References

Cowie, M., Gleizes, A., Grynkewich, G. W., Kalina, D. W., McClure, M. S., Scaringe, R. P., Teitelbaum, R. C., Ruby, S. L., Ibers, J. A., Kannewurf, C. R. & Marks, T. J. (1979). *J. Am. Chem. Soc.* **101**, 2921–2936.

Endres, H. (1982). *Angew. Chem.* **94**, 548–549; *Angew. Chem. Int. Ed. Engl.* **21**, 524; *Angew. Chem. Suppl.* pp. 1309–1321.

Endres, H. (1984*a*). *Angew. Chem.* **96**, 993–994; *Angew. Chem. Int. Ed. Engl.* **23**, 999–1000.

Endres, H. (1984*b*). *Z. Anorg. Allg. Chem.* **513**, 78–88.

Endres, H. (1985). *Acta Cryst.* C**41**, 1047–1049.

Endres, H., Bongart, A., Nöthe, D., Hennig, I., Schweitzer, D., Schäfer, H., Helberg, H. W. & Flandrois, S. (1985). *Z. Naturforsch. Teil B*, **40**, 489–495.

Endres, H. & Jannack, T. (1980). *Acta Cryst.* B**36**, 2136–2138.

Endres, H., Keller, H. J., Mégnamisi-Bélombé, M., Moroni, W., Pritzkow, H., Weiss, J. & Comès, R. (1976). *Acta Cryst.* A**32**, 954–957.

Endres, H. & Schendzielorz, M. (1984). *Acta Cryst.* C**40**, 453–456.

Hoffman, B. M. & Ibers, J. A. (1983). *Acc. Chem. Res.* **16**, 15–21.

Hunziker, M., Hilti, B. & Rihs, G. (1981). *Helv. Chim. Acta*, **64**, 82–89.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Pearse, G. A. Jr & Pflaum, R. T. (1959). *J. Am. Chem. Soc.* **81**, 6505–6508.

Sheldrick, G. M. (1983). *SHELXTL. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

STRUCSY (1984). *Structure System Program Package.* Stoe, Darmstadt, Federal Republic of Germany.

Tschugaeff, L. & Surenjanz, J. (1907). *Chem. Ber.* **40**, 181–185.

Wenger, P. E., Monnier, D. & Kapétanidis, I. (1957). *Helv. Chim. Acta*, **40**, 1456–1468.

Acta Cryst. (1985). C**41**, 1426–1428

Structure of 1,1,2-Tricarbonyl-μ-(dimethyl 2-butynedioate-μ-C^2;μ-C^3)-(2-3-η-dimethyl 2-butynedioate)-μ-(1–5:1′–5′-η-fulvalene)-dimolybdenum(*Mo–Mo*), $[Mo_2(C_{10}H_8)(C_6H_6O_4)_2(CO)_3]$

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(*Received* 20 *February* 1985; *accepted* 31 *May* 1985)

Abstract. $M_r = 687{\cdot}9$, monoclinic, $P2_1/c$, $a = 9{\cdot}6984\,(6)$, $b = 15{\cdot}4379\,(21)$, $c = 16{\cdot}4863\,(17)$ Å, $\beta = 95{\cdot}880\,(7)°$, $V = 2455{\cdot}4\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}86$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 10{\cdot}6$ cm^{-1}, $F(000) = 1368$, $T = 298$ K, final $R = 0{\cdot}022$, $wR = 0{\cdot}029$ for 2692 $[I > 3\sigma(I)]$ unique reflections. Important features include the lack of multiple alkyne coupling, a contracted Mo—Mo distance of 2·906 (1) Å, a bridging (4e$^-$-donating) alkyne C—C distance of 1·374 (4) Å and a singly coordinating (2e$^-$-donating) alkyne C—C distance of 1·265 (4) Å. The bridging alkyne is slightly displaced towards the singly coordinating alkyne ligand, in the more sterically hindered direction.

Introduction. The unusual structural constraints imposed by a fulvalene ligand anchored to a molybdenum dinuclear center should result in interesting structural and chemical properties relative to analogous η^5-C_5H_5Mo dimers. The multiple alkyne coupling in η^5-C_5H_5Mo dimers (Beck, Knox, Stansfield, Stone, Winter & Woodward, 1982; Green, Norman & Orpen, 1981; Knox, Stansfield, Stone, Winter & Woodward, 1978) is nearly always present with rare exceptions (Cotton, Schwortzer & Shamshoum, 1983; Davidson, 1983; Boag, Green, Howard, Spencer, Stansfield, Thomas, Stone & Woodward, 1980) and is especially noteworthy. The study of this class of compounds by Drage and co-workers led to the discovery of novel modes of ligand binding, most notably with respect to alkyne coupling.

Synthetic techniques used are described elsewhere (Drage, Tilset, Voldhardt & Weidman, 1985).

Experimental. Long, thin red-orange tabular single crystal (0·17 × 0·40 × 0·05 mm idealized dimensions), mounted with epoxy glue on a glass fiber. Cell parameters and orientation matrix by least-squares refinement using 24 reflections, $28 \leq 2\theta \leq 33°$, measured on an Enraf–Nonius CAD-4 diffractometer (controlled by a DEC PDP 8/a with an RK05 disk), with graphite-monochromatized Mo $K\alpha$ radiation. Total of 3494 reflections measured using θ–2θ scans for 2θ from 3 to 45° (h −10 to 10, k 0 to 15, l 0 to 15); scan range $(0{\cdot}6 + 0{\cdot}35\tan\theta)°$, scan speeds min. 0·9, max. 6·6° min^{-1}; corrections for Lorentz–polarization and absorption effects (max. transmission 94%, min. 66%, average 91%); intensities of three standard

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reflections $(\bar{2}\bar{3}0, 016, 0\bar{4}\bar{3})$ measured periodically showed no decay during data collection; 3210 unique reflections with 518 reflections $[I \leq 3\sigma(I)]$ considered unobserved; systematic absences $0k0$, k = odd and $h0l$, l = odd uniquely indicated $P2_1/c$. Positions of Mo atoms obtained from Patterson synthesis; Fourier synthesis located all other non-hydrogen atoms; H atoms placed at idealized positions 0·95 Å from appropriate C atoms; final full-matrix least-squares refinements included positional and anisotropic thermal parameters for all non-H atoms; final $R = 0{\cdot}022$, $wR = 0{\cdot}029$, $S = 1{\cdot}25$; quantity minimized was $\sum w(F_o - F_c)^2$; $w = [\sigma_0^2(F_o^2) + (pF^2)^2]$, where p is the factor used to lower the weight of intense reflections; $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0·07; final difference Fourier height maximum 0·610 e Å^{-3}, minimum 0·138 e Å^{-3}; no correction for secondary extinction; atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs: Enraf–Nonius (1980) *SDP* program package.

Table 1. *Positional parameters and their estimated standard deviations*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}(Å^2)
Mo(1)	0·70887 (3)	0·23714 (2)	0·28728 (2)	1·799 (6)
Mo(2)	0·41268 (3)	0·21088 (2)	0·29025 (2)	1·976 (6)
O(1)	0·6608 (3)	0·0544 (2)	0·4302 (1)	3·35 (6)
O(2)	0·5587 (3)	−0·0253 (2)	0·3279 (2)	4·04 (7)
O(3)	0·6801 (3)	0·0759 (2)	0·1273 (2)	4·33 (7)
O(4)	0·4553 (3)	0·0583 (2)	0·1205 (2)	6·03 (8)
O(5)	1·0163 (3)	0·1094 (2)	0·1434 (2)	4·24 (7)
O(6)	0·9372 (3)	0·2379 (2)	0·0982 (2)	4·71 (7)
O(7)	0·9089 (3)	−0·0002 (2)	0·3217 (2)	3·92 (7)
O(8)	1·0245 (3)	0·0957 (2)	0·4045 (2)	3·99 (7)
O(9)	0·2314 (3)	0·0407 (2)	0·2727 (2)	4·19 (7)
O(10)	0·3202 (3)	0·2664 (2)	0·1105 (2)	4·60 (7)
O(11)	0·6395 (3)	0·3078 (2)	0·1080 (2)	4·52 (7)
C(1)	0·7328 (4)	0·2699 (3)	0·4264 (2)	2·83 (8)
C(2)	0·8619 (4)	0·2926 (3)	0·3991 (2)	2·92 (8)
C(3)	0·8394 (4)	0·3587 (3)	0·3403 (2)	3·14 (9)
C(4)	0·6954 (4)	0·3776 (2)	0·3314 (2)	2·77 (8)
C(5)	0·6299 (4)	0·3244 (2)	0·3864 (2)	2·46 (8)
C(6)	0·4816 (4)	0·3118 (2)	0·3869 (2)	2·43 (7)
C(7)	0·4197 (4)	0·2437 (3)	0·4291 (2)	2·90 (8)
C(8)	0·2790 (4)	0·2383 (3)	0·3998 (2)	3·35 (9)
C(9)	0·2507 (4)	0·3030 (3)	0·3394 (2)	3·40 (9)
C(10)	0·3749 (4)	0·3485 (2)	0·3304 (2)	2·99 (8)
C(11)	0·6758 (5)	−0·0221 (3)	0·4807 (3)	4·8 (1)
C(12)	0·6012 (4)	0·0433 (2)	0·3540 (2)	2·33 (8)
C(13)	0·5888 (3)	0·1253 (2)	0·3094 (2)	1·88 (7)
C(14)	0·5670 (4)	0·1424 (2)	0·2273 (2)	2·03 (7)
C(15)	0·5588 (4)	0·0891 (2)	0·1529 (2)	2·30 (8)
C(16)	0·6870 (5)	0·0276 (3)	0·0530 (2)	4·1 (1)
C(17)	1·0886 (5)	0·0995 (3)	0·0720 (3)	4·8 (1)
C(18)	0·9451 (4)	0·1825 (3)	0·1490 (2)	2·55 (8)
C(19)	0·8777 (4)	0·1836 (2)	0·2246 (2)	2·35 (7)
C(20)	0·8766 (4)	0·1446 (2)	0·2919 (2)	2·31 (8)
C(21)	0·9452 (4)	0·0794 (3)	0·3462 (2)	2·78 (8)
C(22)	0·9755 (5)	−0·0699 (3)	0·3689 (3)	5·5 (1)
C(23)	0·2973 (4)	0·1017 (2)	0·2750 (2)	2·71 (8)
C(24)	0·3563 (4)	0·2445 (3)	0·1754 (2)	2·84 (8)
C(25)	0·6651 (4)	0·2825 (3)	0·1722 (2)	2·81 (8)

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

C(1)–C(2)	1·417 (5)	C(1)–C(2)–C(3)	108·50 (32)
C(2)–C(3)	1·408 (5)	C(2)–C(3)–C(4)	107·59 (31)
C(3)–C(4)	1·420 (5)	C(3)–C(4)–C(5)	108·29 (31)
C(4)–C(5)	1·421 (4)	C(4)–C(5)–C(1)	107·50 (30)
C(5)–C(1)	1·415 (5)	C(5)–C(1)–C(2)	108·03 (30)
C(5)–C(6)	1·453 (5)	C(6)–C(7)–C(8)	108·60 (32)
C(6)–C(7)	1·427 (5)	C(7)–C(8)–C(9)	108·15 (32)
C(7)–C(8)	1·402 (5)	C(8)–C(9)–C(10)	108·55 (32)
C(8)–C(9)	1·418 (5)	C(9)–C(10)–C(6)	107·48 (31)
C(9)–C(10)	1·415 (5)	C(10)–C(6)–C(7)	107·22 (30)
C(10)–C(6)	1·436 (5)	C(18)–C(19)–C(20)	141·81 (33)
C(13)–C(14)	1·374 (4)	C(19)–C(20)–C(21)	145·26 (32)
C(14)–C(15)	1·473 (4)	C(12)–C(13)–C(14)	131·13 (28)
C(15)–O(4)	1·187 (4)	C(13)–C(14)–C(15)	134·65 (29)
C(15)–O(3)	1·305 (4)	Mo(1)–C(13)–Mo(2)	85·25 (11)
O(3)–C(16)	1·442 (4)	Mo(1)–C(14)–Mo(2)	83·73 (10)
C(22)–O(7)	1·442 (5)	C(13)–Mo(1)–C(20)	83·15 (11)
O(7)–C(21)	1·330 (4)	C(14)–Mo(1)–C(19)	90·04 (11)
C(21)–O(8)	1·194 (4)	C(13)–Mo(2)–C(14)	36·94 (11)
C(21)–C(20)	1·460 (5)	C(13)–Mo(1)–C(14)	33·83 (11)
C(20)–C(19)	1·265 (4)	C(19)–Mo(1)–C(20)	90·59 (11)
Mo(1)–Mo(2)	2·906 (1)		

Discussion. The final atomic coordinates are listed in Table 1 and pertinent bond distances and angles in Table 2.* Fig. 1 shows a view of the molecule, with the atomic numbering scheme. Fig. 2 shows a stereoview of the crystal packing.

In contrast to the large number of known η^5-C_5H_5Mo dimers, the alkyne units in this configuration remain

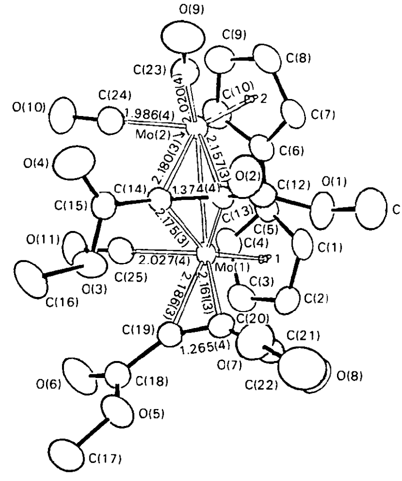

Fig. 1. A view of the molecule showing the atom numbering and some distances (Å) [Mo(1)–C(13) 2·134 (3) Å].

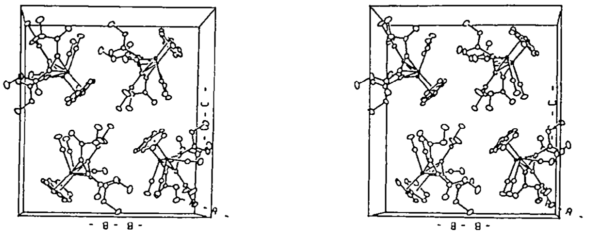

Fig. 2. A stereoview of the molecular packing.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42268 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

uncoupled. The Mo—Mo bond distance is 2·906 (1) Å, shorter by 0·33 Å than in analogous $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ complexes (Adams, Collins & Cotton, 1974) and 0·05–0·08 Å shorter than in alkyne complexes of the latter (Bailey, Chisholm, Cotton & Rankel, 1978). These trends compare favorably with the contracted W—W distance of 2·987 Å in $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4C_2H_2$ (Ginley, Bock, Wrighton, Fischer, Tipton & Bau, 1978) and the W—W distance of 3·347 Å of an alkyne-deficient complex, hexacarbonyl-μ-(1–5:1′–5′-η-fulvalene)-ditungsten (Abrahamson & Heeg, 1985).

The bridging alkyne C—C distance of 1·374 (4) Å and the singly bound alkyne C—C distance of 1·265 (4) Å are consistent with $4e^-$- and $2e^-$-donating ligands. This is also supported by the similarity between the average terminal and average bridging Mo—C(alkyne) distances. Interestingly, the bridging alkyne ligand is not symmetrically oriented with respect to the dinuclear framework; it is displaced slightly towards the singly coordinating alkyne, in the more sterically hindered direction.

The crystal structure analysis was performed by the authors at the UC Berkeley X-ray Diffraction Facility (CHEXRAY) under the supervision of Dr F. J. Hollander, Professor K. Raymond, Professor S. H. Kim and Mr R. Scarrow as part of a requirement for Chemistry 295.

References

Abrahamson, H. B. & Heeg, M. J. (1985). *Inorg. Chem.* In the press.

Adams, R. D., Collins, D. M. & Cotton, F. A. (1974). *Inorg. Chem.* **13**, 1086–1090.

Bailey, W. I., Chisholm, M. H., Cotton, F. A. & Rankel, L. A. (1978). *J. Am. Chem. Soc.* **100**, 5764–5773.

Beck, J. A., Knox, S. A. R., Stansfield, R. F. D., Stone, F. G. A., Winter, M. J. & Woodward, P. (1982). *J. Chem. Soc. Dalton Trans.* pp. 195–200.

Boag, N. M., Green, M., Howard, J. A. K., Spencer, J. L., Stansfield, R. F. D., Thomas, M. D. O., Stone, F. G. A. & Woodward, P. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2182–2190.

Cotton, F. A., Schwortzer, W. & Shamshoum, E. S. (1983). *Organometallics*, **2**, 1167–1171.

Davidson, J. L. (1983). *J. Chem. Soc. Dalton Trans.* pp. 1667–1670.

Drage, J. S., Tilset, M., Volhardt, K. C. & Weidman, T. W. (1985). *J. Am. Chem. Soc.* In the press.

Enraf–Nonius (1980). *SDP* program package. Enraf–Nonius, Delft.

Ginley, D. S., Bock, C. R., Wrighton, M. S., Fischer, B., Tipton, D. L. & Bau, R. (1978). *J. Organomet. Chem.* **157**, 41–50.

Green, M., Norman, N. C. & Orpen, A. G. (1981). *J. Am. Chem. Soc.* **103**, 1269–1271.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor, D. Reidel, Dordrecht.)

Knox, S. A. R., Stansfield, R. F. D., Stone, F. G. A., Winter, M. J. & Woodward, P. (1978). *J. Chem. Soc. Chem. Commun.* pp. 221–223.

Acta Cryst. (1985). C**41**, 1428–1431

cis-Dichlorobis(tetrahydrothiophene 1-oxide)platinum(II), $[PtCl_2(C_4H_8OS)_2]$

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(*Received* 11 *December* 1984; *accepted* 31 *May* 1985)

Abstract. $M_r = 474{\cdot}34$, monoclinic, $P2_1/c$, $a = 11{\cdot}273\ (5)$, $b = 19{\cdot}548\ (7)$, $c = 9{\cdot}885\ (4)$ Å, $\beta = 142{\cdot}61\ (2)^\circ$, $V = 1322{\cdot}9\ (9)$ Å^3, $Z = 4$, $D_x = 2{\cdot}381$, $D_m = 2{\cdot}38\ (1)$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 11{\cdot}407$ mm^{-1}, $F(000) = 896$, $T = 295$ K, $R = 0{\cdot}034$ for 2547 unique observed reflections. Pt has *cis* square-planar coordination to two Cl and to two S atoms of the tetrahydrothiophene 1-oxide ligands. The bond distances are Pt—Cl = 2·309 (3), 2·312 (3) Å and Pt—S = 2·228 (2), 2·248 (3) Å. The packing consists of layers of molecules parallel to the *ab* plane and centered at $z = 0$.

Introduction. For several years, we have been involved in a study of Pt–Me_2SO compounds. The aqueous reaction of K_2PtCl_4 with Me_2SO gives *cis*-$[PtCl_2(Me_2SO)_2]$ (Melanson & Rochon, 1975). The corresponding Pd^{II} complex is the *trans* isomer (Bennett, Cotton, Weaver, Williams & Watson, 1967). With other sulfoxide ligands (L), IR data have shown that the $[PdCl_2L_2]$ complexes have the *trans* S-bonded configuration. In the corresponding Pt^{II} compounds, IR data support a *cis* configuration except when L is a very bulky ligand like bis(3-methylbutyl) sulfoxide (Price, Williamson, Schramm & Wayland, 1972). The $(d\text{–}d)\pi$

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