asymmetric with short bonds to Al(2), mean Al(2)–C(bridge) = 2·05 Å, and long bonds to Al(1), mean Al(1)–C(bridge) = 2·33 Å. The angles in the bridge are 87·1 (6)° at Al(1), 102·7 (7)° at Al(3), 79·7 (6)° at C(21), and 81·3 (6)° at C(11). Fig. 4 shows a schematic representation of the atomic orbitals believed to be involved in the multicentre bonding: one sp^2 hybrid orbital from each of C(11) and C(21), one sp^3 hybrid orbital from Al(1) and two sp^3 hybrid orbitals from Al(3). Note that Al(1) lies twice as far from the mean planes of the C_5H_4 rings (represented by the horizontal dotted lines in Fig. 4) as does Al(3). The bonding scheme represented by Fig. 4 is adequate to explain the observed geometry of the system, particularly the difference between the Al(1)–C(bridge) and Al(3)–C(bridge) distances.

The coordination about Al(3) is a somewhat distorted tetrahedron, with the angle C(4)–Al(3)–C(5) expanded to 114·8 (10)° corresponding to the contraction of the opposite angle, C(11)–Al(3)–C(21), to 102·7 (7)°. Other angles at Al(3) range from 106·2 to 112·6°, and the mean of all angles at Al(3) is 109·3°. None of the five Al–C(terminal) distances differs significantly from the mean value of 2·00 (1) Å, which is equal to the sum of the covalent radii.

The two C_5H_5 and two C_5H_4 groups are all *pentahapto* to the molybdenum atoms, and, assuming that one hydrogen atom is also coordinated to each of the molybdenum atoms, the latter obey the 18-electron rule. If the C_5H_5 and C_5H_4 groups are regarded as formally negatively charged and occupying three coordination sites at the metal atom, the complex may be regarded as a 9-coordinate complex of Mo(II) (assuming the H atom is a one electron donor). The recently reported structure of the niobocene dimer $[(C_5H_5)(C_5H_4)NbH]_2$ (Guggenberger, 1973) also contains *monohapto* and *pentahapto* C_5H_4 ligands. The present structure again demonstrates the versatility of the C_5H_5 ligand in that the C_5H_4 groups derived therefrom are *pentahapto* to a molybdenum atom and are involved *via* the unique carbon atom in multicentre bonding to aluminum atoms.

The mean Mo–C distance is 2·285 Å with individual distance ranging from 2·23 to 2·38 Å and the mean Mo–R (ring centroid) distance is 1·96 Å. The four cyclopentadienyl rings are all planar within experimental error (see Table 6). The mean C–C bond length in the rings is 1·389 Å and the mean C–C–C angle is, as expected, 108°. The Mo–C, C–C (cyclopentadienyl), and Mo–R distances are in good agreement with those of related compounds, which are compiled in Table 8.

The structure may be interpreted in terms of valence-bond theory in a manner analogous to that described for the niobocene dimer (Guggenberger, 1973). The latter approach views structures of this type of bis(cyclopentadienyl)–transition metal complex as having canted rings with three hybrid orbitals in the horizontal mirror plane (Ballhausen & Dahl, 1961) as shown in Fig. 5. Some structures which can be rationalized by this scheme are given by Guggenberger (1973). Both molybdenum atoms in the present molecule have Al(1) in the ψ_1 position and Al(2) in the ψ_2 position, the hydrogen atom is assumed to be in the ψ_3 position. The angles between the C_5H_5 and C_5H_4 planes are 32·9° at Mo(1) and 35·2° at Mo(2), which are similar to those in other molybdenum complexes, *e.g.* 34° in $(C_5H_5)_2MoH_2$ (Gerloch & Mason, 1965) and 35° in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$ (Hoxmeier, Deubzer & Kaesz, 1971). The length of the two Mo–Al(2) bonds (0·3 Å longer than Mo–Al(1) bonds) suggests the possibility of a Mo–H–Al(Me_2)–H–Mo bridging system analogous to the Ti–H–$AlEt_2$ system in $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$ (Corradini & Sirigu, 1967; Tebbe & Guggenberger, 1973).

The three aluminum and five methyl carbon atoms are approximately planar. The two halves of the molecule with respect to this plane are not equivalent, the most interesting difference is that the C_5H_5 and C_5H_4 groups associated with Mo(1) are staggered while those at Mo(2) are eclipsed. This results from steric interaction between the ring 3 and ring 4 hydrogens. The distance between calculated positions for H(31)

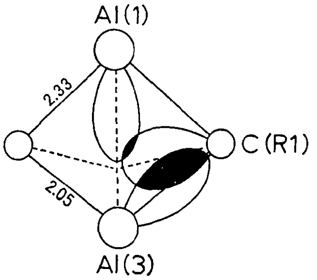

Fig. 4. A representation of the bonding in Al(1)–C(11)–C(21)–Al(3) bridging system. Mean values of the Al–C distances are shown.

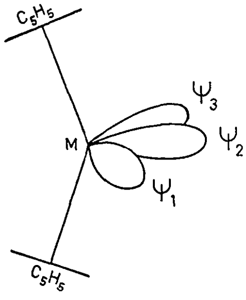

Fig. 5. Idealized structure of bis(cyclopentadienyl)–transition metal complexes with canted Cp rings.

and H(43) is 2·15 Å which is less than the sum of van der Waals radii. If the conformation of the rings were the same at each molybdenum atom there would be even greater steric interference. Inspection of bond lengths and angles shows other small differences between the two halves of the molecule, some of which are significant. The mean Mo–C(C_5H_4) distances are the same, 2·28 Å for each molybdenum atom, while the Mo–Al(2) distances differ by 10σ being 3·003 (6) Å for Mo(2) and 2·944 (6) Å for Mo(1). The mean Mo–C (C_5H_5) also differ being 2·31 Å at Mo(1) and 2·27 Å at Mo(2). The corresponding angles at the two molybdenum atoms show significant differences as well, and may be caused by a small energy difference between the staggered and eclipsed conformation of the C_5H_5 and C_5H_4 rings.

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References

BALLHAUSEN, C. J. & DAHL, J. P. (1961). *Acta Chem. Scand.* **15**, 1333–1336.

CORRADINI, P. & SIRIGU, A. (1967). *Inorg. Chem.* **6**, 601–605.

GERLOCH, M. & MASON, R. (1965). *J. Chem. Soc.* pp. 296–304.

GUGGENBERGER, L. J. (1973). *Inorg. Chem.* **12**, 294–301.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

HOXMEIER, R., DEUBZER, B. & KAESZ. H. D. (1971). *J. Amer. Chem. Soc.* **93**, 536–537.

HUFFMAN, J. C. & STREIB, W. E. (1971). *J. Chem. Soc. Chem. Commun.* pp. 911–912.

International Tables for X-ray Crystallography. (1962). Vol. III. Birmingham: Kynoch Press.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STORR, A. & THOMAS, B. S. (1971). *Canad. J. Chem.* **49**, 2504–2507.

TEBBE, F. N. & GUGGENBERGER, L. J. (1973). *J. Chem. Soc. Chem. Commun.* 227–228.

Acta Cryst. (1974). B30, 673

Structure Cristalline et Moléculaire du Méthyl [Hydroxy-2 phényl-2(diméthyl-2′,4′ phényl)-2] Ethyl Sulfoxyde

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Methyl [2-hydroxy-2-phenyl-2-(2′,4′-dimethylphenyl)]ethyl sulphoxide crystallizes in the monoclinic system, space group $P2_1/c$, with four molecules per unit cell. Unit-cell parameters are $a=7{\cdot}228$, $b=22{\cdot}21$, $c=9{\cdot}618$ Å, $\beta=84{\cdot}88°$. The structure was completely solved by the *MULTAN* program using all reflexions accessible with Cu $K\alpha$ radiation, and refined by the block-diagonal approximation and full-matrix least squares to a conventional R index of 6%. The bond lengths and angles are in agreement with the mean values generally observed. The molecules are packed together by van der Waals contact forces.

Introduction

Dans une note précédente, nous avons étudié par les rayons X la structure du méthyl [phényl-2(diméthyl-3′,4′ phényl)-2] vinyl sulfoxyde, appelé MPVS (Tranqui & Fillion, 1972); cette étude fut entreprise à la suite de la difficulté de tirer des renseignements stéréochimiques de cette molécule à partir des spectres IR, UV et RMN. C'est pour cette même raison et dans le cadre de l'étude structurale des sulfoxydes susceptibles de présenter des activités pharmaceutiques intéressantes que nous étudions ici la structure du méthyl [hydroxy-2, phényl-2(diméthyl-2′,4′ phényl)-2] éthyl sulfoxyde (MHPES); rappelons aussi que le MPVS est préparé à partir de la déshydration en milieu acide du MHPES; il est donc intéressant de comparer leurs structures avant et après la déshydration.

Préparation chimique

Les méthyl [hydroxy-2, phényl-2(diméthyl-2′,4′ phényl)-2] éthyl sulfoxydes s'obtiennent en faisant réagir le carbanion méthyl sulfinyle $\bar{C}H_2$-SO-CH_3 sur des benzophénones substitutés selon le schéma de réaction: