

η^4 -(1-endo-Ethyl)cyclopentadiene- η^5 -cyclopentadienyl(triethylphosphine)-chloromolybdenum(II)

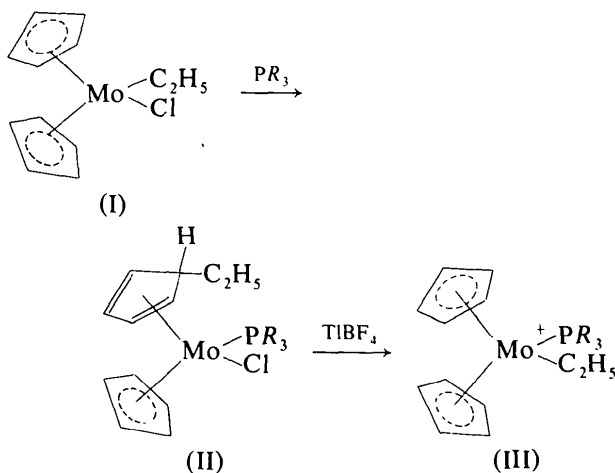
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Abstract. Triclinic, $P\bar{1}$, $a = 15.07$ (2), $b = 8.063$ (6), $c = 7.747$ (6) Å, $\alpha = 78.09$ (2), $\beta = 81.76$ (3), $\gamma = 87.49$ (3)°, $C_{18}H_{30}ClMoP$, $D_c = 1.487$ g cm⁻³ for $Z = 2$. The molecular structure of the title-named compound is confirmed.

Introduction. (η^5 -C₅H₅)₂Mo(C₂H₅)Cl (I), the structure of which has been confirmed by X-ray methods (Prout, Cameron, Forder, Denton, Critchley & Rees, 1974), reacts with tertiary phosphines PR₃, [R₃ = (C₂H₅)₃, (C₆H₅)₂CH₃ and C₆H₅(CH₃)₂] to give purple-pink products (Benfield & Green, 1974). IR and ¹H NMR studies strongly suggest that these are the 1-endo-ethylcyclopentadiene derivatives (η^5 -C₅H₅)(η^4 -1-endo-C₂H₅C₅H₅)MoPR₃Cl (II). These react with thallium tetrafluoroborate to give the BF₄⁻ salt of the cation (η^5 -C₅H₅)₂Mo(PR₃)C₂H₅⁺ (III), the structure of which can be demonstrated by preparation by an unambiguous route. Doubts have been expressed about the reversible transfer of the ethyl group to the cyclopentadiene ring and consequently about the structure of (II). Here we report the X-ray analysis of the structure of this compound.



A crystal, size 0.33 × 0.26 × 0.16 mm, sealed in a Lindemann-glass capillary, was used for data collection on a Philips PW 1100 single-crystal diffractometer with

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Mo radiation monochromatized by a flat graphite crystal. The unique set collected (θ range 2–25°, ω –2 θ scan, scan range 1.6°, scan speed 0.1° s⁻¹), contained 2692 reflexions with $I > \sigma(I)$. These were corrected for Lorentz and polarization effects but not for absorption ($\mu = 8.4$ cm⁻¹).

Table 1. Fractional atomic coordinates ($\times 10^4$; for H $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
Mo	1986.9 (4)	5977.8 (8)	5513.2 (9)
P	3256 (1)	7898 (2)	4088 (2)
Cl	1821 (2)	5995 (3)	2312 (3)
C(11)	452 (5)	6243 (10)	6540 (12)
C(12)	957 (5)	6278 (9)	7912 (10)
C(13)	1510 (5)	7737 (9)	7425 (11)
C(14)	1302 (5)	8605 (9)	5715 (12)
C(15)	661 (5)	7702 (10)	5203 (11)
C(21)	2021 (6)	3148 (9)	5640 (11)
C(22)	2918 (5)	3865 (9)	5213 (11)
C(23)	3109 (5)	4411 (9)	6701 (11)
C(24)	2368 (5)	3988 (9)	8028 (10)
C(25)	1891 (5)	2508 (9)	7615 (10)
C(26)	936 (5)	2099 (9)	8542 (11)
C(27)	895 (5)	1399 (11)	10560 (12)
C(31)	4352 (5)	6972 (10)	3316 (11)
C(32)	4396 (7)	6297 (13)	1606 (12)
C(33)	3616 (6)	9266 (10)	5493 (12)
C(34)	3946 (7)	8366 (12)	7187 (12)
C(35)	3039 (6)	9461 (11)	2067 (11)
C(36)	3742 (7)	10824 (11)	1253 (13)
H(11)	2	563	626
H(12)	93	553	915
H(13)	192	822	822
H(14)	145	961	470
H(15)	24	781	430
H(21)	165	299	433
H(22)	333	405	394
H(23)	379	476	677
H(24)	223	426	915
H(25)	224	134	802
H(261)	55	319	831
H(262)	64	124	797
H(311)	449	583	423
H(312)	477	776	337
H(331)	408	1000	459
H(332)	315	1020	568
H(351)	248	1019	245
H(352)	290	848	159

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

Mo—C(11)	2.351 (8)	C(11)—C(12)	1.40 (1)
Mo—C(12)	2.291 (7)	C(12)—C(13)	1.43 (1)
Mo—C(13)	2.279 (7)	C(13)—C(14)	1.43 (1)
Mo—C(14)	2.340 (7)	C(14)—C(15)	1.38 (1)
Mo—C(15)	2.395 (8)	C(15)—C(11)	1.41 (1)
Mo—C(21)	2.262 (7)	C(21)—C(22)	1.46 (1)
Mo—C(22)	2.188 (7)	C(22)—C(23)	1.39 (1)
Mo—C(23)	2.254 (8)	C(23)—C(24)	1.41 (1)
Mo—C(24)	2.377 (8)	C(24)—C(25)	1.53 (1)
Mo—C(25)	2.931 (8)	C(25)—C(21)	1.50 (1)
Mo—P	2.495 (4)	C(25)—C(26)	1.53 (1)
Mo—Cl	2.526 (3)	C(26)—C(27)	1.54 (1)
P—C(31)	1.85 (1)		
P—C(33)	1.85 (1)	C(15)—C(11)—C(12)	107.8 (6)
P—C(35)	1.85 (1)	C(11)—C(12)—C(13)	109.0 (7)
C(31)—C(32)	1.52 (1)	C(12)—C(13)—C(14)	105.7 (7)
C(33)—C(34)	1.50 (1)	C(13)—C(14)—C(15)	108.9 (7)
C(35)—C(36)	1.53 (1)	C(14)—C(15)—C(11)	108.7 (7)
		C(25)—C(21)—C(22)	105.5 (7)
Cl—Mo—P	82.4 (2)	C(21)—C(22)—C(23)	107.6 (7)
Mo—P—C(31)	119.3 (3)	C(22)—C(23)—C(24)	106.7 (7)
Mo—P—C(33)	115.5 (3)	C(23)—C(24)—C(25)	108.0 (7)
Mo—P—C(35)	115.3 (3)	C(24)—C(25)—C(21)	94.9 (6)
P—C(31)—C(32)	115.6 (6)	C(21)—C(25)—C(26)	117.6 (7)
P—C(33)—C(34)	116.1 (6)	C(24)—C(25)—C(26)	118.6 (6)
P—C(35)—C(36)	118.1 (6)	C(25)—C(26)—C(27)	112.8 (7)

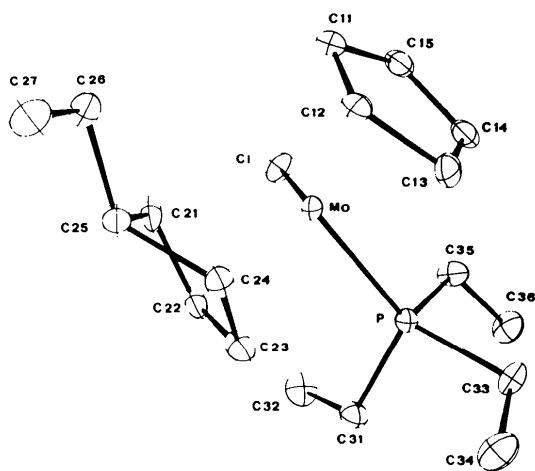


Fig. 1. Atomic numbering in the molecule. No H atoms are shown for reasons of simplicity.

The structure was solved by heavy-atom (Patterson and F_o synthesis) methods and refined by full-matrix least squares. All H atoms, except those of the terminal methyl groups, were located from a difference synthesis calculated at the convergence of the refinement after six cycles (three with isotropic and three with anisotropic temperature factors and unit weights, $R = 0.058$). Inclusion of the H atoms in the structure-factor calculation gave a final conventional R of 0.054. All calculations were performed on a Honeywell 6030 computer with local programs. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). That for Mo was corrected for

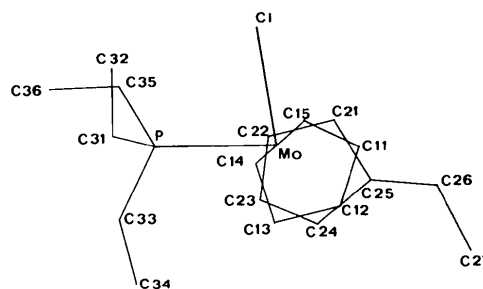


Fig. 2. The molecule seen projected on the Cl—Mo—P plane.

anomalous dispersion. The final atomic parameters are given in Table 1* and the interatomic distances and interbond angles with standard deviations calculated from the variance-covariance matrix in Table 2. The molecule is shown in Figs. 1 and 2.

Discussion. The structure analysis confirmed that the reaction product was the title-named compound (II).

The η^5 -cyclopentadienyl group is planar with the Mo atom 1.995 Å away from the plane. Within the ring the C—C bond lengths are equivalent (1.41 Å mean). In the η^4 -cyclopentadiene ring the atoms of the butadiene residue are planar and lie between 2.188 and 2.377 Å from Mo so that Mo is 1.949 Å from the plane. The fifth atom, C(25), of the ring carries the *endo*-ethyl group and is 0.64 Å out of the butadiene plane on the opposite side to the Mo atom so that C(25)—Mo is 2.931 Å. The ethyl group at C(25) points away from the chloro and phosphine ligands but is nearer the former than the latter (Fig. 2). In the η^5 -cyclopentadiene ring the three C—C bonds of the butadiene are similar in length to those of the η^5 -C₅H₅ ring but C(25)—C(21) and C(25)—C(24) have lengths, 1.50 and 1.53 Å, appropriate for sp^2 — sp^3 single bonds. The rings have the staggered conformation. The normals to the η^5 -C₅H₅ and η^4 -(C₂H₅)C₃H₅ planes are inclined at an angle of 131.2°. The plane containing the normals is almost perpendicular (92.4°) to the plane containing Mo—Cl and Mo—P and the conformation of the molecule is very similar to that found in Mo^{IV} compounds of the type $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoX}_2$ (Prout *et al.*, 1974). The Cl—Mo—P angle, 82.4°, again indicates that the non-bonding electrons are in a ψ_η -type orbital (Green, Green & Prout, 1972). The Mo—Cl bond is somewhat longer than might have been expected: *cf.* 2.500 Å in $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{C}_2\text{H}_5)\text{Cl}$ and 2.471 Å (mean) in $(\eta\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ (Prout *et al.*, 1974), but the Mo—P bond is slightly shorter than in $(\eta\text{-C}_5\text{H}_5)_2\text{MoP}_2\text{H}_2$ (Cannillo, Coda, Prout & Daran, 1977).

The crystal structure contains no short or otherwise unusual contacts.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32887 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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7,7,9,9-Tetramethyl-8-thiosulphinyliminothio-1,4-dioxaspiro[4,5]decane

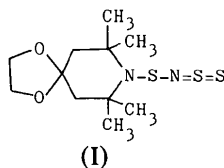
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Abstract. $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_3$, $M_r = 308.5$, monoclinic, $P2_1/n$, $Z = 4$, $a = 15.310$ (2), $b = 9.477$ (1), $c = 10.860$ (2) Å, $\beta = 104.58$ (2)°, $D_x = 1.32$ g cm⁻³. Final residual $R = 0.067$. A new bonding system consisting of one N and three S atoms has been determined. The bonding system is $-\text{S}=\text{N}=\text{S}=\text{S}$ wherein the S=S double-bond distance is 1.912 Å and the N=S=S bond angle is 114.85°.

Introduction. Red crystals of the title compound (I)* were grown from a dilute ether solution. A crystal with dimensions 0.5 × 0.4 × 0.5 mm was selected for the data collection on a Rigaku four-circle diffractometer. 1508 independent reflexions [$F = 3\sigma(F)$] were collected with the ω - 2θ scanning technique with graphite-monochromatized Mo $K\alpha$ radiation. The intensities were corrected for Lorentz-polarization but not for absorption. The structure was solved by symbolic addition procedures using 546 reflexions



with $E \geq 1.54$ and refined by block-diagonal least-squares procedures. On a subsequent difference Fourier map the positions of all the H atoms were discernible. The final coordinates with their estimated

Table 1. Final atomic coordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for H atoms) with e.s.d.'s in parentheses

	x	y	z
S(1)	4589 (1)	4815 (2)	6653 (2)
S(2)	4639 (2)	3130 (3)	8767 (2)
S(3)	5400 (2)	1961 (2)	8046 (3)
O(1)	3066 (4)	9750 (6)	3865 (5)
O(2)	2599 (3)	9271 (5)	5656 (5)
N(1)	4060 (3)	6258 (6)	6069 (5)
N(2)	4286 (4)	4498 (7)	7987 (6)
C(1)	3093 (4)	6125 (7)	5333 (7)
C(2)	2901 (5)	7352 (8)	4370 (6)
C(3)	3181 (4)	8787 (7)	4897 (6)
C(4)	4151 (5)	8784 (7)	5627 (7)
C(5)	4419 (4)	7654 (7)	6641 (7)
C(6)	2477 (7)	10790 (9)	4016 (9)
C(7)	2319 (8)	10613 (10)	5274 (9)
C(8)	2984 (6)	4760 (9)	4552 (8)
C(9)	2440 (5)	6088 (9)	6196 (8)
C(10)	5460 (5)	7604 (9)	6962 (10)
C(11)	4112 (5)	8032 (9)	7845 (7)
H(C2a)	231 (4)	721 (7)	410 (6)
H(C2b)	328 (4)	716 (6)	367 (5)
H(C4a)	432 (3)	975 (6)	592 (5)
H(C4b)	448 (3)	853 (5)	494 (5)
H(C6a)	196 (5)	1065 (8)	346 (7)
H(C6b)	264 (5)	1178 (8)	356 (7)
H(C7a)	171 (5)	1098 (9)	578 (8)
H(C7b)	266 (6)	1125 (10)	563 (8)
H(C8a)	237 (4)	485 (6)	383 (5)
H(C8b)	294 (4)	402 (7)	517 (6)
H(C8c)	346 (4)	476 (6)	413 (5)
H(C9a)	190 (4)	580 (7)	569 (6)
H(C9b)	238 (4)	700 (7)	658 (6)
H(C9c)	263 (4)	513 (7)	688 (6)
H(C10a)	549 (6)	721 (7)	769 (6)
H(C10b)	578 (6)	869 (9)	700 (8)
H(C10c)	575 (5)	696 (9)	641 (8)
H(C11a)	351 (4)	794 (7)	781 (6)
H(C11b)	424 (5)	714 (8)	843 (7)
H(C11c)	447 (4)	884 (7)	831 (6)

* (I) was prepared by reaction of the corresponding N-unsubstituted piperidine with sulphur monochloride followed by treatment with aqueous ammonia. The details will be published elsewhere.