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The Crystal and Molecular Structure of the Novel Molybdenum–Phosphine Complex $(\eta\text{-}C_5H_5)_2MoP_2H_2$

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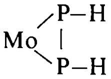
The structure of $(\eta\text{-}C_5H_5)_2MoP_2H_2$ has been determined by X-ray methods [monoclinic, $a = 13{\cdot}209$ (4), $b = 7{\cdot}644$ (2), $c = 11{\cdot}708$ (3) Å, $\beta = 113{\cdot}58$ (2)°, $Z = 4$, space group *Cc*, Mo $K\alpha$ radiation, 1837 reflexions] and refined by full-matrix least squares ($R = 0{\cdot}035$). The presence of the



chelate system has been confirmed (Mo—P 2·54, P—P 2·14 Å, P—Mo—P 49·9, P—P—Mo 65·1°).

Introduction

Bis-η-cyclopentadienylmolybdenum hydride reacts smoothly with excess white phosphorus in toluene at 90°C to give a solution from which, after purification, deep red crystals may be isolated. Analysis, the mass spectrum, and ^1H and ^{31}P NMR spectra are all consistent with the formulation $(\eta\text{-}C_5H_5)_2MoP_2H_2$. Spectroscopic methods do not distinguish between the planar *trans*, the non-planar and the fluxional *cis* or *trans* configurations of the MoP_2H_2 system, although the second was preferred by analogy with related systems (Green, Green & Morris, 1974). Unlike in most phosphines reported, each P in $(\eta\text{-}C_5H_5)_2MoP_2H_2$ behaves as a one-electron ligand.

The structure has been determined by X-ray methods to try to resolve this configurational problem and to derive the dimensions of this novel system.

Experimental

Crystal data

$C_{10}H_{12}MoP_2$, $M_r = 290{\cdot}1$, monoclinic, $a = 13{\cdot}209$ (4), $b = 7{\cdot}644$ (2), $c = 11{\cdot}708$ (3) Å, $\beta = 113{\cdot}58$ (2)°, $V = 1083$ Å^3, D_c (for $Z = 4$) = 1·80 g cm^{-3}. Systematic extinctions hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$ ($h = 2n + 1$); ($0k0$, $k = 2n + 1$), indicated space groups *Cc* or *C*2/*c*. Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 14{\cdot}3$ cm^{-1}, crystal size 0·3 × 0·4 × 0·4 mm.

The lattice parameters were determined with a Philips PW1100 single-crystal automatic diffractometer and refined by least-squares best fit for 25 reflexions. The intensities were collected with Mo $K\alpha$ radiation monochromatized by a flat graphite crystal. A unique set was collected (θ range 2–30°) in the ω–2θ scan mode, with a symmetrical scan range of 1·8° in 2θ from the calculated scattering angles. The scan rate was 0·5 s^{-1}. The data were processed by the Davies & Gatehouse (1974) method. The intensities were not corrected for absorption. Of the 1892 independent reflexions inspected, 55 with $I < \sigma(I)$ were assumed to be unobserved.

An unsharpened Patterson function suggested a centrosymmetric arrangement of Mo atoms on twofold axes. The subsequent Mo-phased F_o synthesis indicated P and C sites for a trial structure in *C*2/*c*. Refinement of the trial (full-matrix least squares with isotropic then with anisotropic temperature factors) to convergence at R 0·048 gave a structure with unsatisfactory dimensions for the $\eta\text{-}C_5H_5$ group. Examination of the Mo- and P-phased difference synthesis showed that the electron density of the $\eta\text{-}C_5H_5$ group was broad and diffuse. To take this into account two further trial structures were set up. One was in *Cc* with the twofold axis removed by small rotations of the C_5 rings about their centroids. The other was a disordered model in *C*2/*c* based on the same displacements of the C_5 rings. All three models were refined by full-matrix least squares with unit weights and anisotropic temperature factors. However, in each case the C_5 ring(s) were constrained to chemically reasonable dimensions by the method of Waser (1963) implemented by Rollett & Carruthers (1975) to avoid ill-conditioned normal matrices. The following constraints were applied: (*a*) C—C 1·40 ± 0·01 Å, (*b*) C—C—C 108 ± 1°, (*c*) C—Mo 2·30 ± 0·01 Å, (*d*) the C_5 ring to be planar with an e.s.d. 0·01 Å, (*e*) the difference in r.m.s. amplitude of vibration in the direction of the C—C bond of two bonded C atoms in the C_5 ring to be 0·000 ± 0·006 $Å^2$. The ordered model in *C*2/*c* reached convergence at R 0·048, the disordered model in *C*2/*c* at 0·042 and the ordered model in *Cc* at 0·0383. An F test indicated the non-centrosymmetric solution was the most probable of the trials. The refinement of this continued with the weighting scheme $w = 1/\Sigma^{n}_{r=1} A_r T^*_r(X)$ with n coefficients, A_r, for the Chebyshev polynomial $T^*_r(X)$ where X is $F_o/F_o(\max)$ (Rollett, 1965) ($n = 3$ and $A_r =$ 1869, 2590 and 781) and a Larson (1970) secondary extinction correction with parameter 25. Convergence was reached at R 0·035 and R_w 0·043 after the removal of constraint (*c*). An unconstrained refinement in *Cc* converged at R 0·033 and R_w 0·0402, but the spread of bond lengths and angles in the C_5 rings was unacceptable (C—C 1·15–1·44 Å; C—C—C 105·1–113·0°). At no stage in any of the refinements could H atoms be unambiguously identified in the region of the P atoms. A difference map in the plane of the C_5 ring calculated for the *Cc* model at R 0·038 indicated H atom sites but when these were included in the refinement there was no improvement in R.

The non-centrosymmetric model is not inconsistent with the $N(Z)$ test (Rogers, Howells & Phillips, 1950) nor with the properties of the normalized structure factors (Karle & Hauptman, 1953).

The initial refinement of the unconstrained *C*2/*c* model was carried out in Pavia on the Honeywell computer at the Centro di calcolo dell'Università di

Table 2. *Interatomic distances* (Å) *and interbond angles* (°)

Standard deviations are in parentheses.

Mo—C(1)	2·280 (8)	*C(1)—C(2)	1·384
Mo—C(2)	2·290 (7)	C(2)—C(3)	1·382
Mo—C(3)	2·282 (8)	C(3)—C(4)	1·396
Mo—C(4)	2·301 (8)	C(4)—C(5)	1·380
Mo—C(5)	2·290 (7)	C(5)—C(1)	1·399
Mo—C(6)	2·296 (9)	C(6)—C(7)	1·394
Mo—C(7)	2·290 (9)	C(7)—C(8)	1·380
Mo—C(8)	2·268 (8)	C(8)—C(9)	1·396
Mo—C(9)	2·289 (8)	C(9)—C(10)	1·382
Mo—C(10)	2·306 (8)	C(10)—C(6)	1·384
*C(1)—C(2)—C(3)	107·5	*C(6)—C(7)—C(8)	107·5
C(2)—C(3)—C(4)	108·9	C(7)—C(8)—C(9)	108·0
C(3)—C(4)—C(5)	107·3	C(8)—C(9)—C(10)	108·3
C(4)—C(5)—C(1)	108·2	C(9)—C(10)—C(6)	107·5
C(5)—C(1)—C(2)	108·1	C(10)—C(6)—C(7)	108·6
Mo—P(1)	2·550 (4)	P(1)—Mo—P(2)	49·91 (7)
Mo—P(2)	2·536 (5)	Mo—P(1)—P(2)	64·7 (2)
P(1)—(2)	2·146 (3)	Mo—P(2)—P(1)	65·4 (2)

* C—C distances were constrained to be 1·40 Å with an e.s.d. of 0·01 Å and C—C—C angles to be 108° with an e.s.d. of 1°.

Table 1. *Fractional atomic coordinates and anisotropic temperature factors*

	x	y	z		x	y	z
Mo	0·0000	0·02376 (4)	0·2500	C(5)	−0·1868 (7)	−0·002 (2)	0·140 (1)
P(1)	0·0391 (5)	0·3272 (5)	0·3486 (4)	C(6)	0·1827 (8)	0·076 (1)	0·293 (2)
P(2)	0·0250 (8)	0·3230 (7)	0·1488 (5)	C(7)	0·133 (1)	0·012 (3)	0·172 (1)
C(1)	0·1679 (7)	0·062 (1)	0·259 (1)	C(8)	0·0981 (7)	−0·156 (3)	0·178 (2)
C(2)	0·1127 (6)	−0·065 (1)	0·3450 (7)	C(9)	0·1276 (9)	−0·197 (1)	0·304 (2)
C(3)	0·0965 (7)	−0·206 (1)	0·280 (1)	C(10)	0·1794 (7)	−0·053 (2)	0·3741 (8)
C(4)	0·1430 (9)	−0·168 (2)	0·153 (1)				

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	0·0287 (1)	0·0310 (2)	0·0330 (2)	−0·0003 (4)	0·0112 (1)	0·0048 (3)
P(1)	0·128 (3)	0·032 (1)	0·062 (2)	−0·010 (1)	0·014 (2)	−0·008 (1)
P(2)	0·271 (9)	0·046 (2)	0·072 (3)	0·018 (2)	0·022 (4)	−0·012 (3)
C(1)	0·060 (6)	0·14 (1)	0·103 (8)	0·027 (7)	0·046 (6)	0·059 (6)
C(2)	0·048 (3)	0·083 (5)	0·051 (3)	0·003 (3)	0·031 (3)	−0·010 (3)
C(3)	0·067 (6)	0·051 (4)	0·118 (8)	−0·006 (4)	0·048 (6)	−0·023 (3)
C(4)	0·064 (6)	0·14 (1)	0·089 (6)	−0·046 (7)	0·036 (5)	−0·056 (7)
C(5)	0·036 (4)	0·17 (1)	0·062 (5)	0·025 (6)	−0·008 (4)	−0·005 (6)
C(6)	0·054 (5)	0·110 (9)	0·16 (1)	0·025 (8)	0·050 (8)	−0·017 (6)
C(7)	0·11 (1)	0·21 (2)	0·11 (1)	0·05 (1)	0·09 (1)	0·07 (1)
C(8)	0·057 (6)	0·18 (2)	0·12 (1)	−0·08 (1)	0·022 (7)	0·031 (9)
C(9)	0·069 (7)	0·052 (4)	0·19 (1)	0·016 (6)	0·060 (9)	0·028 (4)
C(10)	0·047 (5)	0·107 (7)	0·060 (5)	0·016 (4)	0·017 (4)	0·038 (5)

Pavia with local programs. All subsequent calculations were performed in Oxford on the OUCL ICL 1906A computer with the Oxford *CRYSTALS* package (Carruthers, 1976).*

The final atomic parameters are in Table 1. Table 2 gives the interatomic distances and interbond angles with standard deviations calculated from the full variance–covariance matrix.

Discussion

The crystals are made up from isolated molecules of composition (η-C_5H_5)$_2$MoP_2 (Fig. 1). There is no direct evidence from electron density maps to show any H attached to P atoms, although their presence must be inferred from the spectroscopic data.

The normals to the mean planes of the η-C_5H_5 rings at the Mo atom are both 1·961 Å long and are inclined at an angle of 137°. The line of intersection of the P–Mo–P plane and the ring normal plane does not bisect this angle, but makes angles of 72·1 and 64·9° to rings C(6) to C(10) and C(1) to C(5) respectively. The skewness of the molecule can be seen in Fig. 2 in which the molecule is shown projected on the P–Mo–P plane. This deformation is presumed to be related to an intramolecular interaction between H atoms attached to P atoms and one cyclopentadienyl ring. The rings are roughly eclipsed.

The MoP_2 plane is inclined at an angle of 92·3° to the plane of the normals to the cyclopentadienyl rings. The P_2H_2 group forms a three-membered chelate ring at the Mo with a very acute P–Mo–P angle of 49·9°.

The Mo–P bonds, 2·550 and 2·526 Å, are longer than Mo–Cl (2·47 Å, Prout, Cameron, Forder, Critchley, Denton & Rees, 1974) and Mo–S [2·50 Å (mean), Prout, Critchley & Rees, 1974], and this is consistent with the greater covalent radius of P. The P–P bond, 2·146 Å, is somewhat shorter than in black, 2·18, or white, 2·21 Å, phosphorus and in various phosphines, *e.g.* P_2I_4 2·212 (Leung & Waser, 1956); $(C_6H_5P)_5$ 2·217 (Daly, 1964); $(C_6H_5P)_4S$ 2·190 (mean) (Calhoun & Trotter, 1974); $(CF_3P)_4$ 2·21 Å (Palenik &

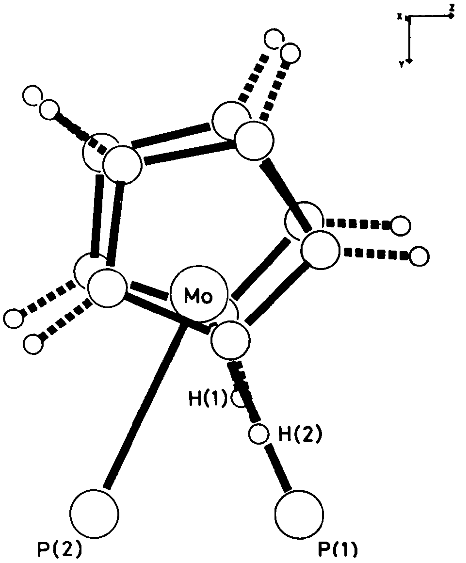


Fig. 2. The (η-C_5H_5)$_2$MoP_2H_2 molecule seen projected onto the P–Mo–P plane.

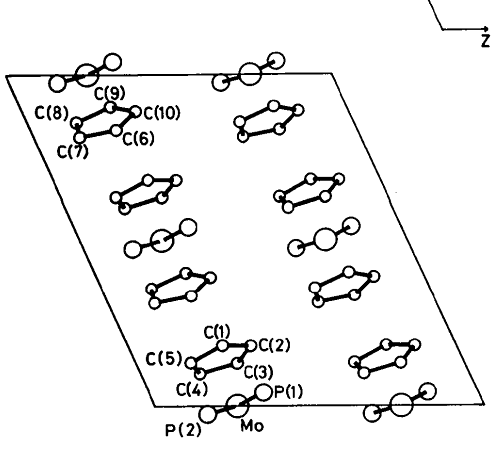


Fig. 1. The crystal structure of (η-C_5H_5)$_2$MoP_2H_2 seen in projection down **b**.

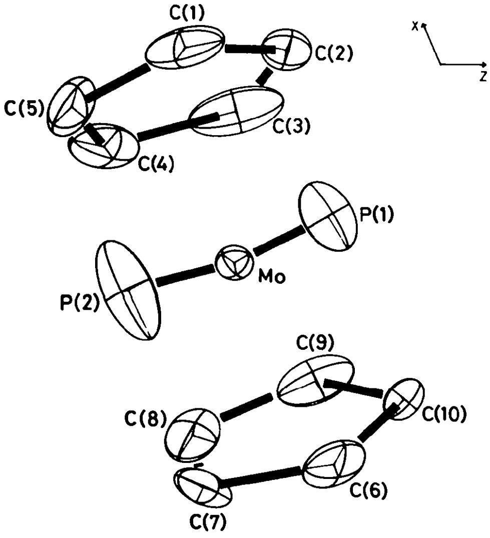


Fig. 3. Thermal ellipsoids of the (η-C_5H_5)$_2$MoP_2H_2 molecule seen in projection down **b**.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32530 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Donohue, 1962), but is substantially longer than in P_2, 1·89 Å (Douglas & Rao, 1958). The P—P linkage appears therefore to be essentially a single bond. In this case the MoP_2H_2 group would be expected to be non-coplanar like the phosphines above and to have angles at P markedly less than the tetrahedral value. Of the possible non-coplanar forms of the phosphine ligand, the *cis* form is consistent with the fact that the Mo—P_2 plane does not bisect the angle formed by the normals to the mean planes of the η-cyclopentadienyl rings, as both H atoms on the same side repulse some C atoms of the corresponding cyclopentadienyl ring, thereby increasing the angle.

Thermal ellipsoids are represented, in projection down **b**, in Fig. 3. The large difference between the two P thermal ellipsoids might have the following explanation. From the estimated H atom positions of the η-C_5H_5 group, Fig. 2, it appears that the surroundings of the P atoms are quite different, and distances from P(2) to H(1) and H(2), 3·35 and 3·00 Å, are longer than those from P(1) to H(1) and H(2), 3·00 and 2·45 Å. The vibration of P(1) is, therefore, restricted while P(2) is free to move.

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Stacking Patterns of Thiopyrimidines: The Crystal Structure of 2-Thiocytosine Picrate

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$C_4H_6N_3S.C_6H_2N_3O_7$, monoclinic, $P2_1/c$, $a = 12{\cdot}430$ (1), $b = 15{\cdot}594$ (1), $c = 7{\cdot}239$ (3) Å, $\beta = 99{\cdot}81$ (3)°, $Z = 4$, $D_x = 1{\cdot}713$, $D_m = 1{\cdot}71$ g cm^{-3}. The structure was solved by use of 2305 symmetry-independent reflections measured on a diffractometer, and was refined by least squares to $R = 0{\cdot}091$. The crystal structure consists of ribbons of stacked thiocytosine cations hydrogen-bonded to the picrate anions and to neighboring thiocytosine moieties. No stacking interactions were observed between thiocytosine cations and picrate anions.

Introduction

The ability of thiopyrimidine residues to stabilize the secondary structure of polynucleotides has been attributed to enhanced base-stacking interactions induced by the sulfur substituents (Faerber, Scheit & Sommer, 1972; Scheit & Gaertner, 1969; Bahr, Faerber & Scheit, 1973). Recent reviews have suggested that the bases in crystal structures of thiopyrimidines generally exhibit characteristic stacking patterns that involve intimate contacts between the sulfur substituent of one base and the ring systems of neighboring bases (Saenger, 1973; Saenger & Suck, 1973). We determined the crystal structure of 2-thiocytosine picrate to