

#### 44. *The Crystal and Molecular Structure of Dihydridodi- $\pi$ -cyclopentadienylmolybdenum.*

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$(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$  crystallises in a monoclinic cell with  $a = 14.30$ ,  $b = 5.90$ ,  $c = 10.41$  Å,  $\beta = 104^\circ$ ; space group  $Cc$  or  $C2/c$ ,  $Z = 4$ . Least-squares analysis of limited three-dimensional  $X$ -ray data shows the molecules to be wedge-like, the angle between the  $\pi$ -cyclopentadienyl rings being  $34 \pm 1^\circ$ . Evidence for asymmetry in the cyclopentadienyl ligand is presented and compared with that from related structures. The Difference Fourier syntheses are described, and the nine-co-ordinate stereochemistry of the complex discussed in relation to the theoretical model of Ballhausen and Dahl.<sup>1</sup>

RECENT studies of transition-metal hydrides led to the preparation of a number of di- $\pi$ -cyclopentadienyl hydrides of general formula  $(\pi\text{-C}_5\text{H}_5)_2\text{MH}_x$  ( $x = 1, 2$ , or  $3$ ). These molecules were originally suggested to be trigonal bipyramids in which parallel cyclopentadienyl rings occupy axial positions; if the cyclopentadienyl anions are formally considered to be terdentate ligands, the proposed structure would then be similar to that of  $\text{Nd}(\text{H}_2\text{O})_9^{3+}$ . The three hydrogen atoms in the trihydride species  $(\pi\text{-C}_5\text{H}_5)_2\text{TaH}_3$  and  $(\pi\text{-C}_5\text{H}_5)_2\text{WH}_3^+$  are

<sup>1</sup> Ballhausen and Dahl, *Acta Chem. Scand.*, 1961, **15**, 1333.

required to occupy the equivalent equatorial positions but the high-resolution proton magnetic resonance spectra of these complexes indicate only two equivalent hydrogen atoms in an  $A_2B$  grouping. The non-equivalence of the third proton was therefore interpreted as favouring a distorted trigonal bipyramidal structure in which the metal-to-ring axes are non-linear, the structures of the dihydrido- and monohydrido-complexes being described in a similar way.<sup>2</sup> It cannot be determined from dipole moment and infrared studies<sup>3</sup> unequivocally whether the cyclopentadienyl rings are parallel, and the present X-ray analysis was undertaken to ascertain the relative conformation of the  $\pi$ -cyclopentadienyl ligands.

*Crystallographic Data.*—The complex was prepared, in high yields, by the reaction of the anhydrous metal chloride with a solution of sodium cyclopentadienide in tetrahydrofuran containing an excess of sodium borohydride.<sup>4</sup> Pale yellow crystals, of acicular habit, were grown from the reaction mixture by slow sublimation *in vacuo*, selected crystals being sealed, under nitrogen, in a Lindemann glass capillary. Weissenberg and precession data (Mo- $K_\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ ) gave the monoclinic unit-cell dimensions as,  $a = 14.30 \pm 0.04$ ,  $b = 5.90 \pm 0.02$ ,  $c = 10.41 \pm 0.03 \text{ \AA}$ ,  $\beta = 104.0 \pm 0.2^\circ$ ,  $U = 852 \text{ \AA}^3$ . With four molecules per unit cell,  $D_c = 1.78$ , the high reactivity of the complex preventing any accurate determination of the density of the crystals. The systematic absences  $h0l$  for  $l = 2n + 1$ , and  $hkl$  for  $h + k = 2n + 1$  indicate the space group as either  $C2/c$  ( $C_{2h}^6$ ) or  $Cc$  ( $C_s^4$ ). In  $C2/c$ , the molybdenum atom must lie in a special position, *i.e.*, either at a centre of symmetry or on the diad axis. In the first case, reflexions with  $\{k + l\}$  even should be systematically weak, and this is not observed. With the molybdenum at  $0\ y\ \frac{1}{2}$ , the reflexions  $\{00l\}$  should be systematically strong; this condition is observed but does not, of course, preclude a choice of the non-centrosymmetric space group. The structure was thus initially determined on the basis of  $Cc$  so as to avoid any *a priori* assumption of the molecular symmetry but the final refinement suggests that the molecule may possess exact  $C_2$  symmetry.

Relative intensities of the Weissenberg  $\{h0l\}$  and  $\{h1l\}$  data were estimated visually by standard methods; the  $\{hk0\}$  and  $\{0kl\}$  precession data were initially measured by a Joyce-Loebl microdensitometer but, since these data appeared to contain systematic errors, these zones were later re-estimated visually. These 274 intensities have not been corrected for absorption, being derived from a crystal of 0.2 mm. average cross-section.

*Determination and Refinement of Atomic Parameters.*—The Patterson series  $P(UV0)$  gave the  $y$ -co-ordinate of molybdenum as 0.33, the  $x$ - and  $z$ -co-ordinates being arbitrarily chosen as 0 in the space group  $Cc$ . The electron-density synthesis  $\rho(x\ y\ 0)$ , phased by the molybdenum atom, showed peaks consistent with a cyclopentadienyl ring together with a mirror-related series of peaks generated by the symmetry of the heavy-atom phased Fourier series. This false additional symmetry was removed when the contributions of one cyclopentadienyl ring were included in the structure factor calculations, the subsequent Fourier map suggesting two possible positions for the second cyclopentadienyl ring. Of these one allowed the reliability factor  $R(hk0)$  to be reduced from 0.23 to 0.07 in three cycles of least-squares refinement of molybdenum positional and anisotropic thermal parameters and carbon co-ordinates and isotropic Debye factors. Approximate  $z$ -co-ordinates for all atoms were obtained from a model used in combination with the previously determined  $x$ - and  $y$ -parameters, these values giving  $R(h0l) = 0.19$  and  $R(0kl) = 0.17$ , respectively. Final scaling together of the three principal zones was *via* the calculated structure factors, least-squares refinement of the 201 two-dimensional reflexions progressing smoothly from 0.17 to 0.098 in eight cycles. The Difference density synthesis  $D(x\ y\ 0)$  and  $D(x\ 0\ z)$  computed at this stage showed significant peaks near the molybdenum atom in positions where the two hydride atoms might be expected.

It was now clear that the molecule was wedge-like (Fig. 1), having essentially two-fold

<sup>2</sup> Green, McCleverty, Pratt, and Wilkinson, *J.*, 1961, 4854.

<sup>3</sup> Fritz, Hristidu, Hummel, and Schneider, *Z. Naturforsch.*, 1959, 15b, 419.

<sup>4</sup> Green, Pratt, and Wilkinson, *J.*, 1958, 3916.

symmetry. A new refinement was begun, placing the molybdenum at  $0y \frac{1}{4}$ , that is on a diad axis in  $C2/c$ , the least-squares analysis being based, now, on the visually estimated intensities of all 274 reflexions from the  $\{hk0\}$ ,  $\{h0l\}$ ,  $\{0kl\}$ , and  $\{h1l\}$  zones. Successive adjustment of the positional and anisotropic thermal parameters of the crystallographically non-equivalent molybdenum and five carbon atoms slowly reduced the reliability index from 0.098 to 0.087 in five cycles, all hydrogen-atom contributions to the structure factors being included. The final atomic co-ordinates are shown in Table 1, the thermal coefficients,  $b_{ij}$ , in Table 2, and observed and calculated structure factors in Table 3.

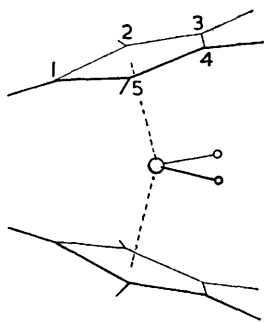


FIG. 1. Molecular configuration and numbering of atoms in  $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ .

Difference density syntheses were calculated at this stage, subtracting the contributions to the structure factors of the molybdenum and cyclopentadienyl carbon and hydrogen atoms.  $D(x\ 0\ z)$  and  $D(x\ y\ 0)$  again show peaks in the hydride atom positions [Figs. 2(a) and (b)], severe overlap preventing a simple interpretation of  $D(0\ y\ z)$ . The peak heights of  $0.3\text{--}0.6\ \text{e}\text{\AA}^{-2}$  are certainly close to the level of significance ( $\sim 2.5\ \sigma$ ) but their appearance in chemically reasonable positions adds some weight to the argument for regarding them as genuine rather than as anomalous "ghost" peaks produced by the molybdenum atom.

TABLE 1.  
Atomic co-ordinates and estimated standard deviations.

Atom	$x/a$	$y/b$	$z/c$	$\sigma(X)$ Å	$\sigma(Y)$ Å	$\sigma(Z)$ Å
Mo(1)	0	0.33188	$\frac{1}{4}$	—	0.0039	—
C(1)	-0.1027	0.0610	0.2712	0.020	0.025	0.029
C(2)	-0.1459	0.1796	0.1634	0.019	0.038	0.037
C(3)	-0.1667	0.4145	0.2027	0.019	0.037	0.032
C(4)	-0.1290	0.4187	0.3423	0.021	0.039	0.027
C(5)	-0.0897	0.1906	0.3849	0.023	0.031	0.026
H(1)	-0.080	-0.113	0.270	} Values not refined (obtained by calculation)		
H(2)	-0.167	0.111	0.058			
H(3)	-0.200	0.548	0.140			
H(4)	-0.131	0.563	0.405			
H(5)	-0.054	0.140	0.485			
H(6)*	-0.033	0.500	0.200			

\* Values obtained from Difference Fourier maps; see text.

TABLE 2.  
Atomic Debye factors.

$$T = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)}$$

Atom	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{13}$	$b_{12}$
Mo(1)	0.00448	0.02685	0.01180	0	0.00407	0
C(1)	0.0046	0.0236	0.0264	0.0181	0.0058	-0.0048
C(2)	0.0031	0.0590	0.0427	-0.0068	0.0094	-0.0149
C(3)	0.0034	0.0791	0.0353	0.0810	0.0040	0.0046
C(4)	0.0063	0.0648	0.0239	-0.0167	0.0176	0.0071
C(5)	0.0086	0.0249	0.0216	0.0133	0.0177	-0.0045

H(1)—H(5) included in the structure-factor calculations with  $b_{ij}$ 's of C(1)—C(5), respectively.

A further Difference synthesis  $D'(x y 0)$  was calculated using coefficients from reflexions with  $\sin \theta \leq 0.5$ , a procedure which minimises Fourier features produced predominantly by any inexact treatment of the thermal vibrations of the heavy atoms. Fig. 2(c) shows only a marginal modification of the peaks assigned to the hydride atoms while all other peaks, especially the large negative feature at (0 0 0), have been greatly diminished. The

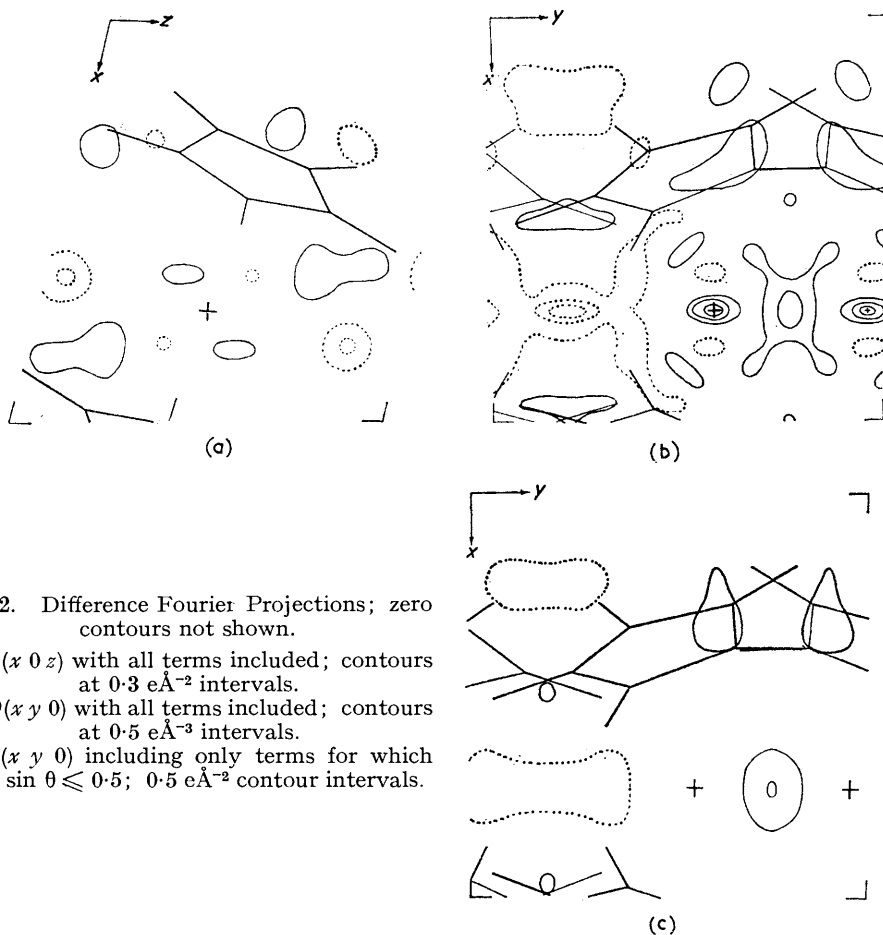


FIG. 2. Difference Fourier Projections; zero contours not shown.

- (a)  $D(x 0 z)$  with all terms included; contours at  $0.3 \text{ e}\text{\AA}^{-2}$  intervals.  
 (b)  $D(x y 0)$  with all terms included; contours at  $0.5 \text{ e}\text{\AA}^{-3}$  intervals.  
 (c)  $D(x y 0)$  including only terms for which  $\sin \theta \leq 0.5$ ;  $0.5 \text{ e}\text{\AA}^{-2}$  contour intervals.

principal reason why the hydrogens have been apparently located may be related to the very small thermal vibrations which these bonded atoms would probably execute; the marked dependence of  $\rho_{\text{obs.}}(\text{hydrogen})$  on temperature factor is well known.<sup>5</sup>

*Discussion.*—The first feature of chemical interest, namely, the mutual orientation of the cyclopentadienyl rings, confirms the suggestions of Green *et al.*,<sup>2</sup> and rules out configurations similar to those of the  $\text{Na}(\text{H}_2\text{O})_9^{3+}$  and  $(\text{TaF}_7)^{2-}$  ions. The cyclopentadienyl rings are essentially planar (r.m.s. deviation,  $0.007 \text{ \AA}$ ), the direction cosines of the normal to the mean plane of the reference ring being  $-0.9486$ ,  $-0.2932$ ,  $0.1190$ , referred to the orthogonal axes  $a$ ,  $b$ , and  $c'$ . The angle between the  $\pi$ -cyclopentadienyl rings of one molecule is, therefore,  $34.1 \pm 1^\circ$  (a typographical error in our earlier Note<sup>6</sup> gave the value as  $25^\circ$ ).

Molecular-orbital calculations on protonated sandwich compounds were reported by Ballhausen and Dahl<sup>1</sup> who showed that the angle of tilt between the rings could not exceed

<sup>5</sup> McDonald, *Acta Cryst.*, 1956, **9**, 162.

<sup>6</sup> Bennett, Gerloch, McCleverty, and Mason, *Proc. Chem. Soc.*, 1962, 357.

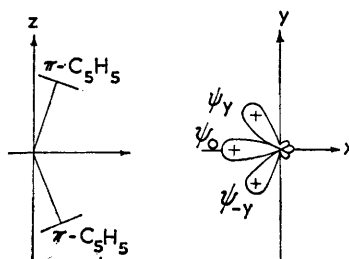
TABLE 3.

Observed and calculated structure factors ( $\times 50$ ).

<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$F_c$
3	1	1	4019	-4207	7	1	11	798	734	0	2	9	1588	1585
5	1	1	5060	-4713	1	1	-11	1144	-1106	0	3	10	981	706
9	1	1	2326	-2589	3	1	-11	1144	-1119	0	3	11	1174	-1159
11	1	1	3083	-2877	5	1	-11	1132	-1461	0	3	12	732	-464
13	1	1	1263	-2347	7	1	-11	1438	-1525	0	2	13	771	649
15	1	1	1349	-1235	9	1	-11	1208	-1153	0	4	1	2128	-2521
17	1	1	854	-988	11	1	-11	761	-732	0	4	2	1703	1851
3	1	-1	938	1572	13	1	-11	798	-816	0	4	3	3623	3639
5	1	-1	2371	2807	0	2	0	2413	-2457	0	4	4	1133	-1119
7	1	-1	6941	6104	0	4	0	2280	-2122	0	4	5	2574	-1189
9	1	-1	4001	3971	0	6	0	1754	1891	0	4	7	1023	651
11	1	-1	2326	2405	0	8	0	1000	-987	0	4	7	1700	1853
13	1	-1	2276	2413	1	1	0	3567	-2769	0	4	8	607	-606
15	1	-1	1530	1603	1	3	0	4068	3735	0	4	9	1676	-1294
17	1	-1	888	948	1	5	0	1027	-932	0	4	10	755	497
19	1	-1	963	981	1	7	0	943	-855	0	4	11	919	911
2	1	2	2887	3174	2	2	0	3274	-3395	0	6	1	763	-399
3	1	2	2359	2510	2	4	0	1292	-1626	0	6	2	1503	-1621
5	1	2	2946	2934	2	6	0	1848	2049	0	6	4	1495	1350
7	1	2	2060	2225	2	8	0	695	-644	0	6	6	1591	-1335
9	1	2	1597	1618	3	1	0	2138	-1777	0	6	7	588	86
11	1	2	1174	1357	3	3	0	5099	5265	0	6	8	969	1175
13	1	2	538	714	3	5	0	2104	-1945	0	8	1	627	721
1	1	-2	2339	2750	3	7	0	695	-543	0	8	2	723	722
3	1	-2	1914	2094	4	0	0	646	-192	0	8	3	801	-642
7	1	-2	3450	3407	4	2	0	3364	-3304	2	0	2	7650	-7493
11	1	-2	1010	1146	4	4	0	1254	-1266	4	0	2	5957	-5818
13	1	-2	2164	2274	4	6	0	2041	2007	6	0	-2	6889	-7237
15	1	-2	1144	1062	4	8	0	277	-180	8	0	-2	7025	-7183
1	1	4	1082	-1627	5	1	0	5347	-4601	4	0	-4	5021	5793
3	1	4	2460	-2500	5	3	0	4592	4607	2	0	-4	5741	6165
5	1	4	2419	-2594	5	5	0	1569	-1545	6	0	2	5073	-4538
7	1	4	1108	-1435	3	7	0	1544	-543	8	0	2	2784	-2916
9	1	4	888	-1146	6	0	0	5844	5921	10	0	2	3585	-3460
11	1	4	1144	-1158	6	2	0	2535	-2319	12	0	2	3215	-3170
1	1	-4	1988	2278	6	4	0	1719	-1687	14	0	2	1310	-1383
3	1	-4	2450	2745	6	6	0	1621	1638	16	0	2	1049	-1098
5	1	-4	3020	3367	7	1	0	3854	-3439	18	0	2	1223	-1328
7	1	-4	2411	2479	7	3	0	3215	3352	18	0	2	0	-397
11	1	-4	1269	-1454	7	5	0	1059	-1009	4	0	-2	3188	-3208
13	1	-4	2096	-2480	7	7	0	393	-378	10	0	-2	2685	-2594
15	1	-4	590	-818	8	0	0	5637	5340	12	0	-2	2284	-2417
1	1	5	2419	-2719	8	2	0	1624	-1692	16	0	-2	1514	-1485
3	1	5	3955	-3690	8	4	0	1318	-1352	18	0	-2	1164	-1256
5	1	5	3575	-3313	8	6	0	1482	1348	20	0	-2	1139	-1196
7	1	5	1816	-2088	9	1	0	1305	-1164	2	0	4	4785	4841
9	1	5	2025	-2204	9	3	0	3219	3153	6	0	4	3256	3506
11	1	5	1889	-1910	9	5	0	1231	-1206	8	0	4	2085	2206
13	1	5	761	-992	9	7	0	671	-621	10	0	4	2659	3120
15	1	5	664	-792	10	0	0	3241	3418	12	0	4	2068	2312
1	1	-5	3715	3954	10	2	0	1363	-1270	16	0	4	1049	999
3	1	-5	5502	5391	10	4	0	960	-816	20	0	4	998	517
5	1	-5	3728	4124	10	6	0	1651	1132	4	0	-4	5804	5495
7	1	-5	2622	2849	11	1	0	1048	-1144	6	0	-4	6139	5433
9	1	-5	2757	2700	11	3	0	2469	2653	8	0	-4	4999	4559
11	1	-5	2326	2446	11	5	0	1148	-866	10	0	-4	3139	2929
13	1	-5	2025	2037	12	0	0	3270	3309	12	0	-4	2944	2624
15	1	-5	1597	1727	12	2	0	1579	-1490	14	0	-4	2153	2235
17	1	-5	1428	1424	12	4	0	877	-713	16	0	-4	1688	1691
1	1	7	2704	2691	12	6	0	1363	1113	18	0	-4	1432	1545
3	1	7	3010	2607	13	1	0	1204	-1214	20	0	-4	1071	1102
5	1	7	1756	1905	13	3	0	1566	1538	2	0	8	3253	2802
7	1	7	1323	1481	13	5	0	584	-357	4	0	8	2390	2327
11	1	7	1038	1218	14	0	0	2051	2141	6	0	8	1424	1551
13	1	7	798	798	14	2	0	1530	-1430	8	0	8	1353	1324
1	1	-7	3010	-3142	14	4	0	1059	-995	10	0	8	1251	1350
3	1	-7	3244	-3399	15	1	0	1589	1273	12	0	8	784	972
5	1	-7	2371	-2364	15	3	0	770	-554	14	0	8	827	716
7	1	-7	1874	-1961	15	5	0	1558	1167	2	0	-8	3320	3056
9	1	-7	2326	-2699	16	0	0	1084	-619	4	0	-8	2654	2350
11	1	-7	2509	-2631	16	2	0	1318	-1016	6	0	-8	1982	2045
13	1	-7	1597	-1681	17	1	0	1460	1389	8	0	-8	3139	2729
15	1	-7	854	-1104	17	3	0	1256	-1214	10	0	-8	3125	3142
17	1	-7	1144	-1105	18	0	0	1445	1256	12	0	-8	1875	1921
3	1	8	938	-922	18	2	0	756	-294	14	0	-8	1114	1032
5	1	8	1292	-1282	19	1	0	770	-384	16	0	-8	1114	1119
7	1	8	706	-912	0	0	2	12229	-11970	18	0	-8	1154	1176
11	1	8	664	-445	0	0	4	4274	4597	20	0	-8	827	854
1	1	-8	1756	-1550	0	0	6	4243	-3693	2	0	10	2017	-1740
3	1	-8	2040	-195	0	0	8	3010	2977	4	0	10	1353	-1466
5	1	-8	1038	-1210	0	0	10	1828	-1788	6	0	10	1045	-1133
7	1	-8	1144	-1053	0	0	12	1546	1065	8	0	10	1103	-951
9	1	-8	1144	-1275	0	0	14	723	-633	2	0	-10	1664	-1658
15	1	-8	888	-767	0	2	1	3602	4596	4	0	-10	1472	-1599
1	1	-10	1108	1091	0	2	2	1371	1431	6	0	-10	2112	-2050
3	1	-10	1082	1139	0	2	3	4993	-5044	8	0	-10	2230	-2416
5	1	-10	761	715	0	2	4	1029	-1038	10	0	-10	1545	-1700
9	1	-10	1010	931	0	2	5	3158	3476	12	0	-10	706	-833
1	1	11	1082	1122	0	2	6	2248	1582	14	0	-10	1103	-950
3	1	11	963	1019	0	2	7	1926	-2001	16	0	-10	1154	-1121
5	1	11	798	855	0	2	8	1286	-1319	18	0	-10	1032	-1006

45°; within this limit, overlap between the ring molecular orbitals and metal hybrid orbitals was not reduced a great deal from the parallel ring model. With these angular bonds it followed, without recourse to *f*-orbitals, that, in addition to the six metal-bonding orbitals, there remained three strongly space-directed orbitals on the metal, orientated in the plane bisecting the angle between the  $\pi$ -cyclopentadienyl rings (Fig. 3). Two orbitals,  $\psi_y$  and  $\psi_{-y}$ , are equivalent ( $sp^2d_{x^2-y^2}$ ,  $d_{z^2}$  hybrids) and different from the third  $\psi_0$  (an  $sp$ -hybrid); together with the six bonding orbitals directed at the rings these make up a new form of nine-co-ordination (see also ref. 7). In the dihydride species, the non-bonding pairs of electrons occupy  $\psi_0$ , a configuration which is more stable than that of the  $(\text{TaF}_7)^{2-}$  ion. It is, however, difficult to understand why the trihydrides as well as the dihydrides have

FIG. 3. The disposition of the cyclopentadienyl rings and available metal orbitals (after Ballhausen and Dahl, 1961).



this asymmetric geometry; it may be that the  $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$  ion finds the Ballhausen–Dahl geometry unfavourable because of the greater steric effects between the  $\text{H}_2\text{O}$  ligands compared with those between the hydride atoms and thus adopts what might otherwise be the more unstable, symmetrical structure.

TABLE 4.

(a) Bond lengths and estimated standard deviations (e.s.d.).

Bond	Length (Å)	e.s.d. (Å)	Bond	Length (Å)	e.s.d. (Å)
Mo–C(1) .....	2.22	0.021	C(1)–C(2) .....	1.34	0.041
Mo–C(2) .....	2.25	0.022	C(2)–C(3) .....	1.51	0.052
Mo–C(3) .....	2.37	0.022	C(3)–C(4) .....	1.42	0.042
Mo–C(4) .....	2.34	0.023	C(4)–C(5) .....	1.49	0.050
Mo–C(5) .....	2.28	0.024	C(5)–C(1) .....	1.39	0.037

(b) Bond angles and estimated standard deviations (e.s.d.).

Bonds	Angle	e.s.d.	Bonds	Angle	e.s.d.
C(1)–Mo–C(2) .....	34.8°	1.1°	C(5)–C(1)–C(2) ...	111.9°	2.7°
C(2)–Mo–C(3) .....	38.1	1.3	C(1)–C(2)–C(3) ...	109.3	2.5
C(3)–Mo–C(4) .....	35.1	1.1	C(2)–C(3)–C(4) ...	104.3	2.7
C(4)–Mo–C(5) .....	37.8	1.2	C(3)–C(4)–C(5) ...	108.1	2.5
C(5)–Mo–C(1) .....	35.9	1.0	C(4)–C(5)–C(1) ...	106.4	2.5

The nature of the molybdenum–cyclopentadienyl bonding can be understood, now, in greater detail in the light of the results of the present analysis. Bond lengths and angles, together with their e.s.d.'s are in Table 4 and some are shown in Fig. 4. The lack of five-fold symmetry in the cyclopentadienyl ring, demonstrated by the carbon–carbon bond lengths, follows a pattern of distortion reported first in 2,3-bis(methoxycarbonyl)norborna-2 $\pi$ ,5-dien-7-yl- $\pi$ -cyclopentadienylnickel<sup>8</sup> and, subsequently, in tricarbonylcyclopentadienylethylmolybdenum,<sup>7</sup>  $\pi$ -cyclopentadienylhexakis(trifluoromethyl)benzenerhodium,<sup>9</sup> and  $\pi$ -cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonecobalt.<sup>10</sup> The localization of electron density in the cyclopentadienyl ring can again be interpreted qualitatively within the framework of molecular-orbital theory. Any removal of the degeneracy of the metal “*d*”-orbitals resulting from the lack of cylindrical symmetry around the metal ion can

<sup>7</sup> Bennett and Mason, *Proc. Chem. Soc.*, 1963, 273.

<sup>8</sup> Dahl and Wei, *Inorg. Chem.*, 1963, 2, 713.

<sup>9</sup> Churchill and Mason, *Proc. Chem. Soc.*, 1963, 365.

<sup>10</sup> Gerloch and Mason, *Proc. Roy. Soc.*, 1964, A, 279, 170.

stabilize some of the cyclopentadienyl molecular orbitals. Elsewhere<sup>11</sup> we have discussed a metal-cyclopentadienyl bonding scheme for this and all the above compounds in such terms, describing the ring formally as in Fig. 5, in which the cyclopentadienyl  $e_1^-$  and  $e_1^+$  molecular orbitals donate unequally to the metal  $d_{xz}$ - and  $d_{yz}$ -orbitals with a concomitant loss of five-fold symmetry in the ligand. While the differences between the carbon-carbon bond lengths in the present complex are on the borderline of statistical significance ( $\sim 3\sigma$ ) the overall pattern of distortions and the large angle C(2)-C(1)-C(5) suggest the value of this description. The differences between the molybdenum-carbon bond lengths are certainly significant ( $5-6\sigma$ ), having the regular pattern around the ring shown in Fig. 4,

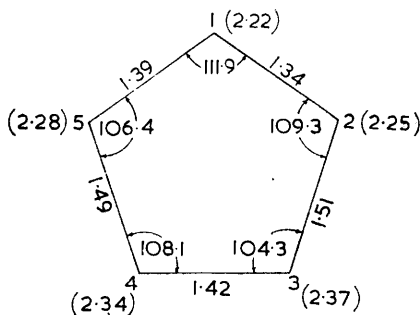


FIG. 4.  $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ . Dimensions in the cyclopentadienyl ring; molybdenum carbon bond lengths in parentheses.

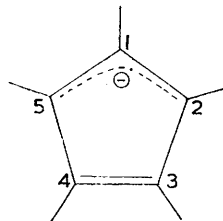


FIG. 5. Electron localization in the cyclopentadienyl ligand.

and are again consistent with the observation that the "allyl" group of the cyclopentadienyl ring is *trans* to the relatively strong field ligands on the opposite side of the molecule in all the above complexes.

The nature of the metal-hydrogen bonding in transition-metal hydrides has been discussed by a number of authors. Several<sup>12,13</sup> assumed that the characteristic high-field lines in the high resolution n.m.r. spectrum of these complexes can be explained by a model involving the embedding of the hydride atoms in the electron density of the metal ion. Bishop *et al.*<sup>13</sup> studied the wide-line n.m.r. spectrum of  $\text{H}_2\text{Fe}(\text{CO})_4$  and found a proton-proton distance of  $1.88 \pm 0.05$  Å from which a most probable Fe-H distance of 1.1 Å can be calculated assuming a value of  $110^\circ$  for the H-Fe-H bond angle. Stevens, Kern, and Lipscomb<sup>14</sup> considered that this simple view of an embedded proton involves a "drastic assumption" and attempt an explanation of the anomalous magnetic resonance shift, without invoking a particularly short metal-hydrogen bond, by suggesting that, when the large diffuse  $4s$ - and  $4p$ -levels of, say, CO are occupied by donation from such ligands as carbon monoxide, the proton can be sufficiently shielded so as to achieve the observed shift to high field, even when the M-H distance is a normal covalent bond length of 1.4–1.6 Å. Some support for these calculations has been provided by the recent report of a Rh-H distance of 1.7 Å.<sup>15</sup> The present Mo-H distance, estimated from the Difference syntheses, is 1.2 Å. The agreement of this value with the n.m.r. data on  $\text{H}_2\text{Fe}(\text{CO})_4$  must be nothing more than fortuitous, both from the standpoint of the large error in the present result (e.s.d.  $\sim 0.3$  Å) and because there is no *a priori* justification for believing that the proton will coincide with the centroid of the electron density of the bonded hydrogen atom. A complete three-dimensional analysis would, of course, have improved the estimated standard deviations of the observed bond lengths but we think

<sup>11</sup> Bennett, Churchill, Gerloch, and Mason, *Nature*, 1964, **201**, 1318.

<sup>12</sup> Cotton, *J. Amer. Chem. Soc.*, 1958, **80**, 4425.

<sup>13</sup> Bishop, Down, Emtage, Richards, and Wilkinson, *J.*, 1959, 2484.

<sup>14</sup> Stevens, Kern, and Lipscomb, *J. Chem. Phys.*, 1962, **37**, 279.

<sup>15</sup> Ibers and La Placa, *J. Amer. Chem. Soc.*, 1963, **85**, 3501.

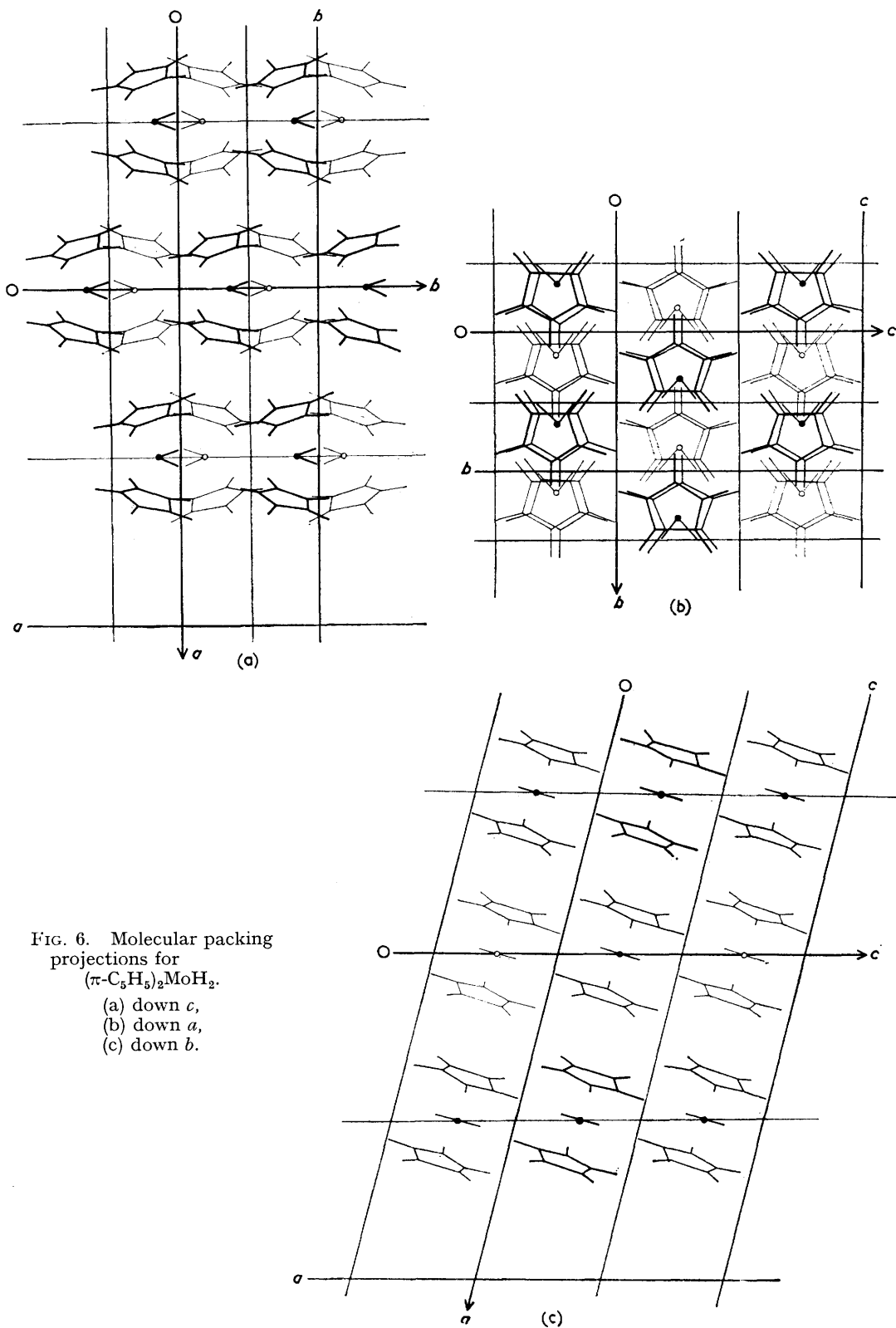


FIG. 6. Molecular packing projections for  $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ .  
 (a) down  $c$ ,  
 (b) down  $a$ ,  
 (c) down  $b$ .



that the problem is more amenable to an accurate neutron-diffraction analysis, and this is now being carried out.<sup>16</sup>

The packing of the molecules in the crystal is illustrated by the three principal crystal projections (Fig. 6). The wedge-like shape of the molecule allows a dove-tailing together

TABLE 5.  
Inter-ring H-H contacts less than 3.0 Å.

	Contact	Å		Contact	Å
1	H(1)-H(1')	2.42	6	H(2)-H(3) ( $-\frac{1}{2} - x, \frac{1}{2} - y, -z$ )	2.62
2	-H(3) ( $x, -1 + y, z$ )	2.77	7	-H(4) ( $x, 1 - y, -\frac{1}{2} + z$ )	2.63
3	-H(4) ( $x, -1 + y, z$ )	2.58	8	-H(5) ( $x, -y, -\frac{1}{2} + z$ )	2.45
4	-H(5) ( $-x, -y, 1 - z$ )	2.80	9	H(3)-H(4) ( $x, 1 - y, -\frac{1}{2} + z$ )	2.93
5	H(2)-H(2) ( $-\frac{1}{2} - x, \frac{1}{2} - y, -z$ )	2.90	10	H(5)-H(5) ( $-x, -y, 1 - z$ )	2.23

The primed symbol refers to the second cyclopentadienyl ring in the reference molecules, related to the first by the diad at  $z = \frac{1}{2}$ .

in the lattice thus forming close packed chains parallel to  $b$ . These chains are quite well separated [Figs. 6(b) and (c)] (cf. the relatively few short intermolecular contacts of Table 5), the high volatility of the crystals presumably resulting from this mode of packing.

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<sup>16</sup> Brown, 1963, personal communication.