Fig. 1. One molecule of the binuclear complex showing the intra-molecular hydrogen bonds. Mo atoms are shown as filled circles.

(Butcher, Penfold & Sinn, 1979). In the latter two compounds, in the absence of oxo bridging there is a simple distinction between long Mo—O_l (O_l = ligand oxygen) bonds trans to terminal O atoms (O_t) and short Mo—O_l cis to O_t, a feature now well established in oxomolybdenum complexes. However, in the present structure, only in the L ligand is there a bond Mo—O(1) trans to O_t and this is indeed 0·48 (2) Å longer than Mo—O(2) in the same ligand. In the L' ligand the bond Mo—O(4) trans to O_b, the bridging O(5) atom, is significantly (six e.s.d.'s) shorter than Mo—O(3).

However, O(3), unlike O(4), is involved in hydrogen bonding and this effect is a likely contributor to relative bond lengthening of Mo—O(3).

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Di-μ-acetato-bis[(trimethylphosphine)(trimethylsilylmethyl)molybdenum(II)](Mo—Mo)

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Abstract. [$Mo_2(C_2H_3O_2)_2(C_3H_9P)_2(C_4H_{11}Si)_2$], $C_{18}H_{46}$-$Mo_2O_4P_2Si_2$, $M_r = 636·6$, triclinic, $P\bar{1}$, $a = 8·501$ (2), $b = 9·844$ (3), $c = 10·294$ (3) Å, $\alpha = 99·54$ (3), $\beta = 111·72$ (4), $\gamma = 98·69$ (4)°, $U = 767·7$ Å^3, $Z = 1$, $D_c = 1·377$ Mg m^{-3}, $F(000) = 328$, μ(Mo $K\alpha$) $= 0·92$ mm^{-1}, λ(Mo $K\alpha$) $= 0·71069$ Å. The structure has been refined to $R = 0·0273$ for 3810 diffractometer data. The dimeric molecules lie on crystallographic inversion centres. The short Mo—Mo distance [2·0984 (5) Å] is consistent with the presence of a quadruple bond.

Introduction. The title compound was obtained as orange-red prisms by reacting $Mo_2(O_2CMe)_4$ with $Mg(CH_2SiMe_3)_2$ in the presence of trimethylphosphine (Anderson, Jones, Wilkinson, Hursthouse & Malik, 1977; Anderson, Jones & Wilkinson, 1978). We undertook an X-ray study of this material both for complete structural characterization and as part of a general investigation of the structures of molecules containing bulky alkyl ligands. Since the compound is air-sensitive, suitable crystals were sealed under nitrogen in Lindemann capillaries. The cell parameters were initially determined from oscillation and Weissenberg photographs and later refined on a Nonius CAD-4 diffractometer from the setting angles for fifteen high-angle [$16 < \theta$(Mo $K\alpha$) $< 17°$] reflections. Intensities of

Table 1. Fractional coordinates of the non-hydrogen atoms (Mo $\times 10^5$, others $\times 10^4$)

	x	y	z
Mo	2957 (2)	8865 (1)	8444 (2)
P(1)	2579 (1)	2685 (1)	580 (1)
Si(2)	−441 (1)	2148 (1)	3737 (1)
O(1)	2378 (2)	198 (2)	2231 (2)
O(2)	1709 (2)	−1718 (2)	472 (2)
C(1)	2643 (3)	−978 (2)	1743 (2)
C(2)	4109 (4)	−1491 (4)	2699 (3)
C(11)	3543 (7)	4180 (5)	2122 (6)
C(12)	1930 (8)	3434 (6)	−974 (6)
C(13)	4539 (5)	2114 (5)	581 (6)
C(21)	−1144 (3)	570 (2)	2236 (2)
C(22)	−1786 (5)	2039 (4)	4830 (3)
C(23)	−669 (4)	3770 (3)	3018 (3)
C(24)	1876 (4)	2374 (4)	5008 (3)

Table 2. Hydrogen-atom coordinates ($\times 10^3$) and isotropic temperature factors ($\text{Å}^2 \times 10^3$)

H atoms are numbered according to the parent C atom and distinguished by a, b, or c.

	x	y	z	U
H(2a)	423 (6)	−139 (5)	380 (2)	114 (14)
H(2b)	392 (7)	−257 (2)	279 (6)	160 (21)
H(2c)	514 (6)	−160 (9)	234 (7)	268 (21)
H(11a)	247 (4)	465 (4)	212 (5)	124 (16)
H(11b)	457 (5)	495 (5)	209 (5)	158 (18)
H(11c)	368 (6)	370 (5)	302 (4)	140 (19)
H(12a)	134 (4)	404 (3)	−39 (3)	75 (10)
H(12b)	261 (8)	453 (2)	−49 (7)	208 (22)
H(12c)	163 (9)	245 (6)	−176 (8)	315 (21)
H(13a)	403 (9)	201 (7)	−57 (1)	198 (22)
H(13b)	549 (7)	290 (6)	48 (7)	203 (21)
H(13c)	509 (7)	179 (7)	158 (4)	183 (21)
H(21a)	−254 (5)	32 (3)	165 (3)	68 (8)
H(21b)	−96 (4)	−41 (2)	256 (3)	65 (8)
H(22a)	−122 (6)	296 (3)	573 (3)	137 (17)
H(22b)	−312 (3)	197 (8)	412 (7)	228 (21)
H(22c)	−140 (5)	117 (3)	529 (4)	114 (13)
H(23a)	17 (5)	480 (2)	360 (4)	134 (16)
H(23b)	−190 (3)	403 (4)	289 (4)	122 (14)
H(23c)	6 (5)	406 (5)	240 (4)	139 (17)
H(24a)	240 (6)	347 (2)	559 (5)	141 (18)
H(24b)	274 (4)	257 (4)	448 (4)	106 (13)
H(24c)	234 (8)	146 (3)	531 (6)	208 (20)

Table 3. Bond distances (Å) and angles (°)

The primed atoms are related to the unprimed ones by the centre of symmetry at (0,0,0).

Mo–Mo'	2·0984 (5)	Si(2)–C(21)	1·844 (2)
Mo–P(1)	2·547 (1)	Si(2)–C(22)	1·881 (3)
Mo–C(21)	2·231 (2)	Si(2)–C(23)	1·876 (3)
Mo–O(1)	2·108 (1)	Si(2)–C(24)	1·872 (3)
Mo–O(2')	2·119 (1)		
P(1)–C(11)	1·805 (4)	C(1)–O(1)	1·271 (3)
P(2)–C(12)	1·808 (4)	C(1)–O(2)	1·270 (3)
P(1)–C(13)	1·837 (4)	C(1)–C(2)	1·491 (3)
Mo'–Mo–O(1)	92·0 (1)	Mo–P(1)–C(11)	111·1 (2)
Mo'–Mo–O(2')	91·4 (1)	Mo–P(1)–C(12)	118·5 (2)
Mo'–Mo–P(1)	104·3 (1)	Mo–P(1)–C(13)	116·7 (2)
Mo'–Mo–C(21)	113·6 (1)	C(11)–P(1)–C(12)	105·4 (3)
O(1)–Mo–O(2')	176·2 (1)	C(11)–P(1)–C(13)	100·3 (2)
O(1)–Mo–P(1)	87·0 (1)	C(12)–P(1)–C(13)	102·7 (3)
O(1)–Mo–C(21)	90·1 (1)		
P(1)–Mo–O(2')	90·4 (1)	Mo–C(21)–Si(2)	110·0 (1)
P(1)–Mo–C(21)	142·1 (1)		
O(2')–Mo–C(21)	90·2 (1)	C(21)–Si(2)–C(22)	112·2 (3)
		C(21)–Si(2)–C(23)	109·9 (1)
Mo–O(1)–C(1)	117·3 (1)	C(21)–Si(2)–C(24)	111·3 (1)
Mo'–O(2)–C(1)	117·2 (1)	C(22)–Si(2)–C(23)	107·4 (2)
		C(22)–Si(2)–C(24)	106·8 (2)
O(1)–C(1)–C(2)	122·1 (2)	C(23)–Si(2)–C(24)	109·1 (2)
O(1)–C(1)–C(2)	118·4 (2)		
O(2)–C(1)–C(2)	119·4 (2)		

Table 4. Least-squares planes in the form Ax + By + Cz = D, where x,y,z are fractional coordinates

Deviations (Å $\times 10^3$) of the relevant atoms are given in square brackets. E.s.d.'s are $\sim$0·005 Å.

Plane (1): through all atoms in the $(MoO_2C)_2$ unit

$$6·4008 x + 4·4648 y - 7·1817 z = 0·0$$

[Mo −21, O(1) 8, C(1) 3, O(2) −12, C(2) 25]

Plane (2): through all atoms in the $(MoCP)_2$ unit

$$5·2930 x - 5·9882 y + 4·2539 z = 0·0$$

[Mo −15, C(21) 5, P(1) 4]

The angle between the normals to planes (1) and (2) = 91·0 (2)°.

5786 reflections ($1·5 < \theta < 30°$) were recorded on the same diffractometer with graphite-monochromated Mo $K\alpha$ radiation and the ω–2θ scan method with a crystal 0·45 $\times$ 0·32 $\times$ 0·22 mm (Bonnett, Charalambides, Hursthouse, Malik, Nicolaidou & Sheldrick, 1979). All data were corrected for Lorentz and polarization factors but not for absorption or extinction. Averaging equivalent reflections and omitting those with $F_o < 3\sigma(F_o)$ yielded 3811 unique data.

The structure was solved in the space group $P\bar{1}$, a choice confirmed by successful refinement. The position of the unique Mo atom was obtained from a Patterson map and all other atoms were located from difference syntheses. Full-matrix least-squares refinement of the non-hydrogen atoms, first with isotropic and then anisotropic temperature factors, gave R values of 0·064 and 0·034 respectively. All the H atoms were then located from difference maps and isotropically refined with C–H constrained to remain at 1·08 Å. The structure finally refined to $R = 0·0273$ and $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2} = 0·0389$. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0·0005F_o^2]$, and this gave satisfactory variance analyses. Neutral-atom scattering factors were taken from Stewart, Davidson & Simpson (1965) for H and from Cromer &

Mann (1968) for other atoms. The final atomic co-ordinates are presented in Tables 1 and 2, inter-atomic distances and angles in Table 3.* Results of least-squares-plane calculations are presented in Table 4.

Discussion. The structure of the dimeric molecule is shown in Fig. 1 with the atom numbering. The molecule contains a crystallographic inversion centre but the effective symmetry of the core is C_{2h}. The short Mo—Mo distance of 2·0984 (5) Å is indicative of a quadruple bond and is comparable to those [2·065 (1)–2·183 (2) Å] in other Mo≡Mo systems (Chisholm, 1978; Cotton, 1975; Garner, Parkes, Walton & Clegg, 1978).

The immediate coordination around each metal may be described as a distorted trigonal bipyramid with two O atoms from the bridging carboxylate ligands occupying axial positions [O(1)—Mo—O(2') = 176·2 (1)°], but should perhaps more properly be considered as the usual square-pyramidal coordination strained towards the trigonal-bipyramidal structure by intramolecular steric interactions between the phosphine and alkyl ligands on different metals. The relevant contacts P(1)···C(21') = 3·644 (5), C(12)···C(21') = 3·812 (5) and C(13)···C(21') = 3·561 (5) Å, are all shorter than the corresponding van der Waals sums. The angles in the MoCP plane, Mo'—Mo—C(21) = 113·6 (1) and Mo'—Mo—P(1) = 104·3 (1)°, seem to reflect the relative steric properties of the alkyl and phosphine ligands. Very similar parameters have been found in the centrosymmetric {Mo₂Br₂[O₂CPh]₂-[P(Buⁿ)₃]₂} (Potenza, Johnson & San Filippo, 1976) which is not surprising since the Br and CH₂ groups have similar (~1·95 Å) van der Waals radii.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34617 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
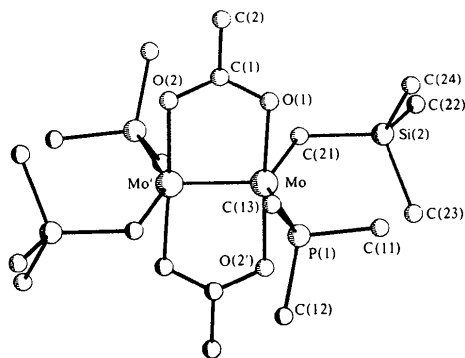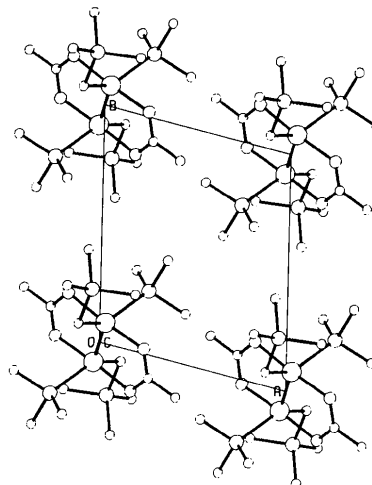

Fig. 2. The packing of the molecules in the unit cell.

The remaining molecular-geometry parameters mostly correspond to expected values. The Mo—O distances of 2·108 (1) and 2·119 (1) Å lie in the range found for all other Mo₂ carboxylate species (Potenza, Johnson & San Filippo, 1976, and references therein) and the Mo—C distance of 2·231 (2) Å compares with a value of 2·29 (2) Å in $[Mo_2Me_8]^{4-}$ (Cotton, Troup, Webb, Williamson & Wilkinson, 1974). The Mo—P distance of 2·547 (1) Å would appear to be long for an Mo^{II}—P bond (Potenza, Johnson & San Filippo, 1976) and may again be a reflection of the steric crowding in the molecule.

The $(MoO_2C)_2$ group is planar within 0·017 Å and perpendicular to the $(MoCP)_2$ plane (Table 4). Bond lengths and angles within the alkyl and phosphine ligands are normal, with Si—Me = 1·872 (3)–1·881 (3) Å and P—Me = 1·805 (4)–1·837 (4) Å. The tetrahedral angles at P show greater variations than those at Si; in particular, the Mo—P(1)—C(12) [118·5 (2)°] and Mo—P(1)—C(13) [116·7 (2)°] angles have opened up as a result of alkyl–phosphine repulsions discussed above. The closest approach between two methyl groups [C(2) and C(24)] on neighbouring molecules is 3·687 (5) Å. A packing diagram is presented in Fig. 2.

Fig. 1. Structure of $[Mo_2(CH_2SiMe_3)_2(OAc)_2(PMe_3)_2]$ showing the atom numbering. The primed atoms are related to the unprimed ones by a centre of symmetry at (0,0,0).

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Structure du Bis(hexaméthylphosphoramide)bis(isothiocyanato)dioxomolybdène(VI)

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Abstract. $[Mo(C_6H_{18}N_3OP)_2(NCS)_2O_2]$, $C_{14}H_{36}MoN_8O_4P_2S_2$, monoclinic, $P2_1/b$, $a = 23.17$ (1), $b = 18.16$ (1), $c = 14.780$ (4) Å, $\gamma = 112.21$ (5)°, $Z = 8$, $d_m = 1.39$, $d_x = 1.40$ Mg m^{-3}. The structure was solved by the heavy-atom method and refined by least-squares procedures from single-crystal diffractometer data with 2911 independent structure factors; $R = 0.058$. The H atoms were not searched for. The NCS ligands are shown to be linked to molybdenum(VI) by the N atom and occupy *trans* positions in the octahedral Mo coordination.

Introduction. Le bis(hexaméthylphosphoramide)-bis(isothiocyanato)dioxomolybdène(VI) {[Mo-(hmpa)$_2$(NCS)$_2$O$_2$]} a été préparé par action du thiocyanate d'ammonium sur le dichlorobis(hexaméthyl-phosphoramide)dioxomolybdène(VI) en solution dans l'acétone. On obtient un précipité de chlorure d'ammonium et une solution qui, par évaporation lente, laisse déposer des cristaux de couleur jaune pâle. La formule du composé a été établie en faisant l'analyse élémentaire de ces cristaux.

Le monocristal utilisé mesure environ $0,30 \times 0,25 \times 0,20$ mm. Les spectres d'oscillation et de Weissenberg montrent que le réseau présente la symétrie mono-clinique. Les dimensions de la maille ont été déter-minées à l'aide d'un diffractomètre automatique Enraf–

Nonius CAD-4 utilisant le rayonnement Mo $K\alpha$ à partir des données angulaires de 15 réflexions. Les extinctions systématiques sont celles du groupe $P2_1/b$. En admettant la présence dans la maille de huit unités formulaires, donc de deux groupements [Mo(hmpa)$_2$-(NCS)$_2$O$_2$] dans l'unité asymétrique, la masse volumi-que calculée ($d_x = 1,40$ Mg m^{-3}) est en bon accord avec la masse volumique mesurée à l'aide de mono-cristaux ($d_m = 1,39$ Mg m^{-3}).

Les intensités des réflexions appartenant au domaine défini par $0 \le \theta \le 18°$, $-20 \le h \le 20$, $0 \le k \le 15$ et $0 \le l \le 12$ ont été mesurées avec le diffractomètre déjà cité. Sur les 3915 réflexions mesurées, 2911 vérifient la relation $I > 2\sigma(I)$. Elles ont été corrigées des facteurs de Lorentz et de polarisation et conservées pour la résolution et l'affinement de la structure.

Pour le rayonnement utilisé, le coefficient d'ab-sorption est égal à 0,724 mm^{-1} et les valeurs extrêmes du produit μl sont respectivement 0,145 et 0,217. Aussi, il n'a pas été fait de correction d'absorption.

Les coordonnées approchées des atomes de molyb-dène ont été déduites de la fonction de Patterson tri-dimensionnelle $P(u,v,w)$. Les autres atomes, à l'excep-tion des atomes d'hydrogène, ont ensuite été déterminés progressivement en calculant la densité électronique, puis la série de Fourier des différences ($F_o - F_c$), à l'aide des atomes déjà connus. Le programme d'affine-