dihedral angle of 114·9 (7)°. The C–C distances for the naphthalene fragments are similar to those for naphthalene itself (Pawley & Yeats, 1969); the angles are however distorted as the naphthalene parts are fused to five-membered and to four-membered rings. The distortions due to the five-membered ring are similar to those found in acenaphthene (Ehrlich, 1957), those due to the four-membered ring are smaller as in naphtho[*b*]cyclobutene (Crawford & Marsh, 1973) and in (II).

C (7)–C (18) is very long for a single bond, 1·601 (10) Å; the weakening of the bond is presumably caused by the strain due to the fusion of the four- and five-membered rings. Similar long bonds are found in (II) [1·606 (4)] and (III) [1·591 (6) Å]. The cyclobutene ring is not quite planar, the angle between the planes through C (7), C (8), C (17) and C (7), C (18), C (17) is 177·5 (9)°, so that the molecule as a whole is slightly twisted. We attribute the deformation to packing forces. A stereo view of the unit-cell contents is shown in Fig. 2.

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cis-Tetracarbonyl (1,3-tetramethyl-2-t-butyltriphosphane-^1P,^3P)molybdenum(0)

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Abstract. $C_{12}H_{21}O_4P_3Mo$, monoclinic, $P2_1$, $a=8·432$ (11), $b=12·751$ (14), $c=9·243$ (6) Å, $\beta=107·51$ (8)°, $M=418·16$, $Z=2$, $D_x=1·47$ g cm^{-3}. Considerable distortion from perfect octahedral coordination is observed at Mo with a small P–Mo–P angle of 72·7 (1)°. The four-membered MoPPP chelate ring is non-planar [distances from the least-squares plane: Mo, −0·104; P(1), 0·284; P(2), −0·345; P(3), 0·383 Å] and contains a remarkably small P(1)–P(2)–P(3) angle of 85·0 (1)°. The P–P distances of 2·193 (4) and 2·186 (4) Å are normal.

Introduction. Cell dimensions were determined by a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$, 0·71069 Å). Intensities from a prismatic crystal, elongated *c*, with approximate dimensions 0·16 × 0·19 × 0·42 mm, were collected on the diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Measurements were carried out in the θ–2θ mode ($3·0 \le 2\theta \le 50·0°$) at scan speeds varying linearly between 2·93° min^{-1} (150 c.p.s. and below) and 8·37° min^{-1} (5000 c.p.s. and above). Scan and background times were equal. Three standard reflexions, monitored at regular intervals, did not display any significant variations. Lorentz and polarization but no absorption [μ(Mo $K\alpha$) = 9·4 cm^{-1}] corrections were applied. From the 1886 reflexions recorded (one quadrant of reciprocal space) 1417 were retained for use in the structure analysis, after application of the criterion $F \ge 2·5\sigma(F)$ and averaging, where $\sigma(F)$ is based on the counting statistics.

The structure was solved by conventional Patterson and difference Fourier methods. Refinement with anisotropic temperature factors for all non-hydrogen atoms was by full-matrix least squares, $\sum w\Delta^2$ being minimized. A final difference synthesis revealed possible coordinates for some but not all of the H atoms. In view of the ambiguous nature of this information no attempt was made to include any H atoms in the final cycles. The terminal value of $R_G=[\sum w\Delta^2/\sum wF_o^2]^{1/2}$ was 0·069, with $R_w=\sum w^{1/2}\Delta/\sum w^{1/2}F_o=0·054$ and $R=0·050$. The weights were given by $w=k/[\sigma^2(F_o)+gF_o^2]$ where k and g refined to 0·6609 and 0·005354 respectively. In the final cycle the largest observed shift/e.s.d. was −0·006. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed. The atom coordinates are listed in Table 1 and the temperature factors in Table 2. The

full covariance matrix was used in the estimation of the bond lengths and angles presented in Tables 3 and 4.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31389 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atom positional parameters* ($\times 10^4$)

	x	y	z
Mo	−455 (1)	2500	1367 (1)
P(1)	2241 (3)	3388 (2)	2649 (3)
P(2)	1878 (3)	3337 (2)	4900 (3)
P(3)	437 (3)	1918 (2)	4067 (3)
C(1)	817 (18)	1334 (10)	747 (18)
O(1)	1517 (18)	702 (11)	325 (20)
C(2)	−2502 (14)	1675 (11)	809 (16)
O(2)	−3736 (13)	1166 (9)	540 (13)
C(3)	−793 (13)	3159 (12)	−687 (17)
O(3)	−939 (12)	3530 (10)	−1863 (17)
C(4)	−1766 (14)	3714 (9)	1863 (14)
O(4)	−2569 (13)	4370 (9)	2121 (13)
C(5)	4180 (13)	2761 (13)	2612 (13)
C(6)	2662 (23)	4766 (12)	2306 (18)
C(7)	3798 (14)	3228 (11)	6592 (13)
C(71)	4732 (19)	4250 (15)	6683 (21)
C(72)	3156 (23)	3113 (25)	7941 (19)
C(73)	4949 (16)	2300 (14)	6534 (16)
C(8)	1606 (20)	709 (11)	4539 (18)
C(9)	−1005 (18)	1828 (15)	5237 (17)

Table 3. *Bond lengths* (Å)

Mo –P(1)	2·497 (3)	Mo –P(3)	2·493 (3)
P(1)–P(2)	2·193 (4)	P(3)–P(2)	2·186 (4)
Mo –C(1)	2·015 (13)	C(1)–O(1)	1·135 (16)
Mo –C(2)	1·954 (11)	C(2)–O(2)	1·187 (13)
Mo –C(3)	2·016 (16)	C(3)–O(3)	1·158 (16)
Mo –C(4)	2·033 (11)	C(4)–O(4)	1·145 (14)
P(1)–C(5)	1·830 (11)	P(1)–C(6)	1·839 (15)
P(3)–C(8)	1·811 (15)	P(3)–C(9)	1·858 (12)
P(2)–C(7)	1·887 (11)	C(7)–C(71)	1·51 (2)
C(7)–C(72)	1·51 (2)	C(7)–C(73)	1·54 (2)

Table 4. *Bond angles* (°)

P(1)—Mo –P(3)	72·7 (1)	P(2)—P(1)–Mo	94·0 (1)
P(2)—P(3)–Mo	94·3 (1)	P(1)—P(2)–P(3)	85·0 (1)
P(1)—Mo –C(1)	89·0 (4)	P(1)—Mo –C(2)	167·3 (4)
P(1)—Mo –C(3)	96·2 (3)	P(1)—Mo –C(4)	91·5 (3)
P(3)—Mo –C(1)	92·2 (4)	P(3)—Mo –C(2)	94·6 (4)
P(3)—Mo –C(3)	168·9 (4)	P(3)—Mo –C(4)	91·2 (4)
C(1)—Mo –C(2)	91·8 (6)	C(1)—Mo –C(3)	88·7 (6)
C(1)—Mo –C(4)	176·5 (6)	C(2)—Mo –C(3)	96·5 (6)
C(2)—Mo –C(4)	88·4 (5)	C(3)—Mo –C(4)	87·9 (5)
Mo—C(1)–O(1)	176·4 (15)	Mo—C(2)–O(2)	176·9 (12)
Mo—C(3)–O(3)	178·0 (10)	Mo—C(4)–O(4)	176·8 (11)
C(5)—P(1)–Mo	118·9 (5)	C(5)—P(1)–P(2)	112·7 (4)
C(5)—P(1)–C(6)	101·2 (8)	C(6)—P(1)–Mo	123·2 (6)
C(6)—P(1)–P(2)	106·4 (6)	C(8)—P(3)–Mo	118·2 (5)
C(8)—P(3)–P(2)	114·5 (5)	C(8)—P(3)–C(9)	102·2 (8)
C(9)—P(3)–Mo	123·2 (6)	C(9)—P(3)–P(2)	103·8 (5)
C(7)—P(2)–P(1)	118·6 (4)	C(7)—P(2)–P(3)	117·3 (4)
C(71)–C(7)–P(2)	106·6 (9)	C(71)–C(7)–C(72)	110·4 (16)
C(71)–C(7)–C(73)	110·0 (11)	C(72)–C(7)–P(2)	105·1 (9)
C(72)–C(7)–C(73)	109·9 (14)	C(73)–C(7)–P(2)	114·8 (9)

Discussion. It has recently been shown that the dilithium salt *cis*-$Mo(CO)_4(Me_2PLi)_2$ reacts with $MePCl_2$ to yield the novel chelate complex *cis*-$Mo(CO)_4$-(PMe_2–PMe–PMe–PMe_2) of the unknown hexamethyltetraphosphane Me_2P–PMe–PMe–PMe_2 instead of the expected triphosphane complex (Stelzer & Unger, 1975). Confirmation of this result was provided by a crystal structure determination (Sheldrick, 1975*a*), which was noteworthy for the fact that the molecule displayed two significantly different P–P lengths. A short (P)P–P(P) distance of 2·142 (12) was observed, contrasting with that of 2·200 (9) Å for the (Mo)P–P(P) bond, which falls within the range (2·18–2·22 Å) nor-

Table 2. *Anisotropic temperature factors* ($Å^2 \times 10^3$) *in the form*
$$exp\,[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
Mo	58 (1)	51 (1)	49 (1)	−5 (1)	15 (1)	0 (1)
P(1)	52 (1)	50 (1)	44 (2)	6 (1)	17 (1)	−2 (1)
P(2)	44 (1)	45 (1)	46 (2)	−3 (1)	13 (1)	0 (1)
P(3)	56 (2)	47 (2)	44 (2)	1 (1)	18 (1)	−9 (1)
C(1)	93 (10)	51 (7)	82 (11)	−1 (7)	34 (8)	7 (7)
O(1)	133 (11)	87 (9)	171 (15)	−54 (10)	68 (11)	22 (9)
C(2)	50 (6)	66 (7)	73 (9)	−27 (7)	21 (6)	−19 (6)
O(2)	89 (7)	84 (7)	94 (8)	−22 (6)	24 (6)	−27 (6)
C(3)	49 (6)	75 (8)	56 (10)	−5 (7)	16 (6)	9 (6)
O(3)	97 (7)	117 (9)	51 (7)	27 (7)	31 (5)	13 (7)
C(4)	60 (7)	56 (7)	45 (8)	−14 (5)	18 (6)	3 (6)
O(4)	96 (7)	83 (7)	91 (8)	−3 (6)	44 (6)	21 (6)
C(5)	48 (5)	123 (16)	65 (8)	10 (8)	30 (5)	18 (7)
C(6)	154 (15)	61 (9)	82 (12)	19 (8)	45 (10)	−25 (10)
C(7)	56 (6)	75 (8)	38 (7)	−1 (6)	7 (5)	4 (6)
C(71)	71 (9)	87 (11)	100 (13)	−6 (9)	−18 (8)	−18 (8)
C(72)	102 (12)	213 (26)	55 (11)	4 (14)	17 (9)	12 (16)
C(73)	59 (6)	90 (14)	70 (9)	8 (7)	8 (6)	24 (7)
C(8)	101 (10)	49 (7)	86 (11)	11 (7)	18 (8)	−1 (7)
C(9)	100 (10)	143 (15)	62 (9)	−25 (9)	57 (8)	−70 (10)

mally observed for the P–P bond (Cowley, 1965). Interestingly, if Bu^tPCl_2 is used instead of $MePCl_2$ in the reaction with the Li salt, then the expected triphosphane complex *cis*-$Mo(CO)_4(Me_2P–Bu^tP–PMe_2)$ (I) is obtained in low yield (Stelzer & Unger, 1975. In an analogous compound *cis*-$Mo(CO)_4(Ph_2P–CH_2–PPh_2)$ (II) an approximately planar four-membered chelate ring was observed with a small P–Mo–P angle of 67·3 (1) and other ring angles Mo–P–C 96·3 (3) and 97·5 (3), P–C–P 95·6 (4)°, which deviate significantly from tetrahedral (Cheung, Lai & Mok, 1971). A crystal structure determination of (I) was accordingly undertaken in order to provide information on the molecular geometry of a triphosphane chelate ring system.

The molecule of (I) displays approximate C_v symmetry with a mirror plane passing through Mo, O(1), O(4), C(1), C(4), P(2), C(7) and C(73) (Fig. 1). In contrast to the MoPCP chelate ring in (II), that in (I) is very sharply buckled, with atoms at the following distances from the weighted least-squares plane: Mo, −0·104; P(1), 0·284; P(2), −0·345; P(3), 0·383 Å. The P–Mo–P angle of 72·7 (1) in (I) is larger than that of 67·3 (1)° in (II) which is to be expected in view of the geometric constraints imposed on (II) by the shorter P–C distance [1·88 (1) *vs* 2·19 (1) Å for P–P in (I)]. The P–P–Mo angles of 94·0 (1) and 94·3 (1) in (I) are slightly smaller than the C–P–Mo angles of 97·5 (3) and 96·3 (3)° in (II). However, the most remarkable feature of the ring geometry in (I) is the very small P–P–P angle of 85·0 (1) which contrasts with the P–C–P angle of 95·6 (4)° in (II). There are no particularly short intra- or intermolecular contacts which may be invoked to explain this phenomenon. The P–P distances of 2·193 (4) and 2·186 (4) Å in (I) lie within the range normally associated with this bond.

In (II) the Mo–C bonds (mean 1·93 Å) *trans* to P were found to be significantly shorter than those (mean 2·04 Å) *trans* to CO groups. No significant differences were observed between these bonds, however, in the tetraphosphane (III) or (dimethylphosphino-1,2-dimethyl)diarsine (IV) derivatives (Sheldrick, 1975*b*). This is also the state of affairs in (I) where values in the range 1·954–2·033 Å were obtained for the Mo–C bond. The Mo–P distance of 2·497 (3) in (I) is shorter, though not significantly, than the mean value in (II) of 2·518 (17), but longer than those of 2·489 (6) and 2·453 (7) Å in (III) and (IV). A comparison of these values with the sum of the covalent radii for Mo^0 and P (2·71 Å) suggests the presence of $(d \rightarrow d)\pi$-bonding from Mo to P and indicates that this effect is probably less strong in (I) and (II) where the P–Mo–P angle is forced by geometric constraints to take up a value much smaller than 90°. The P–C lengths in (I) are unexceptional.

The crystal structure is shown in Fig. 2.

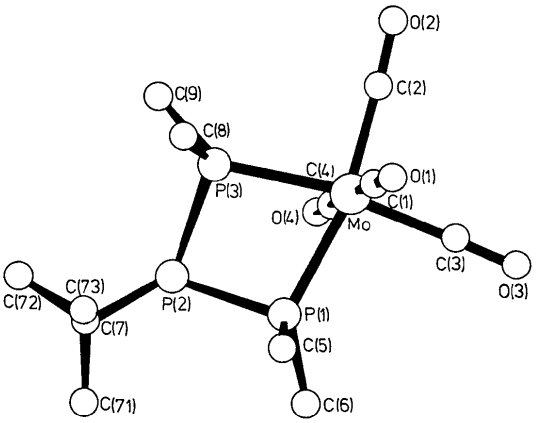

Fig. 1. Atom numbering in the molecule.

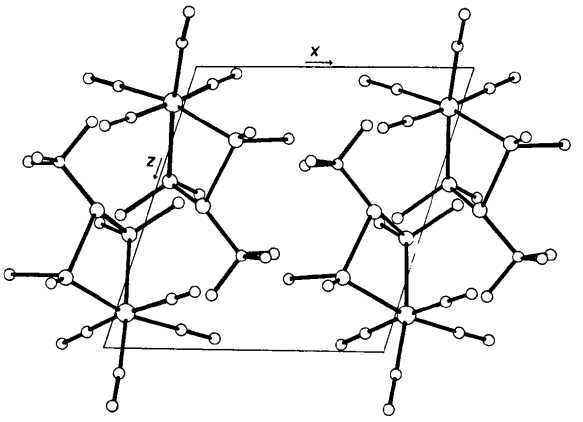

Fig. 2. Projection of the structure perpendicular to [010].

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