

μ -(η^5 : η^5 -Fulvalene)-bis[dicarbonyl(trimethylphosphine)molybdenum](Mo–Mo)

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Abstract. $[\text{Mo}_2(\text{C}_{10}\text{H}_8)(\text{CO})_4\{\text{P}(\text{CH}_3)_3\}_2]$, $M_r = 584.26$, orthorhombic, $P2_12_12_1$, $a = 12.005$ (1), $b = 12.070$ (1), $c = 15.991$ (1) Å, $V = 2317.1$ (1) Å³, $Z = 4$, $D_m = 1.67$, $D_x = 1.675$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 12.14$ cm⁻¹, $F(000) = 1168$, $T = 293$ K, $R_{\text{final}} = 0.0144$ for 2859 unique observed reflections. The structure of $[(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Mo}_2(\text{CO})_4\{\text{P}(\text{CH}_3)_3\}_2]$ consists of a fulvalene π -bonded to two $\text{Mo}(\text{CO})_2[\text{P}(\text{CH}_3)_3]$ groups. The Mo–Mo bond distance is 3.220 (1) Å. The fulvalene ligand is distorted from planarity with a dihedral angle between the C₅ rings of 27.0° and a torsion angle [Cp(1)–Mo(1)–Mo(2)–Cp(2)] of –24.2°.

Introduction. The synthesis of the title complex was previously reported (Tilset & Volhardt, 1985). The crystal-structure determination was undertaken as part of a continuing study of a series of compounds in which two metals, bound to a common fulvalene ligand, are forced to remain in close proximity.

Experimental. Dark bluish-purple crystals obtained from Dr Mats Tilset. D_m measured by flotation method in a mixture of CCl_4 and CH_2I_2 . Crystals mounted on glass fibers in air using polycyanoacrylate cement. Sample crystal was 0.18 × 0.20 × 0.22 mm. Enraf–Nonius CAD-4 diffractometer; 2θ from 3 to 45°; index range $0 \leq h \leq 12$, $0 \leq k \leq 13$, $-17 \leq l \leq 17$; θ – 2θ scan technique with Mo K α ; 25 reflections with $16 < 2\theta < 23^\circ$ used to refine cell parameters. 3321 total reflections; 3031 unique reflections; 2859 reflections with $(F_o)^2 > 3\sigma(F_o)^2$. No indication of crystal decomposition, no absorption correction needed, ψ -scan variation $\pm 1\%$. Three standard reflections, $\pm 0.1\%$ intensity variation. Structure solved by Patterson methods and refined *via* standard least-squares and Fourier techniques with a PDP 11/60 computer using modified Nonius (Frenz, 1982) SDP software. Function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma(F_o)^2$; p factor = 0.02; non-H atoms refined anisotropically. All H atoms located on a difference map, their positions calculated using idealized geometry and C–H distances constrained to 0.95 Å, but not refined. Isotropic thermal parameters assigned by $B(\text{CH}) = 1 + B_{\text{eq}}(\text{C})$.

The structure factors were calculated for both possible enantiomers, and the set of coordinates giving the better R_{all} , $\Delta R_{\text{all}} = 0.0017$, was assumed the correct choice. Final number of parameters refined = 254, $R = 0.0144$, $wR = 0.0185$, $R_{\text{all}} = 0.0173$; $S = 1.12$. Max. shift/ $\sigma = 0.36$ on final cycle; largest peak on final difference map 0.27 e \AA^{-3} ; secondary-extinction coefficient = $1.38(6) \times 10^{-7}$. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974).

Discussion. The structure of $[(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Mo}_2(\text{CO})_4\{\text{P}(\text{CH}_3)_3\}_2]$ consists of a fulvalene ligand π -bonded to two $\text{Mo}(\text{CO})_2[\text{P}(\text{CH}_3)_3]$ fragments. The Mo atoms are separated by a distance of 3.220 (1) Å. An approximate twofold axis bisects the metal–metal bond. Each trimethylphosphine ligand is coordinated to one Mo atom in a roughly *trans* position relative to the metal–metal bond. Trimethylphosphine and carbonyl ligands bonded to one Mo are staggered with respect to equivalent ligands on the adjacent Mo atom. A drawing of the molecule with the numbering scheme is shown in Fig. 1. Atomic coordinates and final equivalent isotropic thermal parameters are given in Table 1.† Table 2 lists interatomic bond distances and angles.

The cyclopentadienyl rings are twisted 24.2° about the C(15)–C(16) bond axis as a result of the staggered conformation of the ligands. This large torsion angle of 24.2° [measured as Cp(1)–Mo(1)–Mo(2)–Cp(2), where Cp is the centroid of a cyclopentadienyl moiety] is the largest known torsion angle of any compound reported containing a metal–metal bond and the fulvalene ligand (Drage & Volhardt, 1986). Other reported fulvalene complexes containing a metal–metal bond have small torsion angles and eclipsed conformations of the non-fulvalene ligands (Drage & Volhardt, 1986; Abrahamson & Heeg, 1984). To date, one other fulvalene complex, μ -fulvalene-(1-oxacyclopent-2-ylidene)bis(dicarbonylmolybdenum), which con-

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43439 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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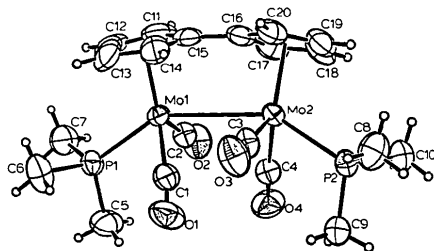


Fig. 1. ORTEP (Johnson, 1965) drawing and numbering scheme of the $[(\eta^2:\eta^2\text{-C}_{10}\text{H}_8)\text{Mo}_2(\text{CO})_4\{\text{P}(\text{CH}_3)_3\}_2]$ molecule. The ellipsoids are scaled to represent 50% of the probability surface. H atoms are shown as arbitrarily small spheres for clarity.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters

	x	y	z	$B_{\text{eq}}^*(\text{\AA}^2)$
Mo(1)	0.03059 (2)	0.06767 (2)	0.07762 (1)	3.325 (4)
Mo(2)	0.01332 (2)	-0.15651 (2)	-0.03077 (1)	2.957 (4)
P(1)	0.08791 (6)	0.25958 (6)	0.08036 (5)	3.63 (1)
P(2)	0.00719 (6)	-0.23860 (6)	-0.16909 (4)	3.45 (1)
O(1)	-0.0394 (2)	0.1574 (2)	-0.0972 (1)	6.25 (5)
O(2)	0.2853 (2)	0.0353 (2)	0.0625 (2)	6.05 (6)
O(3)	-0.1957 (2)	-0.0428 (2)	-0.1046 (2)	5.86 (6)
O(4)	0.2132 (2)	-0.0378 (2)	-0.1187 (1)	5.81 (5)
C(1)	-0.0134 (2)	0.1190 (2)	-0.0340 (2)	4.02 (6)
C(2)	0.1899 (3)	0.0479 (2)	0.0619 (2)	4.10 (6)
C(3)	-0.1131 (2)	-0.0789 (2)	-0.0790 (2)	3.73 (6)
C(4)	0.1389 (2)	-0.0780 (2)	-0.0845 (2)	3.88 (6)
C(5)	0.1703 (3)	0.3074 (3)	-0.0077 (2)	6.23 (9)
C(6)	-0.0228 (3)	0.3622 (3)	0.0852 (3)	6.64 (9)
C(7)	0.1761 (3)	0.3000 (3)	0.1668 (2)	5.25 (8)
C(8)	-0.1236 (3)	-0.3011 (3)	-0.2017 (2)	5.52 (8)
C(9)	0.0352 (4)	-0.1453 (3)	-0.2556 (2)	5.65 (8)
C(10)	0.1023 (3)	-0.3527 (2)	-0.1883 (2)	4.66 (7)
C(11)	0.0385 (4)	-0.0252 (3)	0.2060 (2)	6.52 (9)
C(12)	-0.0025 (4)	0.0812 (3)	0.2213 (2)	8.1 (1)
C(13)	-0.1063 (4)	0.0925 (3)	0.1813 (2)	7.76 (9)
C(14)	-0.1294 (3)	-0.0064 (3)	0.1390 (2)	5.85 (8)
C(15)	-0.0383 (3)	-0.0804 (2)	0.1531 (2)	4.77 (7)
C(16)	-0.0197 (3)	-0.1852 (2)	0.1100 (2)	4.06 (6)
C(17)	-0.1008 (2)	-0.2470 (2)	0.0665 (2)	4.35 (6)
C(18)	-0.0440 (3)	-0.3288 (2)	0.0197 (2)	4.88 (7)
C(19)	0.0703 (3)	-0.3201 (2)	0.0369 (2)	5.23 (7)
C(20)	0.0866 (3)	-0.2323 (3)	0.0910 (2)	4.77 (7)

* Anisotropically refined atoms. The equivalent isotropic thermal parameter is: $B_{\text{eq}} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

tains a metal-metal bond and a staggered ligand conformation, is known. This molecule has a ligand torsion angle of 21.1° (Drage & Volhardt, 1986).

In dinuclear fulvalene complexes, the fulvalene ligand is generally bent from coplanarity to accommodate metal-metal bonding interactions. The dihedral angle, measured between the two planes of the C₅ rings, increases with decreasing metal-metal interatomic distances. Bond distances between the metal centers are longer in the fulvalene complexes than those in similar

Table 2. Bond distances (\AA) and bond angles ($^\circ$)

Mo(1)—Mo(2)	3.220 (1)	P(1)—C(6)	1.818 (4)
Mo(1)—P(1)	2.417 (1)	P(1)—C(7)	1.808 (3)
Mo(1)—C(1)	1.962 (3)	P(2)—C(8)	1.818 (3)
Mo(1)—C(2)	1.943 (3)	P(2)—C(9)	1.815 (3)
Mo(1)—C(11)	2.341 (3)	P(2)—C(10)	1.815 (3)
Mo(1)—C(12)	2.338 (3)	O(1)—C(1)	1.155 (3)
Mo(1)—C(13)	2.354 (4)	O(2)—C(2)	1.156 (4)
Mo(1)—C(14)	2.335 (3)	O(3)—C(3)	1.158 (3)
Mo(1)—C(15)	2.309 (3)	O(4)—C(4)	1.153 (3)
Mo(1)—Cp(1)	2.003 (1)	C(11)—C(12)	1.397 (6)
Mo(2)—P(2)	2.425 (1)	C(12)—C(13)	1.406 (7)
Mo(2)—C(3)	1.943 (3)	C(13)—C(14)	1.401 (5)
Mo(2)—C(4)	1.978 (3)	C(14)—C(15)	1.430 (5)
Mo(2)—C(16)	2.311 (2)	C(15)—C(11)	1.417 (5)
Mo(2)—C(17)	2.343 (3)	C(15)—C(16)	1.458 (4)
Mo(2)—C(18)	2.335 (3)	C(16)—C(17)	1.411 (4)
Mo(2)—C(19)	2.353 (3)	C(17)—C(18)	1.413 (4)
Mo(2)—C(20)	2.324 (3)	C(18)—C(19)	1.404 (5)
Mo(2)—Cp(2)	2.001 (1)	C(19)—C(20)	1.382 (5)
P(1)—C(5)	1.815 (3)	C(20)—C(16)	1.430 (5)
Mo(2)—Mo(1)—P(1)	146.46 (2)	C(7)—P(1)—Mo(1)	116.06 (11)
Mo(2)—Mo(1)—C(1)	76.02 (7)	C(8)—P(2)—C(9)	101.49 (18)
Mo(2)—Mo(1)—C(2)	83.71 (8)	C(8)—P(2)—C(10)	100.38 (15)
Mo(2)—Mo(1)—Cp(1)	97.46 (1)	C(9)—P(2)—C(10)	103.01 (15)
P(1)—Mo(1)—C(1)	77.89 (7)	C(8)—P(2)—Mo(2)	117.21 (11)
P(1)—Mo(1)—C(2)	80.79 (8)	C(9)—P(2)—Mo(2)	115.86 (10)
P(1)—Mo(1)—Cp(1)	116.00 (2)	C(10)—P(2)—Mo(2)	116.42 (11)
C(1)—Mo(1)—C(2)	100.69 (12)	O(1)—C(1)—Mo(1)	174.7 (2)
C(1)—Mo(1)—Cp(1)	136.35 (9)	O(2)—C(2)—Mo(1)	172.0 (3)
C(2)—Mo(1)—Cp(1)	121.74 (8)	O(3)—C(3)—Mo(2)	172.2 (2)
Mo(1)—Mo(2)—P(2)	146.75 (2)	O(4)—C(4)—Mo(2)	175.9 (3)
Mo(1)—Mo(2)—C(3)	81.89 (8)	C(11)—C(12)—C(13)	108.8 (3)
Mo(1)—Mo(2)—C(4)	77.41 (8)	C(12)—C(13)—C(14)	108.2 (4)
Mo(1)—Mo(2)—Cp(2)	97.58 (1)	C(13)—C(14)—C(15)	107.7 (4)
P(2)—Mo(2)—C(3)	79.12 (8)	C(14)—C(15)—C(11)	107.4 (3)
P(2)—Mo(2)—C(4)	79.78 (9)	C(15)—C(11)—C(12)	107.9 (4)
P(2)—Mo(2)—Cp(2)	115.64 (2)	C(11)—C(15)—C(16)	126.2 (4)
C(3)—Mo(2)—C(4)	101.06 (11)	C(14)—C(15)—C(16)	125.7 (3)
C(3)—Mo(2)—Cp(2)	122.82 (8)	C(17)—C(16)—C(15)	125.9 (3)
C(4)—Mo(2)—Cp(2)	134.93 (9)	C(20)—C(16)—C(15)	125.6 (3)
C(5)—P(1)—C(6)	102.40 (18)	C(16)—C(17)—C(18)	107.3 (3)
C(5)—P(1)—C(7)	100.84 (15)	C(17)—C(18)—C(19)	108.4 (3)
C(6)—P(1)—C(7)	102.23 (17)	C(18)—C(19)—C(20)	108.6 (3)
C(5)—P(1)—Mo(1)	116.47 (11)	C(19)—C(20)—C(16)	108.2 (3)
C(6)—P(1)—Mo(1)	116.45 (12)	C(20)—C(16)—C(17)	107.5 (3)

metal dimers, due to the geometric constraints imposed by the ligand (Drage & Volhardt, 1986; Abrahamson & Heeg, 1984; Olthof, 1977; Guggenberger & Tebbe, 1976). The dihedral angle in the title complex has a value of 27.0° which is much larger than expected for the observed metal-metal bond length. In the analogous μ -fulvalene-bis(tricarbonylmolybdenum) complex, the metal-metal bond length is only 0.051 \AA longer while the dihedral angle is 11.7° smaller (Drage & Volhardt, 1986). The unusually large dihedral angle and decrease in the metal-metal bond length were both unexpected and are currently under investigation.

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References

- ABRAHAMSON, H. B. & HEEG, M. J. (1984). *Inorg. Chem.* **23**, 2281–2286.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101, 148–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- DRAGE, J. & VOLHARDT, K. P. C. (1986). *Organometallics*, **5**, 280–297.
- FRENZ, B. A. (1982). *Structure Determination Package*. College Station, Texas, and Enraf–Nonius, Delft. Revised locally by Dr F. J. HOLLANDER.
- GUGGENBERGER, L. J. & TEBBE, F. N. (1976). *J. Am. Chem. Soc.* **98**, 4137–4143.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- OLTHOF, G. J. (1977). *J. Organomet. Chem.* **128**, 367–373.
- TILSET, M. & VOLHARDT, K. P. C. (1985). *Organometallics*, **4**, 2230–2232.

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Structure of *trans*-Bis(aminoethylaminoethanol-*N,N'*)bis(isothiocyanato)nickel(II)

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Abstract. $[\text{Ni}(\text{NCS})_2(\text{C}_4\text{H}_{12}\text{N}_2\text{O})_2]$, $M_r = 383.2$, orthorhombic, *Pbca*, $a = 8.8954$ (11), $b = 14.3450$ (12), $c = 13.6824$ (16) Å, $V = 1745.9$ (3) Å³, $Z = 4$, $D_x = 1.458$ Mg m⁻³, Cu *K*α radiation (graphite-crystal monochromator, $\lambda = 1.54178$ Å), $\mu(\text{Cu } K\alpha) = 3.907$ mm⁻¹, $F(000) = 808$, $T = 290$ K. Final $R = 0.032$, $wR = 0.034$ for 1337 'observed' reflections and 133 variables. The structure is centrosymmetric with Ni²⁺ octahedrally coordinated by the N atoms of the NCS⁻ ions, and the N atoms of the bidentate *N*-(2-hydroxyethyl)ethylenediamine ligands. The five-membered ring Ni–N(1)–C(1)–C(2)–N(2) in the Ni coordination adopts a twist (*T*) conformation with C_2 symmetry. There is an OH...S internal hydrogen bond of 3.332 Å with O–H...S angle of 171°.

Introduction. In continuation of our studies of metal complexes of amino alcohols, we have determined the X-ray structure of the title compound as part of the series. The X-ray crystal structure will complement our spectroscopic studies which indicate a five-membered ring in the Ni coordination as well as reveal the possibility of any hydrogen bonding in the complex. The title compound was prepared by adding 10 cm³ of aminoethylaminoethanol to 10 g of hydrated nickel(II) perchlorate dissolved in 50 cm³ of methanol. To the resulting blue solution a solution of 10 g sodium thiocyanate in 30 cm³ of methanol was added. Mauve

crystals of the title compound separated out overnight. Crystallization was from hot methanol. Elemental analysis confirmed the identity of the complex {found: Ni 15.38, C 31.45, H 6.31, S 16.80, N 22.20%; calculated for $[\text{Ni}(\text{NCS})_2(\text{C}_8\text{H}_{24}\text{N}_4\text{O}_2)]$: Ni 15.34, C 31.36, H 6.27, S 16.72, N 22.18%}.

Experimental. A mauve crystal of dimensions approximately 0.15 × 0.25 × 0.29 mm was used during the measurements. Throughout the experiment Cu *K*α radiation was used with a graphite-crystal monochromator on a Nonius CAD-4 single-crystal diffractometer ($\lambda = 1.54178$ Å). The unit-cell dimensions were determined from the angular settings of 25 high-order reflections. The space group was inferred as *Pbca* (No. 61) from systematic absences ($0kl$ with $k = 2n + 1$; $h0l$ with $l = 2n + 1$ and $hk0$ with $h = 2n + 1$) and from the structure determination. The intensity data of 3692 reflections up to $\theta = 70^\circ$ in the range $0 \leq h \leq 10$, $-17 \leq k \leq 17$, $0 \leq l \leq 16$ were measured, using the ω - 2θ scan technique with a scan angle of 1.00° and a variable scan rate with a maximum scan time of 20 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 minutes. The final drift correction factors were between 1.00 and 1.04. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); an empirical absorption correction was applied, using ψ scans (North, Phillips & Mathews, 1968) (correction factors were in the range 0.88 to 1.00). Symmetry-equivalent

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