Fig. 1. A single anion showing 30% probability ellipsoids.

1987). Comparison of bond lengths and angles in free and complexed ligands has rarely been possible due to the lack of structures of the free ligands. The only structures known to date of this type of ligand are the potassium salt of the present anion determined from photographic data (Coppens, McGillavry, Hovenkamp & Douwes, 1962), the dimethylammonium salt of the isopropyl analog (Kalinin, Andrianov & Struchkov, 1979) and the potassium salt of the benzyl-substituted anion (Hazel & Collin, 1972).

In general the P—S bond lengths are essentially equivalent (in the potassium salt by symmetry). The small asymmetry here [1·954 (3) *vs* 1·944 (2) Å] is much less than observed in the free acids *e.g.* in

diphenyldithiophosphinic acid, P=S = 1·954 (1) Å and P—SH = 2·077 (1) Å (Krebs & Henkel, 1981). The value for the potassium salt was 1·96 (1) Å and in the isopropyl and benzyl analogs the values were 1·974 (6), 1·965 (6), 1·969 (2) and 1·945 (2) Å respectively. The P atoms are formally tetrahedral, the major distortion being the larger angle between the two S atoms [120·1 (1)°] owing to steric effects as has been observed for the cited analogs [118·2° in the potassium salt, 116·6 (3)° for the isopropyl analog and 120·0 (1)° for the benzyl-substituted anion].

On complexation there is typically a small lengthening of the P—S bonds and a concomitant closing of the S—P—S angle.

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Structure of Hexacarbonylbis(pentamethylcyclopentadienyl)dimolybdenum(*Mo—Mo*)

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Abstract. [Mo$_2$(C$_{10}$H$_{15}$)$_2$(CO)$_6$], $M_r = 630\cdot4$, monoclinic, $P2_1/n$, $a = 9\cdot3922$ (4), $b = 9\cdot1125$ (3), $c = 15\cdot5643$ (6) Å, $\beta = 97\cdot319$ (4)°, $V = 1321\cdot24$ Å^3, $Z = 2$, $D_x = 1\cdot584$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0\cdot71073$ Å, $\mu = 0\cdot96$ mm^{-1}, $F(000) = 636$, $T = 293$ K, $R = 0\cdot0245$ for 1818 unique reflections with $F > 4\sigma(F)$. The molecule consists of a mutually bonded dimolybdenum core, each Mo atom being additionally bonded to three carbonyl and one pentamethylcyclopentadienyl ligand, and contains the longest recorded unsupported Mo—Mo bond, 3·281 (1) Å.

Experimental. The compound was isolated in good yield from a reaction between bismuth metal and [Mo$_2$-(η-C$_5$Me$_5$)$_2$(CO)$_4$](Mo$\equiv$Mo), the only other major product being the *cis* isomer of the dimolybdenum tetraoxo compound, [Mo$_2$(η-C$_5$Me$_5$)$_2$(μ-O)$_2$(O)$_2$], which has been previously characterized by X-ray crystallography (Arzoumanian, Baldy, Pierrot & Petrignani, 1985). Reaction is presumed to occur by oxo transfer from the bismuth surface to [Mo$_2$(η-C$_5$Me$_5$)$_2$(CO)$_4$] and subsequent carbonyl loss to give [Mo$_2$(η-C$_5$Me$_5$)$_2$-(μ-O)$_2$(O)$_2$]. Additional molecules of [Mo$_2$(η-C$_5$Me$_5$)$_2$-

Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^4)$

$U_{eq} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$

	x	y	z	U_{eq}
Mo	4636·7 (2)	5000·2 (3)	6003·4 (1)	285 (1)
C(1)	2623 (3)	3514 (3)	6199 (2)	338 (8)
C(2)	3671 (3)	2540 (3)	5940 (2)	307 (8)
C(3)	4905 (3)	2586 (3)	6580 (2)	332 (8)
C(4)	4610 (3)	3592 (3)	7235 (2)	365 (9)
C(5)	3196 (3)	4159 (3)	6998 (2)	371 (9)
C(6)	1096 (3)	3643 (4)	5786 (2)	560 (12)
C(7)	3461 (4)	1481 (3)	5195 (2)	453 (10)
C(8)	6178 (3)	1577 (3)	6628 (2)	522 (11)
C(9)	5547 (4)	3800 (4)	8087 (2)	619 (13)
C(10)	2396 (4)	5115 (4)	7557 (2)	628 (13)
C(11)	5121 (3)	6664 (3)	6769 (2)	412 (9)
O(11)	5395 (3)	7634 (2)	7235 (1)	662 (9)
C(12)	3448 (3)	6589 (3)	5415 (2)	452 (10)
O(12)	2672 (3)	7527 (3)	5183 (1)	721 (10)
C(13)	6716 (3)	5267 (3)	5936 (2)	425 (10)
O(13)	7942 (2)	5393 (3)	6048 (1)	598 (9)

Table 2. *Bond lengths* (Å) *and angles* (°)

Mo–Mo'	3·281 (1)	Mo–C(1)	2·378 (3)
Mo–C(2)	2·416 (3)	Mo–C(3)	2·377 (3)
Mo–C(4)	2·310 (3)	Mo–C(5)	2·313 (3)
Mo–C(11)	1·946 (3)	Mo–C(12)	1·979 (3)
Mo–C(13)	1·984 (3)	C(1)–C(2)	1·421 (4)
C(1)–C(5)	1·418 (4)	C(1)–C(6)	1·499 (4)
C(2)–C(3)	1·429 (3)	C(2)–C(7)	1·503 (4)
C(3)–C(4)	1·424 (4)	C(3)–C(8)	1·503 (4)
C(4)–C(5)	1·429 (4)	C(4)–C(9)	1·508 (4)
C(5)–C(10)	1·499 (5)	C(11)–O(11)	1·151 (4)
C(12)–O(12)	1·152 (4)	C(13)–O(13)	1·148 (4)

C(1)–Mo–C(2)	34·5 (1)	C(1)–Mo–C(3)	58·1 (1)
C(2)–Mo–C(3)	34·7 (1)	C(1)–Mo–C(4)	58·9 (1)
C(2)–Mo–C(4)	58·3 (1)	C(3)–Mo–C(4)	35·3 (1)
C(1)–Mo–C(5)	35·2 (1)	C(2)–Mo–C(5)	58·1 (1)
C(3)–Mo–C(5)	58·9 (1)	C(4)–Mo–C(5)	36·0 (1)
C(1)–Mo–C(11)	119·5 (1)	C(2)–Mo–C(11)	143·6 (1)
C(3)–Mo–C(11)	119·0 (1)	C(4)–Mo–C(11)	87·2 (1)
C(5)–Mo–C(11)	87·7 (1)	C(1)–Mo–C(12)	93·7 (1)
C(2)–Mo–C(12)	118·2 (1)	C(3)–Mo–C(12)	151·4 (1)
C(4)–Mo–C(12)	136·5 (1)	C(5)–Mo–C(12)	102·0 (1)
C(11)–Mo–C(12)	77·7 (1)	C(1)–Mo–C(13)	151·8 (1)
C(2)–Mo–C(13)	118·6 (1)	C(3)–Mo–C(13)	94·3 (1)
C(4)–Mo–C(13)	103·1 (1)	C(5)–Mo–C(13)	137·7 (1)
C(11)–Mo–C(13)	77·4 (1)	C(12)–Mo–C(13)	112·8 (1)
C(1)–Mo–Mo'	112·8 (1)	C(2)–Mo–Mo'	94·8 (1)
C(3)–Mo–Mo'	109·5 (1)	C(4)–Mo–Mo'	144·6 (1)
C(5)–Mo–Mo'	147·9 (1)	C(11)–Mo–Mo'	121·5 (1)
C(12)–Mo–Mo'	74·5 (1)	C(13)–Mo–Mo'	67·9 (1)
Mo–C(1)–C(2)	74·2 (2)	Mo–C(1)–C(5)	69·9 (2)
C(2)–C(1)–C(5)	108·0 (2)	Mo–C(1)–C(6)	129·3 (2)
C(2)–C(1)–C(6)	125·9 (2)	C(5)–C(1)–C(6)	125·4 (3)
Mo–C(2)–C(1)	71·3 (1)	Mo–C(2)–C(3)	71·2 (1)
C(1)–C(2)–C(3)	108·3 (2)	Mo–C(2)–C(7)	129·7 (2)
C(1)–C(2)–C(7)	126·3 (2)	C(3)–C(2)–C(7)	124·9 (2)
Mo–C(3)–C(2)	74·1 (1)	Mo–C(3)–C(4)	69·7 (1)
C(2)–C(3)–C(4)	107·7 (2)	Mo–C(3)–C(8)	129·1 (2)
C(2)–C(3)–C(8)	125·9 (2)	C(4)–C(3)–C(8)	125·7 (2)
Mo–C(4)–C(3)	74·9 (2)	Mo–C(4)–C(5)	72·1 (2)
C(3)–C(4)–C(5)	107·9 (2)	Mo–C(4)–C(9)	126·4 (2)
C(3)–C(4)–C(9)	124·5 (3)	C(5)–C(4)–C(9)	126·9 (3)
Mo–C(5)–C(1)	74·9 (2)	Mo–C(5)–C(4)	71·9 (2)
C(1)–C(5)–C(4)	108·2 (2)	Mo–C(5)–C(10)	125·1 (2)
C(1)–C(5)–C(10)	126·0 (3)	C(4)–C(5)–C(10)	125·3 (2)
Mo–C(11)–O(11)	178·7 (3)	Mo–C(12)–O(12)	170·2 (3)
Mo–C(13)–O(13)	168·2 (3)		

Symmetry operator for Mo': $1-x$, $1-y$, $1-z$.

$[(\text{CO})_4]$ react with free CO to afford $[\text{Mo}_2(\eta\text{-C}_5\text{-Me}_5)_2(\text{CO})_6]$. Crystallization by slow diffusion of hexane into a THF solution of the title compound at 253 K afforded block orange crystals. Crystal size $0·45 \times 0·45 \times 0·15$ mm, Siemens AED2 diffractometer, cell parameters from 2θ values of 32 reflections $(20 < 2\theta < 25°)$, 3807 reflection intensities measured in ω/θ scan mode, scan width 0·47° below $K\alpha_1$ to 0·47° above $K\alpha_2$, scan time 17–68 s, 2θ 3→50°, h 0→11, k −10→4, l −18→18. Semi-empirical absorption correction, transmission factors 0·568–0·652. No significant variation of three standard reflections. 2323 unique reflections $(R_{int} = 0·015)$, 1818 with $F > 4\sigma(F)$. Structure solved by Patterson and difference syntheses, refined by blocked-cascade least squares to minimize $\sum w\Delta^2$; $w^{-1} = \sigma^2(F) + 0·00005F^2$. Anisotropic thermal parameters for all non-H atoms, H atoms constrained to give C–H = 0·96 Å, H–C–H = 109·5°, $U(\text{H}) = 1·2U_{eq}(\text{C})$. $R = 0·0245$, $wR = 0·0271$, slope of normal probability plot = 1·59, $(\Delta/\sigma)_{max} = 0·010$, $(\Delta/\sigma)_{mean} = 0·003$, $(\Delta\rho)_{max} = 0·36$, $(\Delta\rho)_{min} = -0·25$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs: *SHELXTL* (Sheldrick, 1985). Table 1 gives atom parameters and Table 2 bond lengths and angles.* Fig. 1 shows a view of the molecule.

Related literature. The title compound is the permethyl derivative of $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ which has been previously characterized by X-ray diffraction (Adams, Collins & Cotton, 1974) and found to have an Mo—Mo bond length of 3·235 Å. Other examples of compounds containing unsupported Mo—Mo single bonds are $[\text{Mo}_2(\text{CO})_{10}]^{2-}$, 3·123 Å (Handy, Ruff &
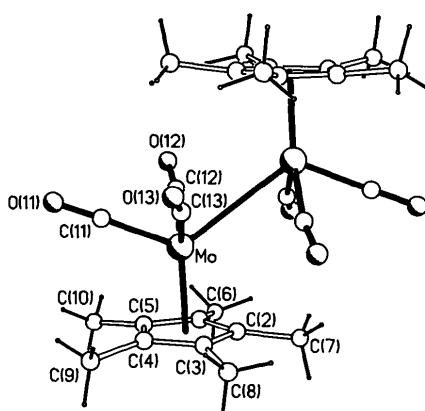
Fig. 1. The molecular structure with the atom-labelling scheme.

Dahl, 1970), $[Mo_2(\eta\text{-}C_5H_4CHPh_2)_2(CO)_6]$, 3·227 Å (Drews & Behrens, 1985), $[Mo_2(\eta\text{-}C_5H_4CH_2CH_2CH_2\text{-}OH)_2(CO)_6]$, 3·213 Å (Coolbaugh, Coots, Santarsiero & Grubbs, 1985), $[Mo_2(\eta\text{-}C_5H_5)_2(CH_3NC)(CO)_5]$, 3·230 Å (Adams, Brice & Cotton, 1973), and $[Mo_2\text{-}(\eta\text{-}C_5H_5)_2\{C(C_6H_4CH_3)_2\}\{N_2C(C_6H_4CH_3)_2\}(CO)_3]$, 3·052 Å (Messerle & Curtis, 1982). The bond length in $[Mo_2(\eta\text{-}C_5Me_5)_2(CO)_6]$ is 3·281 (1) Å and is the longest unsupported Mo–Mo single bond so far observed. Additional features of interest are the *trans* disposition of the C_5Me_5 ligands and the slight bending at carbon in the four carbonyls *cis* to the Mo–Mo bond. Both features are observed in the parent compound, $[Mo_2\text{-}(\eta\text{-}C_5H_5)_2(CO)_6]$ (Adams, Collins & Cotton, 1974).

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Di-μ-carbonyl-nonacarbonyl-μ4-(α–α'-η-diphenylacetylene)-(μ4-diphenylnitrene)-tetraruthenium(4 Ru–Ru)

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Abstract. $[Ru_4(C_{14}H_{10})(C_6H_5N)(CO)_{11}]$, $M_r = 981\cdot71$, monoclinic, $P2_1/c$, $a = 16\cdot315$ (3), $b = 20\cdot037$ (4), $c = 19\cdot749$ (4) Å, $\beta = 95\cdot75$ (1)°, $V = 6424$ (2) Å^3, $Z = 8$, 2 independent molecules/asymmetric unit, $D_x = 2\cdot030$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71073$ Å, $\mu = 18\cdot70$ cm^{-1}, $F(000) = 3680$, $T = 296$ K, $R_F = 2\cdot99\%$ for 7583 observed reflections and 776 parameters. The structure is the phenyl analog of a previously reported (μ4-NH)-(diphenylacetylene)tetraruthenium cluster. The two independent molecules are chemically indistinguishable. The structure is a pentagonal bipyramid with an equatorial plane containing two Ru atoms, the acetylene residue and the nitrene N atom. This plane is capped by two Ru(CO)2 units with two edge-bridging carbonyl groups.

Experimental. Orange crystals from hexane (0·41 × 0·41 × 0·41 mm); Nicolet *R3m* diffractometer with

graphite monochromator; ω scans; lattice parameters from least-squares fit of 25 reflections ($30 \le 2\theta \le 35°$); no absorption correction ($\mu = 18\cdot7$ cm^{-1}, uniform crystal shape, $T_{max}/T_{min} = 1\cdot11$); $2\theta_{max} = 48°$ ($h = \pm19$, $k = +23$, $l = +23$); standard reflections 12,0,2, $\bar{6}$,15,1, $\bar{5}$,4,14. 10 933 reflections collected, 10 090

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

U_{eq} is the equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	2285·1 (3)	5232·5 (2)	4721·1 (2)	33·4 (1)
Ru(2)	3160·3 (3)	6192·3 (2)	4060·3 (2)	32·1 (1)
Ru(3)	1223·9 (3)	6261·2 (2)	4804·5 (2)	30·6 (1)
Ru(4)	2310·9 (3)	7214·8 (2)	4555·0 (2)	29·9 (1)
Ru(1')	3256·6 (2)	4628·6 (2)	8647·6 (2)	28·7 (1)
Ru(2')	4034·6 (3)	3731·5 (2)	9517·2 (2)	29·6 (1)
Ru(3')	3095·1 (3)	2684·7 (2)	9092·7 (2)	28·4 (1)
Ru(4')	2045·3 (2)	3629·1 (2)	8542·7 (2)	28·1 (1)

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