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Acta Cryst. (1988). C**44**, 461–463

gauche Conformer of Bis[tricarbonyl(cyclopentadienyl)molybdenum]

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(*Received* 12 *October* 1987; *accepted* 2 *December* 1987)

Abstract. $[\{Mo(CO)_3(C_5H_5)\}_2]$, $M_r = 490{\cdot}1$, monoclinic, $I2$ (non-conventional setting of $C2$, No. 5), $a = 10{\cdot}332\,(1)$, $b = 8{\cdot}009\,(1)$, $c = 10{\cdot}366\,(1)$ Å, $\beta = 109{\cdot}063\,(9)°$, $V = 810{\cdot}8$ Å^3, $Z = 2$, $D_x = 2{\cdot}01$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 15{\cdot}4$ cm^{-1}, $F(000) = 476$, $T = 295$ K, $R = 0{\cdot}047$ for 613 observed reflections. The asymmetric unit is one-half of the dimeric molecule, which has C_2 (2) symmetry. The Mo—Mo bond is 3·2239 (11) Å. Each Mo atom is coordinated to three C (carbonyl) at 1·94–1·97 Å and five C (Cp) at 2·27–2·39 Å. A remarkable feature of the structure is an intramolecular contact of 2·44 (2) Å between two carbon atoms separated by three bonds.

Introduction. The stable (*trans*) conformer (1) of the title compound (2) was one of the first organometallic structures to be reported (Wilson & Shoemaker, 1956, 1957), its preparation having been reported only slightly earlier (Wilkinson, 1954; Cotton, Liehr & Wilkinson, 1955). We obtained crystals of (2) as a minor product in the reaction of $Mo(Cp)(CO)_3Cl$ (3) with Me_3SiNMe_2 (4), a reaction being carried out to prepare the species $[\{Mo(Cp)(CO)(NMe_2)\}_2]$ (Keable & Kilner, 1987).

Experimental. A freshly prepared toluene solution of (4) (from $LiNMe_2$ and Me_3SiCl in toluene, the precipitated LiCl having been filtered off) was reacted with (3) at 320 K. Small bright-red plates were found in the crude yield of this reaction, and one with dimensions $0{\cdot}25 \times 0{\cdot}25 \times 0{\cdot}025$ mm was selected for a structure determination. Enraf–Nonius CAD-4 diffractometer. Mo $K\alpha$ radiation, graphite monochromator. Lattice parameters refined from the setting angles for 18

0108-2701/88/030461-03$03.00

reflections with θ between 8·8 and 11·0°. 817 data collected, $2 < \theta < 25°$, $-12 \le h \le 12$, $0 \le k \le 9$, $0 \le l \le 12$. Intensities of two standard reflections were followed during data collection, and no significant decay was observed. A small (maximum 15%) absorption correction was applied based on azimuthal data for 031 (North, Phillips & Mathews, 1968). Merging of equivalent data ($R = 0{\cdot}02$) left 772 independent data, of which the 613 with $I > 3\sigma(I)$ were used to solve and refine the structure.

Scattering factors and anomalous corrections from *International Tables for X-ray Crystallography* (1974). Structure solution by heavy-atom method, a cyclopentadienyl ring being easily selected from the pseudo-centrosymmetric electron density synthesis phased on Mo. Molybdenum atom refined anisotropically, other non-H atoms isotropically. Attempts to refine other atoms anisotropically did not improve the results, so, in view of the poor quality of crystals and data, refinement was terminated at this stage. H atoms included in idealized positions to give C—H 1·08 Å and both H—C—C angles equal to $\frac{1}{2}(360° - \angle\text{C—C—C})$. Full-matrix least-squares refinement on F (*SHELX76*; Sheldrick, 1976) with $w^{-1} = \sigma^2(F) + 0{\cdot}0011F^2$. Final $R = 0{\cdot}047$, $wR = 0{\cdot}064$, $S = 1{\cdot}3$ based on 53 parameters. Maximum shift/e.s.d. in last cycle 0·13, max. and min. ripple in difference electron density map: 1·1 and $-1{\cdot}0$ e Å^{-3}. Final atomic coordinates and thermal parameters are given in Table 1.*

Table 1. *Fractional coordinates of atoms with e.s.d.'s*

	x	y	z	U_{eq}(Å^2)
Mo	0·13874 (9)	0	−0·03909 (10)	0·0354 (6)
C(0)	0·2982 (21)	0·145 (3)	0·0163 (21)	0·054 (4)
O(0)	0·3874 (15)	0·2337 (23)	0·0483 (15)	0·067 (4)
C(1)	0·0546 (16)	0·2197 (20)	−0·0880 (16)	0·037 (3)
O(1)	0·0142 (14)	0·3482 (18)	−0·1273 (14)	0·059 (3)
C(2)	0·1854 (13)	0·0294 (21)	0·1596 (12)	0·034 (3)
O(2)	0·2251 (11)	0·0386 (16)	0·2781 (11)	0·051 (3)
C(3)	0·0780 (21)	−0·115 (3)	−0·2590 (22)	0·058 (5)
C(4)	0·2144 (20)	−0·086 (3)	−0·2106 (21)	0·057 (5)
C(5)	0·2729 (19)	−0·198 (3)	−0·0980 (21)	0·053 (5)
C(6)	0·1633 (18)	−0·2905 (23)	−0·0744 (18)	0·046 (4)
C(7)	0·0461 (20)	−0·241 (3)	−0·1739 (21)	0·054 (5)

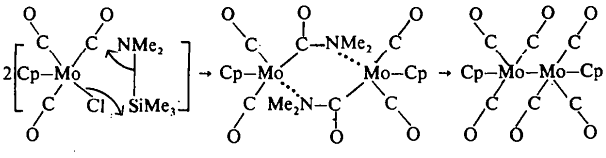
Anisotropic vibration parameters for molybdenum

U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
0·0257 (5)	0·0385 (6)	0·0393 (5)	0·0014 (16)	0·0138 (4)	0·0051 (13)

Discussion. A stereoscopic drawing of the molecular structure, together with its numbering system, is given as Fig. 1 (*PLUTO*; Motherwell & Clegg, 1978). Bond lengths, angles, and selected torsion angles about the Mo—Mo bond are given in Table 2 (*CALC*; Gould & Taylor, 1983). In this table atoms with a prime (′) are related to those without by the symmetry operation $(-x, y, -z)$. The unit cell of (2) is very similar to that of (1) (Wilson & Shoemaker, 1956), which may be transformed to give $a = 10{\cdot}38$, $b = 8{\cdot}04$, $c = 10{\cdot}38$ Å, $\beta = 109{\cdot}0°$, space group $P2_1/n$.

In both conformers, the geometry at Mo can be least unsatisfactorily described as distorted octahedral, with Mo′ occupying one site, and the Cp ring occupying two. These two positions may be taken to correspond roughly to C(3) and the midpoint of C(5)—C(6), given as Y in the tables. The *trans* positions are then occupied by Mo′ and C(0), C(1) and Y, and C(2) and C(3). The conformational difference between the molecules of (1) (site symmetry $\bar{1}$) and (2) (site symmetry 2) may be expressed in terms of the dihedral angle X—Mo—Mo′—X', where X is the centre of gravity of a Cp ring. In (1), this is required by symmetry to be 180°, while in (2), it is ±69·9 (8)°. We would assume that in the absence of chirally selective reagents equal amounts of both enantiomers were formed. While the absolute hand of the crystal used is probably as given, no significant degree of discrimination was possible. The bond lengths and angles in (2) are very similar to those in (1). The metal–metal bond is very slightly longer in (2). In both compounds, the Mo—C (carbonyl) bond lengths are essentially equal, while the bonds from Mo to the C (Cp) atoms furthest from the other Mo atom [here C(4) and C(5)] are shorter than the other Mo—C(Cp) bonds. Also, both compounds have one carbonyl group [here C(0)—O(0)] which makes a much larger angle with the Mo—Mo′ bond than do the other two, and the distortion from 180° of the Mo—C—O angle is least for this carbonyl. The other two Mo—C—O angles deviate significantly from linearity, and these are bent to minimize oxygen contacts where C···C contacts are particularly close in both (1) and (2). The shortest in (2) is C(1)···C(1′): 2·44 (2), while C(1)···C(2′) is 2·80 (2) Å. As may be seen in Fig. 1, relief of strain by rotation about Mo—Mo′ to lengthen C(1)···C(1′) would shorten both C(1)···C(2′) and the symmetry related C(2)···C(1′) as well as bringing the two Cp groups closer to an unfavourable eclipsed conformation. In (1), there is also a symmetry-related pair of C···C contacts at 2·80 Å.

The formation of this unexpected conformer is probably best explained by the following scheme:



(5) (*trans*) (1) (*trans*)

(3) (4) (6) (*cis*) (2) (*gauche*)

$+2\text{SiMe}_3\text{Cl}$

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* Lists of structure factors, complete bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44591 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *selected bond angles* (°) *and torsion angles* (°)

Mo—Mo′	3·2239 (11)	Mo—*Y*	2·234 (19)
Mo—C(0)	1·943 (21)	C(0)—O(0)	1·12 (3)
Mo—C(1)	1·955 (16)	C(1)—O(1)	1·135 (22)
Mo—C(2)	1·971 (14)	C(2)—O(2)	1·163 (19)
Mo—C(3)	2·345 (22)	C(3)—C(4)	1·35 (3)
Mo—C(4)	2·271 (21)	C(3)—C(7)	1·45 (3)
Mo—C(5)	2·316 (21)	C(4)—C(5)	1·44 (3)
Mo—C(6)	2·382 (19)	C(5)—C(6)	1·44 (3)
Mo—C(7)	2·395 (21)	C(6)—C(7)	1·37 (3)
Mo—*X*	2·011 (19)		

Mo′—Mo—C(0)	131·6 (6)	C(1)—Mo—*X*	128·6 (7)
Mo′—Mo—C(1)	73·1 (5)	C(1)—Mo—*Y*	153·4 (7)
Mo′—Mo—C(2)	70·8 (4)	C(2)—Mo—C(3)	163·6 (7)
Mo′—Mo—C(3)	105·5 (5)	C(2)—Mo—*X*	135·6 (7)
Mo′—Mo—*X*	115·3 (5)	C(2)—Mo—*Y*	110·6 (6)
Mo′—Mo—*Y*	118·4 (5)	C(3)—Mo—*Y*	56·3 (7)
C(0)—Mo—C(1)	78·5 (8)	Mo—C(0)—O(0)	177·5 (19)
C(0)—Mo—C(2)	74·1 (8)	Mo—C(1)—O(1)	171·7 (15)
C(0)—Mo—C(3)	116·9 (8)	Mo—C(2)—O(2)	173·1 (13)
C(0)—Mo—*X*	113·1 (8)		
C(0)—Mo—*Y*	104·5 (8)		
C(1)—Mo—C(2)	95·7 (6)		
C(1)—Mo—C(3)	98·4 (7)		

C(0)—Mo—Mo′—C(0′)	73·9 (12)	C(1)—Mo—Mo′—*Y*′	166·5 (7)
C(0)—Mo—Mo′—C(1′)	17·2 (10)	C(2)—Mo—Mo′—C(2′)	165·5 (6)
C(0)—Mo—Mo′—C(2′)	119·7 (10)	C(2)—Mo—Mo′—C(3′)	−31·3 (7)
C(0)—Mo—Mo′—C(3′)	−77·0 (10)	C(2)—Mo—Mo′—*X*′	−62·3 (7)
C(0)—Mo—Mo′—*X*′	−108·1 (10)	C(2)—Mo—Mo′—*Y*′	−91·0 (7)
C(0)—Mo—Mo′—*Y*′	−136·8 (10)	C(3)—Mo—Mo′—C(3′)	132·0 (8)
C(1)—Mo—Mo′—C(1′)	−39·6 (7)	C(3)—Mo—Mo′—*Y*′	72·3 (8)
C(1)—Mo—Mo′—C(2′)	62·9 (7)	*X*—Mo—Mo′—*X*′	69·9 (8)
C(1)—Mo—Mo′—C(3′)	−133·8 (8)	*Y*—Mo—Mo′—*Y*′	12·6 (8)
C(1)—Mo—Mo′—*X*′	−164·8 (8)		

The reaction of (3) with (4) could result in the attack of the nitrogen at a carbonyl to form $SiMe_3Cl$ and a reactive (16-electron) intermediate which will dimerize to (5) or (6). These are two stereoisomers, in which the entering nitrogen is *trans* or *cis* respectively to the other carbamoyl ligand, the *cis*-form being statistically twice as likely. Subsequent cleavage of the carbamoyl groups with the formation of a Mo—Mo bond would give (1) or (2) and organonitrogen material (not identified). Restricted rotation about the Mo—Mo bond, as noted above, will prevent conversion of (2) to (1).

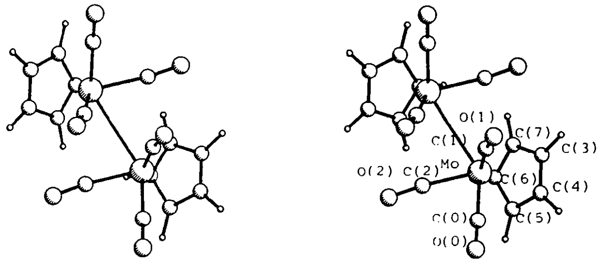

Fig. 1. View of (2) along the molecular twofold axis.

We thank the Science and Engineering Council (UK) for a studentship (to JB).

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Acta Cryst. (1988). C**44**, 463–465

Structure of *cis*-Bis(2,2′-bipyridine-*N*,*N*′)dichloromanganese(II)

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(*Received* 23 *June* 1987; *accepted* 23 *November* 1987)

Abstract. $[Mn(C_{10}H_8N_2)_2Cl_2]$, $M_r = 438{\cdot}22$, monoclinic, $P2_1/c$, $a = 8{\cdot}590\,(2)$, $b = 14{\cdot}415\,(5)$, $c = 15{\cdot}735\,(5)$ Å, $\beta = 98{\cdot}09\,(2)°$, $V = 1929\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}51$, $D_x = 1{\cdot}51$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 10{\cdot}1$ cm^{-1}, $F(000) = 892$, $T = 295$ K, $R = 0{\cdot}041$ for 2173 observed reflections. The Mn atom is distorted octahedral, being coordinated to four N and two Cl atoms. The basal plane is formed by the two Cl and two N atoms [N(2), N(4)] of the different bpy molecules and the apical positions are occupied by the two remaining N atoms [N(1), N(3)]. The *M*—N bond lengths vary from 2·264 (3) to 2·353 (3) Å; the

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0108-2701/88/030463-03$03.00