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The Crystal and Molecular Structures of (*pentahapto*-Cyclopentadienyl)hydridomolybdenum-μ-dimethylaluminum-μ-{methylaluminumdi-[μ-*pentahapto*(*monohapto*)-cyclopentadienyl]-dimethylaluminum}-(*pentahapto*-cyclopentadienyl)hydridomolybdenum, $[MoH(C_5H_5)(C_5H_4)]_2Al_3(CH_3)_5$, and Dimolybdenumbis-μ-{methylaluminumdi-[μ-*pentahapto*(*monohapto*)-cyclopentadienyl]-dimethylaluminum}, $[Mo(C_5H_4)_2Al_2(CH_3)_3]_2$

BY ROGER A. FORDER AND KEITH PROUT

Chemical Crystallography Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QS, England

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The structures of two crystalline products obtained from the reaction of bis-(π-cyclopentadienyl)-molybdenum dihydride with trimethylaluminum have been determined from four-circle diffractometer data and refined by least-squares methods. $C_{25}H_{35}Al_3Mo_2$ crystallizes in space group $P2_12_12_1$ with $a=19{\cdot}383$, $b=14{\cdot}458$, $c=9{\cdot}009$ Å, $Z=4$, and has been refined to $R=0{\cdot}069$ for 2670 reflexions. $C_{26}H_{34}Al_4Mo_2$ crystallizes in space group $P\bar{1}$ with $a=9{\cdot}029$, $b=9{\cdot}125$, $c=9{\cdot}748$ Å, $\alpha=64{\cdot}9$, $\beta=70{\cdot}3$, $\gamma=86{\cdot}9°$, $Z=1$, and has been refined to $R=0{\cdot}097$ for 2379 reflexions. In both cases Mo–Al bonds are present and σ-bonding between Al atoms and the π-cyclopentadienyl rings is an important feature of the structure. In $C_{25}H_{35}Al_3Mo_2$, an Mo–H–Al bridge system is postulated.

The reaction of bis-(π-cyclopentadienyl)molybdenum dihydride with trimethylaluminum in toluene yields two crystalline compounds depending on the conditions. Their composition and structure have been elucidated by single-crystal X-ray diffraction and they have thereby been formulated as $C_{25}H_{35}Al_3Mo_2$ (compound I, orange crystals) and $C_{26}H_{34}Al_4Mo_2$ (compound II, yellow crystals). This work has been the subject of a preliminary communication (Forder, Green, MacKenzie, Poland & Prout, 1973), and it was later learnt that a full description of the structure of $C_{25}H_{35}Al_3Mo_2$ had been submitted for publication by Rettig, Storr, Thomas & Trotter (1974).*

Experimental

Samples were kindly provided by Drs R. E. MacKenzie, J. S. Poland and M. L. H. Green. The insolubility of the materials prevented recrystallization and crystals obtained directly from the reaction mixture were employed. 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.

After survey photography by oscillation and Weissenberg techniques, the crystals were 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

Compound I: $C_{25}H_{35}Al_3Mo_2$, $M=608{\cdot}4$.
Orthorhombic, $a=19{\cdot}383\ (7)$, $b=14{\cdot}458\ (6)$, $c=9{\cdot}009\ (5)$ Å, $U=2524{\cdot}7$ Å^3.
Systematic extinctions: $h00$, $h=2n+1$; $0k0$, $k=2n+1$, $00l$, $l=2n+1$.
Space group $P2_12_12_1$ (D_2^4, No. 19), $d_{\text{calc}}=1{\cdot}60$ g cm^{-3} for $Z=4$, $F(000)=1232$. Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å, $\mu=96$ cm^{-1}.

Compound II: $C_{26}H_{34}Al_4Mo_2$, $M=646{\cdot}4$.
Triclinic, $a=9{\cdot}029\ (5)$, $b=9{\cdot}125\ (5)$, $c=9{\cdot}748\ (5)$ Å, $\alpha=64{\cdot}86\ (2)$, $\beta=70{\cdot}34\ (2)$, $\gamma=86{\cdot}88\ (2)°$, $U=681{\cdot}0$ Å^3.
Space group $P\bar{1}$ (C_i^1, No. 2), $d_{\text{calc}}=1{\cdot}58$ g cm^{-3} for $Z=1$ (molecule on $\bar{1}$), $F(000)=326$, Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å, $\mu=92$ cm^{-1}.

For each crystal, the intensities of every independent reflexion with $\theta<70°$ (and, in the case of the orthorhombic compound, at least one other equivalent reflexion) were measured with an $\omega/2\theta$ scan and the ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970) in 50 steps of 0·02°. The 25 consecutive steps giving the highest total count were treated as peak, and the remaining 25 as background. Counting times at each step ranged from 1 to 3 s depending on the Bragg angle. Cu $K\alpha$ radiation was used with a nickel β-filter, except for data with $\theta<10°$ where

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* The authors have been privileged to see this paper before publication and found no significant differences between the two analyses.

balanced filters (nickel and cobalt) were used. Reflexions with intensity less than 3σ, 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 2670 (compound I) and 2379 (compound II) reflexions.

Absorption problems were severe, especially in the triclinic material, which crystallized in a tabular habit. Empirical corrections were applied by the method of North, Phillips & Mathews (1968), but it is clear from the final agreement indices that the quality of the data was still impaired.

Structure solution and refinement

Both structures were solved by Patterson and Fourier techniques. In the orthorhombic structure molecules were found to occupy general positions in $P2_12_12_1$, whilst in the triclinic material molecules proved to consist of two asymmetric units related by the centre of symmetry in $P\bar{1}$. Full-matrix least-squares refinement converged to an R of 0·091 (compound I) and 0·121 (compound II) with isotropic temperature factors, and 0·069 (I) and 0·097 (II) when anisotropic variation was permitted. Hydrogen atoms were not located. In the last stages of refinement, each reflexion

Table 1. *Compound* I ($C_{25}H_{35}Al_3Mo_2$): *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)	0·4032 (1)	0·5991 (1)	0·4304 (1)	0·026 (1)	0·033 (1)	0·055 (1)	−0·005 (1)	−0·001 (1)	−0·002 (1)
Mo(2)	0·2971 (1)	0·8512 (1)	0·6816 (2)	0·024 (1)	0·036 (1)	0·060 (1)	−0·002 (1)	0·003 (1)	0·002 (1)
Al(1)	0·3723 (2)	0·6976 (3)	0·6693 (6)	0·031 (2)	0·033 (2)	0·061 (3)	0·005 (2)	−0·002 (2)	−0·002 (2)
Al(2)	0·5039 (2)	0·7688 (4)	0·7469 (8)	0·032 (2)	0·055 (3)	0·079 (3)	−0·021 (3)	−0·015 (2)	0·003 (2)
Al(3)	0·3437 (2)	0·7847 (3)	0·3830 (6)	0·039 (2)	0·041 (2)	0·055 (3)	0·007 (2)	0·002 (2)	0·001 (2)
C(1)	0·3621 (10)	0·6204 (13)	0·8587 (21)	0·066 (11)	0·060 (10)	0·052 (10)	0·013 (8)	0·003 (9)	0·000 (9)
C(2)	0·5316 (12)	0·7149 (21)	0·9498 (36)	0·065 (13)	0·114 (21)	0·123 (22)	−0·007 (18)	−0·050 (15)	0·033 (14)
C(3)	0·5730 (8)	0·8513 (16)	0·6507 (34)	0·029 (7)	0·076 (13)	0·146 (22)	−0·026 (16)	0·016 (11)	−0·006 (8)
C(4)	0·2653 (10)	0·7787 (14)	0·2372 (23)	0·053 (10)	0·073 (13)	0·058 (10)	0·004 (9)	−0·004 (9)	0·006 (9)
C(5)	0·4134 (11)	0·8709 (15)	0·2973 (24)	0·066 (12)	0·066 (12)	0·074 (12)	0·009 (10)	0·026 (10)	−0·008 (10)
C(11)	0·4989 (8)	0·6898 (13)	0·4330 (22)	0·028 (7)	0·073 (10)	0·055 (10)	−0·002 (9)	−0·006 (7)	−0·019 (7)
C(12)	0·4826 (7)	0·6688 (9)	0·5913 (16)	0·035 (7)	0·034 (6)	0·041 (7)	−0·004 (5)	−0·015 (6)	−0·002 (5)
C(13)	0·4882 (8)	0·5699 (11)	0·6013 (22)	0·045 (8)	0·041 (7)	0·071 (11)	−0·006 (8)	−0·009 (8)	0·020 (6)
C(14)	0·5082 (9)	0·5322 (14)	0·4654 (19)	0·055 (10)	0·071 (11)	0·048 (10)	−0·012 (8)	−0·021 (8)	0·039 (9)
C(15)	0·5157 (7)	0·6071 (17)	0·3588 (26)	0·018 (6)	0·090 (14)	0·089 (15)	−0·030 (13)	0·002 (7)	0·001 (8)
C(21)	0·2907 (11)	0·5695 (16)	0·3870 (38)	0·056 (12)	0·062 (12)	0·132 (26)	0·001 (14)	−0·051 (15)	−0·025 (10)
C(22)	0·3097 (14)	0·5201 (19)	0·5046 (29)	0·083 (17)	0·089 (18)	0·087 (16)	−0·026 (14)	0·022 (14)	−0·078 (17)
C(23)	0·3589 (13)	0·4554 (11)	0·4550 (48)	0·094 (16)	0·014 (6)	0·208 (35)	0·016 (13)	−0·046 (21)	−0·035 (18)
C(24)	0·3680 (16)	0·4711 (23)	0·3073 (52)	0·103 (20)	0·089 (19)	0·174 (33)	−0·104 (23)	−0·009 (23)	−0·047 (17)
C(25)	0·3246 (17)	0·5399 (22)	0·2638 (22)	0·137 (25)	0·125 (22)	0·030 (10)	0·017 (12)	−0·049 (13)	−0·090 (20)
C(31)	0·4108 (7)	0·8414 (11)	0·7572 (21)	0·032 (6)	0·044 (8)	0·068 (10)	0·007 (8)	−0·002 (7)	0·004 (6)
C(32)	0·4023 (7)	0·9188 (10)	0·6616 (24)	0·025 (6)	0·038 (7)	0·085 (12)	0·011 (8)	−0·001 (7)	−0·014 (6)
C(33)	0·3549 (9)	0·9846 (10)	0·7254 (28)	0·045 (8)	0·030 (7)	0·110 (18)	−0·011 (9)	−0·012 (10)	0·000 (6)
C(34)	0·3352 (10)	0·9461 (14)	0·8666 (21)	0·070 (11)	0·079 (12)	0·063 (11)	−0·057 (10)	−0·043 (9)	0·013 (10)
C(35)	0·3684 (8)	0·8603 (14)	0·8900 (18)	0·042 (7)	0·077 (12)	0·045 (8)	−0·025 (8)	−0·009 (6)	0·004 (8)
C(41)	0·2014 (12)	0·8484 (35)	0·8256 (28)	0·048 (11)	0·238 (49)	0·049 (12)	−0·023 (23)	0·011 (10)	−0·027 (21)
C(42)	0·1842 (7)	0·8887 (16)	0·6900 (36)	0·018 (6)	0·085 (14)	0·151 (24)	−0·028 (17)	0·024 (10)	0·008 (8)
C(43)	0·1884 (10)	0·8292 (22)	0·5726 (36)	0·033 (9)	0·116 (21)	0·122 (20)	−0·010 (19)	0·016 (12)	−0·023 (11)
C(44)	0·2108 (9)	0·7469 (15)	0·6351 (37)	0·030 (9)	0·063 (10)	0·167 (26)	−0·035 (14)	0·010 (12)	−0·020 (8)
C(45)	0·2181 (12)	0·7575 (28)	0·7909 (50)	0·039 (12)	0·163 (30)	0·200 (37)	0·124 (30)	−0·016 (17)	−0·044 (16)

Table 2. *Compound* II ($C_{26}H_{34}Al_4Mo_2$): *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	0·1085 (1)	0·2596 (1)	0·0602 (1)	0·051 (1)	0·044 (1)	0·046 (1)	−0·014 (1)	−0·005 (1)	0·017 (1)
Al(1)	0·1520 (3)	0·5825 (4)	−0·0759 (4)	0·047 (1)	0·052 (1)	0·050 (2)	−0·023 (1)	−0·012 (1)	0·012 (1)
Al(2)	0·2763 (4)	0·6406 (4)	−0·4006 (4)	0·048 (2)	0·055 (2)	0·047 (2)	−0·020 (1)	−0·002 (1)	0·002 (1)
C(1)	0·3387 (17)	0·6830 (19)	−0·0728 (20)	0·070 (8)	0·082 (8)	0·104 (11)	−0·051 (8)	−0·030 (7)	0·003 (6)
C(2)	0·2168 (17)	0·6023 (19)	−0·5614 (21)	0·096 (10)	0·098 (10)	0·062 (7)	−0·041 (7)	−0·028 (7)	0·039 (8)
C(3)	0·4722 (20)	0·7807 (22)	−0·4870 (18)	0·063 (7)	0·076 (8)	0·090 (9)	−0·037 (7)	0·011 (6)	−0·021 (6)
C(11)	−0·0797 (12)	0·2656 (14)	0·2822 (12)	0·048 (5)	0·059 (5)	0·041 (4)	−0·019 (4)	−0·004 (4)	0·009 (4)
C(12)	−0·0739 (15)	0·0977 (14)	0·3037 (14)	0·065 (6)	0·050 (5)	0·048 (5)	−0·007 (4)	0·000 (5)	0·006 (5)
C(13)	0·0779 (19)	0·0515 (16)	0·3102 (14)	0·101 (10)	0·059 (6)	0·042 (5)	0·000 (5)	−0·027 (6)	0·028 (7)
C(14)	0·1665 (17)	0·1815 (24)	0·2899 (14)	0·072 (8)	0·124 (13)	0·040 (5)	−0·021 (6)	−0·029 (5)	0·035 (8)
C(15)	0·0711 (14)	0·3164 (17)	0·2752 (14)	0·064 (6)	0·079 (7)	0·051 (5)	−0·039 (5)	−0·017 (5)	0·015 (5)
C(21)	0·3629 (13)	0·3350 (15)	−0·1225 (16)	0·045 (5)	0·059 (6)	0·080 (7)	−0·028 (6)	−0·006 (5)	0·019 (4)
C(22)	0·2574 (12)	0·4157 (13)	−0·2073 (10)	0·047 (5)	0·060 (5)	0·027 (4)	−0·013 (4)	0·009 (3)	−0·003 (4)
C(23)	0·1640 (17)	0·2870 (16)	−0·1968 (12)	0·086 (8)	0·071 (7)	0·032 (5)	−0·017 (5)	−0·002 (5)	−0·017 (6)
C(24)	0·2045 (19)	0·1334 (17)	−0·1015 (17)	0·092 (9)	0·072 (7)	0·072 (8)	−0·019 (6)	0·013 (7)	0·004 (7)
C(25)	0·3283 (17)	0·1621 (17)	−0·0579 (17)	0·070 (7)	0·061 (7)	0·072 (8)	−0·053 (7)	0·006 (6)	0·029 (6)

was assigned a weight according to the expression $w=(A+|F_o|+BF_o^2)^{-1}$, where A and B were chosen to minimize the variation of mean $w(|F_o|-|F_c|)^2$ with F_o. For compound I, A was 20 and B was 0·011, the final weighted R being 0·083; for compound II the corresponding values were 20, 0·10, and 0·111. The complex neutral atom scattering factors of Cromer (1965) and Cromer & Waber (1965) were used.

Table 3. *Compound* I ($C_{25}H_{35}Al_3Mo_2$): *interatomic distances* (Å) *and bond angles* (°)

Mo(1)—Al(1)	2·650 (5)	Mo(2)—Al(1)	2·657 (4)
Mo(1)—Al(3)	2·951 (4)	Mo(2)—Al(3)	2·996 (5)
Al(1)—C(1)	2·05 (2)	Al(2)—C(2)	2·06 (3)
Al(1)—C(12)	2·29 (2)	Al(2)—C(3)	1·99 (2)
Al(1)—C(31)	2·35 (2)	Al(2)—C(12)	2·06 (2)
Al(3)—C(4)	2·01 (2)	Al(2)—C(31)	2·09 (2)
Al(3)—C(5)	1·99 (2)		
Mo(1)···Mo(2)	4·756 (2)	Al(1)···Al(2)	2·838 (6)
		Al(1)···Al(3)	2·923 (7)
Mo(1)—C(11)	2·27 (1)	Mo(2)—C(31)	2·31 (1)
Mo(1)—C(12)	2·34 (1)	Mo(2)—C(32)	2·27 (1)
Mo(1)—C(13)	2·30 (2)	Mo(2)—C(33)	2·27 (1)
Mo(1)—C(14)	2·28 (1)	Mo(2)—C(34)	2·28 (1)
Mo(1)—C(15)	2·28 (1)	Mo(2)—C(35)	2·33 (1)
Mo(1)—C(21)	2·26 (2)	Mo(2)—C(41)	2·26 (2)
Mo(1)—C(22)	2·24 (2)	Mo(2)—C(42)	2·26 (1)
Mo(1)—C(23)	2·26 (1)	Mo(2)—C(43)	2·35 (2)
Mo(1)—C(24)	2·26 (2)	Mo(2)—C(44)	2·29 (2)
Mo(1)—C(25)	2·30 (2)	Mo(2)—C(45)	2·27 (2)
C(11)—C(12)	1·49 (2)	C(31)—C(32)	1·42 (2)
C(12)—C(13)	1·44 (2)	C(32)—C(33)	1·44 (2)
C(13)—C(14)	1·40 (2)	C(33)—C(34)	1·44 (3)
C(14)—C(15)	1·45 (3)	C(34)—C(35)	1·41 (3)
C(15)—C(11)	1·41 (3)	C(35)—C(31)	1·48 (2)
C(21)—C(22)	1·33 (4)	C(41)—C(42)	1·39 (4)
C(22)—C(23)	1·41 (4)	C(42)—C(43)	1·37 (4)
C(23)—C(24)	1·36 (5)	C(43)—C(44)	1·39 (4)
C(24)—C(25)	1·36 (4)	C(44)—C(45)	1·42 (5)
C(25)—C(21)	1·36 (4)	C(45)—C(41)	1·39 (5)

Results

Atomic coordinates and temperature factors are shown in Tables 1 and 2, and bond lengths and angles, with estimated standard deviations calculated from the full variance–covariance matrix, in Tables 3 and 4. Projections of the molecules are shown in Figs. 1 and 2. Details of important molecular planes are given in Table 5. The observed structure amplitudes and structure factors calculated from the parameters of Tables 1 and 2 are available.*

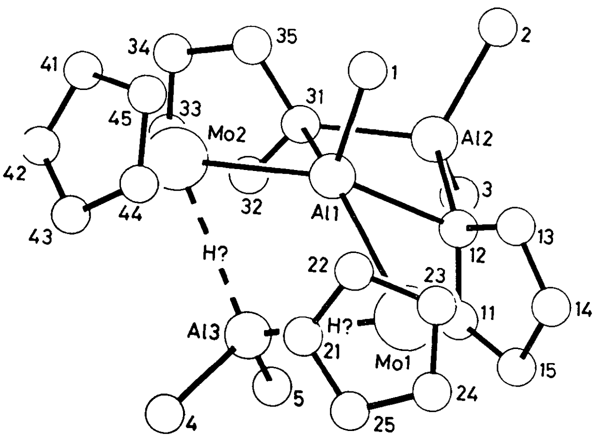

Fig. 1. The $C_{25}H_{35}Al_3Mo_2$ molecule. For clarity, carbon atoms are denoted by their number only.

Table 3 (*cont.*)

Al(1)—Mo(1)-Al(3)	62·7 (1)	Al(1)—Mo(2)-Al(3)	61·9 (1)
Mo(1)-Al(1)—Mo(2)	127·3 (2)	C(2)—Al(2)—C(3)	116·0 (11)
Mo(1)-Al(1)—C(1)	113·9 (6)	C(2)—Al(2)—C(12)	113·1 (9)
Mo(1)-Al(1)—C(12)	56·0 (3)	C(2)—Al(2)—C(31)	112·1 (9)
Mo(1)-Al(1)—C(31)	132·7 (4)	C(3)—Al(2)—C(12)	105·0 (8)
Mo(2)-Al(1)—C(1)	111·6 (6)	C(3)—Al(2)—C(31)	107·4 (8)
Mo(2)-Al(1)—C(12)	132·6 (4)	C(12) -Al(2)—C(31)	102·1 (6)
Mo(2)-Al(1)—C(31)	54·6 (3)	Mo(1)-Al(3)—Mo(2)	106·2 (1)
C(1)—Al(1)—C(12)	104·2 (7)	C(4)—Al(3)—C(5)	106·7 (9)
C(1)—Al(1)—C(31)	103·4 (7)		
C(12) -Al(1)—C(31)	88·1 (5)		
Al(1)—C(12) -Al(2)	81·4 (5)	Al(1)—C(31) -Al(2)	79·3 (5)
Al(1)—C(12) -C(13)	104 (1)	Al(1)—C(31) -C(32)	117 (1)
Al(1)—C(12) -C(11)	117 (1)	Al(1)—C(31) -C(35)	105 (1)
Al(2)—C(12) -C(13)	130 (1)	Al(2)—C(31) -C(32)	118 (1)
Al(2)—C(12) -C(11)	118 (1)	Al(2)—C(31) -C(35)	128 (1)
C(11) -C(12) -C(13)	104 (1)	C(31) -C(32) -C(33)	111 (2)
C(12) -C(13) -C(14)	111 (2)	C(32) -C(33) -C(34)	105 (1)
C(13) -C(14) -C(15)	109 (2)	C(33) -C(34) -C(35)	111 (2)
C(14) -C(15) -C(11)	107 (2)	C(34) -C(35) -C(31)	107 (2)
C(15) -C(11) -C(12)	109 (2)	C(35) -C(31) -C(32)	106 (1)
C(21) -C(22) -C(23)	107 (3)	C(41) -C(42) -C(43)	114 (3)
C(22) -C(23) -C(24)	107 (3)	C(42) -C(43) -C(44)	104 (3)
C(23) -C(24) -C(25)	109 (3)	C(43) -C(44) -C(45)	110 (3)
C(24) -C(25) -C(21)	107 (2)	C(44) -C(45) -C(41)	108 (2)
C(25) -C(21) -C(22)	110 (2)	C(45) -C(41) -C(42)	105 (2)

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No SUP 30479 (35 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

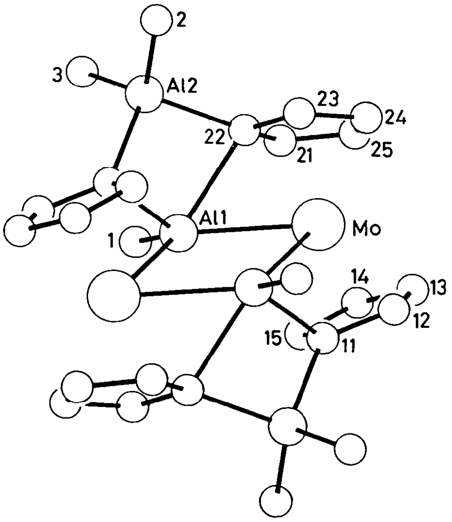

Fig. 2. The $C_{26}H_{34}Al_4Mo_2$ molecule. For clarity, carbon atoms are denoted by their number only.

Table 4. *Compound* II ($C_{26}H_{34}Al_4Mo_2$): *interatomic distances* (Å) *and bond angles* (°)

Mo——Al(1)	2·656 (3)	Mo——Al(1)′	2·685 (3)
Al(1) -C(1)	1·98 (1)	Al(2)——C(2)	1·98 (2)
Al(1) -C(11)′	2·19 (1)	Al(2)——C(3)	1·95 (1)
Al(1) -C(22)	2·35 (1)	Al(2)——C(11)′	2·12 (1)
		Al(2)——C(22)	2·08 (1)
Mo···Mo′	4·551 (1)	Al(1)···Al(2)	2·795 (4)
		Al(1)···Al(1)′	2·796 (6)
Mo——C(11)	2·28 (1)	Mo——C(21)	2·30 (1)
Mo——C(12)	2·28 (1)	Mo——C(22)	2·31 (1)
Mo——C(13)	2·30 (1)	Mo——C(23)	2·29 (1)
Mo——C(14)	2·28 (1)	Mo——C(24)	2·25 (1)
Mo——C(15)	2·28 (1)	Mo——C(25)	2·28 (1)
C(11)–C(12)	1·46 (2)	C(21)——C(22)	1·44 (2)
C(12)–C(13)	1·43 (2)	C(22)——C(23)	1·43 (2)
C(13)–C(14)	1·37 (2)	C(23)——C(24)	1·42 (2)
C(14)–C(15)	1·45 (2)	C(24)——C(25)	1·40 (2)
C(15)–C(11)	1·43 (2)	C(25)——C(21)	1·44 (2)

Table 5. *Some least-squares best planes*

In the equations, x, y and z represent fractional coordinates with respect to the crystallographic axes. The tables give the displacement (Å) of the specified atom from the plane. Atoms in parentheses were not included in the calculation of that particular plane.

Compound I ($C_{25}H_{35}Al_3Mo_2$)

(1) Al_3C_5 skeleton

Equation of plane: $-8{\cdot}331x+11{\cdot}207y+4{\cdot}172z=7{\cdot}522$

Al(1)	−0·013	C(3)	−0·041
Al(2)	0·006	C(4)	−0·016
Al(3)	0·011	C(5)	0·034
C(1)	−0·004	(Mo(1)	−2·371)
C(2)	0·023	(Mo(2)	2·385)

(2) Ring C(11) to C(15)

Equation of plane: $18{\cdot}648x+1{\cdot}485y+2{\cdot}277z=11{\cdot}326$

C(11)	−0·013	C(14)	0·000
C(12)	0·012	C(15)	0·009
C(13)	−0·008	(Mo(1)	−1·939)

Normal to Mo(1) meets plane 0·05 Å from centroid.

(3) Ring C(21) to C(25)

Equation of plane: $14{\cdot}050x+0{\cdot}570y+1{\cdot}719z=10{\cdot}193$

C(21)	0·006	C(24)	0·014
C(22)	0·002	C(25)	−0·012
C(23)	−0·010	(Mo(1)	1·945)

Normal to Mo(1) meets plane 0·05 Å from centroid.

(4) Ring C(31) to C(35)

Equation of plane: $14{\cdot}916x+6{\cdot}739y+3{\cdot}933z=14{\cdot}785$

C(31)	−0·010	C(34)	−0·002
C(32)	0·008	C(35)	0·007
C(33)	−0·004	(Mo(2)	−1·938)

Normal to Mo(2) meets plane 0·07 Å from centroid.

(5) Ring C(41) to C(45)

Equation of plane: $18{\cdot}479x+3{\cdot}913y-1{\cdot}211z=6{\cdot}041$

C(41)	0·000	C(44)	0·008
C(42)	0·005	C(45)	−0·005
C(43)	−0·008	(Mo(2)	1·954)

Normal to Mo(2) meets plane 0·07 Å from centroid.

Table 4 (*cont.*)

Al(1)-Mo-Al(1)′	63·1 (1)	C(15)–C(11)–C(12)	106 (1)
Mo——Al(1)—Mo′	116·9 (1)	C(2)——Al(2)–C(3)	115·4 (8)
Mo——Al(1)—C(1)	117·0 (5)	C(2)—Al(2)–C(11)′	106·0 (6)
Mo——Al(1)—C(11)′	122·7 (3)	C(2)——Al(2)–C(22)	107·6 (6)
Mo——Al(1)—C(22)	54·5 (2)	C(3)—Al(2)–C(11)′	112·0 (6)
Mo′—Al(1)—C(1)	117·9 (5)	C(3)—Al(2)–C(22)	116·3 (7)
Mo′—Al(1)—C(11)′	54·6 (3)	C(11)′-Al(2)–C(22)	97·8 (4)
Mo′—Al(1)—C(22)	131·4 (3)		
C(1)—Al(1)—C(11)′	113·2 (6)		
C(1)—Al(1)—C(22)	104·4 (5)		
C(11)′-Al(1)—C(22)	88·3 (4)	Al(1)—C(22)- Al(2)	77·9 (4)
Al(1)—C(11)′-Al(2)	80·7 (4)	Al(1)—C(22)-C(23)	122·9 (8)
Al(1)—C(11)′-C(12)′	111·5 (8)	Al(1)—C(22)-C(21)	99·7 (7)
Al(1)—C(11)′-C(15)′	115·8 (8)	Al(2)—C(22)-C(23)	115·5 (8)
Al(2)—C(11)′-C(12)′	125·4 (8)	Al(2)—C(22)-C(21)	133·3 (8)
Al(2)—C(11)′-C(15)′	115·4 (8)	C(21)–C(22)–C(23)	105 (1)
C(11)–C(12)–C(13)	108 (1)	C(22)–C(23)–C(24)	110 (1)
C(12)–C(13)–C(14)	109 (1)	C(23)–C(24)-C(25)	108 (1)
C(13)–C(14)–C(15)	109 (1)	C(24)–C(25)-C(21)	108 (1)
C(14)–C(15)–C(11)	108 (1)	C(25)–C(21)-C(22)	109 (1)

Table 5 (*cont.*)

Compound II ($C_{26}H_{34}Al_4Mo_2$)

(1) Al_4C_6 skeleton

Equation of plane: $-4{\cdot}357x+7{\cdot}435y-0{\cdot}228z=-3{\cdot}718$

Al(1)	0·031	Al(1)′	−0·031
Al(2)	−0·067	Al(2)′	0·067
C(1)	0·098	C(1)′	−0·098
C(2)	−0·056	C(2)′	0·056
C(3)	0·141	C(3)′	−0·141
(Mo	2·274)	(Mo′	−2·274)

(2) Ring C(11) to C(15)

Equation of plane: $0{\cdot}077x+1{\cdot}146y+8{\cdot}737z=-2{\cdot}765$

C(11)	0·001	C(14)	0·011
C(12)	0·005	C(15)	−0·008
C(13)	−0·010	(Mo	1·934)

Normal to Mo meets plane 0·03 Å from centroid.

(3) Ring C(21) to C(25)

Equation of plane: $-3{\cdot}459x+3{\cdot}363y+7{\cdot}2232z=1{\cdot}005$

C(21)	0·008	C(24)	−0·013
C(22)	−0·016	C(25)	0·003
C(23)	0·018	(Mo	−1·937)

Normal to Mo meets plane 0·04 Å from centroid.

Discussion

The two molecules represent a new type of metal cluster compound involving Mo–Al bonds. The bis-(π-cyclopentadienyl)molybdenum groups of the original dihydride remain essentially intact; in both molecules, two such groups are bonded, one on either side, to an approximately planar Al–methyl skeleton.

A striking feature of this skeleton, in both cases, is the presence of pairs of Al atoms [Al(1) and Al(2)] arranged in a way reminiscent of the trialkyl- and triarylaluminum dimers, with bridging C atoms provided by the adjacent cyclopentadienyl rings, which are therefore formulated as C_5H_4. Al(2) carries two methyl groups, whilst Al(1) bears only one, but is also bonded to the two Mo atoms. One such pair is present in compound I, while compound II contains two equivalent pairs related by the centre of symmetry. A comparison of the relevant molecular dimensions with those observed by Malone & McDonald (1972) in di-μ-phenyl-bis(dimethylaluminum) is set out in Table 6. There is a general similarity, but a number of significant differences are apparent, most of which can be attributed to the 5-coordinate nature of Al(1). Thus, the angles at the bridging atoms, Cμ, are smaller, and, except for Al(1)–C(11) in compound II, the Al(1)–Cμ bonds are longer. These effects in turn cause the Al(1)···Al(2) distance to increase. The constraint imposed on the bridging C_5H_4 groups by the bonding to the Mo is important, especially in compound II where it leads to the short Al(1)–C(11) bond.

Atoms Al(1) are essentially 5-coordinate, with similar coordination geometries in the two molecules (Table 7); once again, most of the differences are associated with the position of C(11) in compound II. The small Cμ–Al–Mo angle of about 55° is a consequence of the Cμ–Mo bond.

Table 6. *Comparative stereochemistries of carbon-bridged aluminum dimer systems*

Distances are in Å and angles in degrees. C_μ denotes bridging carbon atoms which are part of π-cyclopentadienyl rings in $C_{25}H_{35}Al_3Mo_2$ and $C_{26}H_{34}Al_4Mo_2$, and of phenyl groups in di-μ-phenyl-bis(dimethylaluminum).

	$C_{25}H_{35}Al_3Mo_2$	$C_{26}H_{34}Al_4Mo_2$	$(Me_2AlPh)_2^*$
Al···Al	2·84	2·80	2·69
Al—CH_3(mean)	2·03	1·97	1·98
Al—C_μ	2·06–2·35	2·08–2·35	2·16
Al—C_μ—Al	79–81	78–81	78
CH_3–Al(2)–CH_3	116	115	121
CH_3–Al(2)–C_μ	105–113	106–116	108
C_μ—Al(1)–C_μ	88	88	102
C_μ—Al(2)–C_μ	102	98	102

* Mean values.

Table 7. *Coordination geometry of* Al(1)

The bond angles about Al(1) in the two compounds are given in degrees. C_μ has the same meaning as in Table 6.

	$C_{25}H_{35}Al_3Mo_2$	$C_{26}H_{34}Al_4Mo_2$
Mo –Al(1)–Mo	127	117
CH_3–Al(1)–Mo	112, 114	117, 118
C_μ—Al(1)–Mo	55, 56	54, 55
	133, 133	131, 123
CH_3–Al(1)–C_μ	103, 104	104, 113
C_μ—Al(1)–C_μ	88	88

There is no report of a comparable Mo–Al bond length, but a range of reasonable values may be predicted from covalent radii. The Mo–Mo single bond in $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ is 3·22 Å long (Wilson & Shoemaker, 1957), leading to a radius of Mo in this compound of 1·6 Å. The halving of a homonuclear bond length usually leads to a maximum, rather than a typical, effective radius; various Mo–alkyl bonds lead to values in the region of 1·5 Å. The covalent radius of Al can be put at about 1·2 Å, so it might be expected that the length of a single, covalent Mo–Al bond would be something less than 2·8 Å. The Mo–Al(1) bond lengths in both compounds I and II are therefore seen to be of about the right magnitude.

However, compound I also has a single dimethylaluminum group whose contact distances to the Mo atoms are much longer (2·95–3·00 Å), leading us to postulate the presence of bridging H atoms, as in Fig. 1. Attempts to obtain independent evidence for this formulation from neutron diffraction and spectroscopic techniques have not so far proved successful. M–H–Al bridges have also recently been proposed in $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$ (Corradini & Sirigu, 1967; Tebbe & Guggenberger, 1973) and $[(C_5H_5)_2Zr(H)HAlMe_2]_2$ (Wailes, Weigold & Bell, 1972).

The bis-(π-cyclopentadienyl)molybdenum groupings in these two molecules have significantly different geometries from those observed in many other systems. The Mo–ring perpendicular distances are in the range 1·93–1·95 Å, and the angles between the rings are 144·5 and 143·2° in compound I, and 151·2° in compound II. Typical values in simple Cp_2MX_2 systems are 1·96–1·99 Å and 130–133° (Prout, Allison, Delbaere & Gore, 1972; Green, Green & Prout, 1972). This difference in behaviour, especially the large angle in compound II, could well be a result of the geometrical requirements of σ-bonding to Al, though it should be noted that no such effects are present in $(C_5H_5)_2MoH_2$ (Gerloch & Mason, 1965) or $[(C_5H_5)_2Mo(H)Li]_4$ (Benfield, Forder, Green, Moser & Prout, 1973) where short metal–ring distances and wide angles are also observed.

In simple $(C_5H_5)_2MoX_2$ systems the projection of the metal atom onto the best plane of a cyclopentadienyl ring typically lies within about 0·1 Å of the ring centroid (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). It might have been expected that one of the effects of Al–C_5H_4 σ-bonding would have been to pull the ring away from this idealized position; however, this is not so and these distances are quite normal in both compounds (Table 5).

The variation of C–C bond lengths in the cyclopentadienyl groups does appear to show some definite features. The mean of 1·393 Å in the two C_5H_5 rings of compound I is similar to that observed in many other compounds, but is less than that in the four C_5H_4 groups (1·432 Å). This can probably be accounted for principally by the greater librational motion permitted to the non-σ-bonded ligands. Nevertheless it is noticeable that in each of the C_5H_4 groups, the longest C–C bond is one of those associated with the σ-bonding C atom. There is, however, no systematic or significant variation in the other C–C bonds, so the present data offer no real evidence for any significant loss of π-character from these rings.

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