

## CRYSTAL AND MOLECULAR STRUCTURE OF TRICLINIC $[\text{C}_5\text{H}_5(\text{CO})_2\text{Mo}]_2(\mu, \eta^2\text{-C}\equiv\text{NC}_6\text{H}_5)$ AND COMPARISON WITH ITS MONOCLINIC FORM

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### Summary

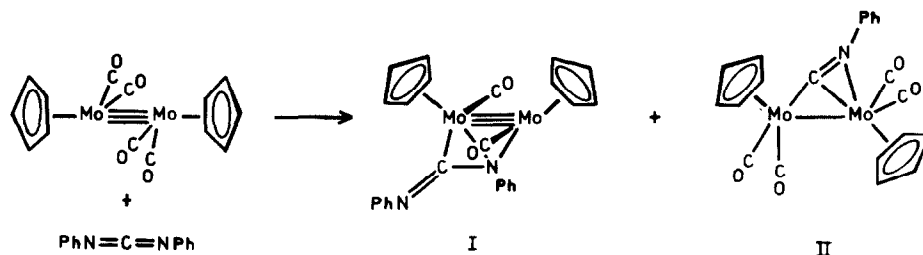
The crystal and molecular structure of  $[\text{C}_5\text{H}_5(\text{CO})_2\text{Mo}]_2(\mu, \eta^2\text{-C}\equiv\text{NC}_6\text{H}_5)$  were determined for a new polymorphic form in which the substance crystallizes in the triclinic system, as opposed to the monoclinic form previously described. The space group is  $P\bar{1}$  and the lattice constants are  $a$  9.795(2),  $b$  10.219(3),  $c$  11.505(3) Å,  $\alpha$  81.53(2),  $\beta$  70.83(2) and  $\gamma$  66.91(2)°,  $V$  997.70 Å<sup>3</sup> and  $D(Z=2) = 1.788 \text{ g cm}^{-3}$ . The Niggli matrix rules out the possibility that the triclinic cell is a sub-cell of the monoclinic one previously described. Detailed comparison of bond lengths, angles, torsional angles and superposition of the two molecules through the BMFIT program show that the two determinations yield very close but not identical results, and that the largest deviations are associated with those groups (Cp and phenyl), which are able to respond readily to differences in packing forces. It is clear, however, that the general conformation of the molecules is not dictated by such forces, which merely modify the intramolecular forces controlling conformation and configuration.

### Introduction

The reaction of  $\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Mo}(\text{CO})_2\text{Cp}$  ( $\text{Cp} = \eta\text{-C}_5\text{H}_5$ ) with an excess of diphenylcarbodiimide,  $\text{C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5$ , leads to the new asymmetrically bridged complex  $\text{Cp}_2(\text{CO})_2\text{Mo}_2\mu(\eta^1 : \eta^2\text{-C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5)$ , I, and to  $\text{Cp}_2(\text{CO})_4\text{Mo}_2\mu(\eta^1 : \eta^2\text{-C}\equiv\text{NC}_6\text{H}_5)$ , II [1] (Scheme 1).

During our attempts to prepare single crystals of complex I, in which the  $\text{Mo}\equiv\text{Mo}$  bond is preserved, thus giving rise to a compound having reactivity similar to that of  $[\text{Cp}(\text{CO})_2\text{Mo}]_2$ , we separated a substance crystallizing in the triclinic system with

## SCHEME 1



space group  $P\bar{1}$ . Analysis by X-ray diffraction showed this compound to be  $\text{Cp}_2(\text{CO})_4\text{Mo}_2$  ( $\eta^1 : \eta^2\text{-C}\equiv\text{NC}_6\text{H}_5$ ). This result was somewhat surprising, since the same complex was reported by Adams et al. [2] to be monoclinic ( $P2_1/n$ ), although both structure determinations were carried out at about the same temperature. Consequently, this study constitutes a separate and independent determination of the crystal and molecular structure of compound II. The phenomenon of polymorphism is somewhat rare for organometallic compounds [3], but it is of interest, for it allows us to see the effect of packing on molecular conformation and configuration. Thus, therefore in this paper we compare our and Adams' results, for they are of

TABLE 1

## SUMMARY OF DATA COLLECTION AND PROCESSING PARAMETERS

Space group	$P\bar{1}$
Cell constants	$a$ 9.795(2) Å $b$ 10.219(3) $c$ 11.505(3) $\alpha$ 81.53(2)° $\beta$ 70.38(2) $\gamma$ 66.91(2)
Cell volume	$V$ 997.70 Å <sup>3</sup>
Crystal aligned nearly along	[0,1,2]
Molecular formula	$\text{C}_{21}\text{H}_{15}\text{NO}_4\text{Mo}_2$
Molecular weight	537.238
Density (calc.; $Z = 2$ )	1.788 g cm <sup>-3</sup>
Radiation	Mo- $K_\alpha$
Absorption coefficient	$\mu$ 11.51 cm <sup>-1</sup>
Data collection range	$4.0^\circ \leq 2\theta \leq 60.0^\circ$
Scan width	$\Delta\theta = (1.0 + 0.35\tan\theta)$
Maximum scan time	180 seconds
Scan speed range	0.53 to 6.70 deg min <sup>-1</sup>
Total data collected	6419 data <sup>a</sup>
Data with $I > 3\sigma(I)$	3688
Total variables	144 (Cp and Ph as rigid bodies).
$R = \Sigma  F_o  -  F_c   / \Sigma F_o $	0.0526
$R_w = [\Sigma w^2( F_o  -  F_c )^2 / \Sigma w^2 F_o ^2]^{1/2}$	0.0471
Weights	$w = [\sigma(F_o)]^{-2}$
Goodness of fit	3.81

<sup>a</sup> Of these, 2731 were eliminated because they were intensity standards, were redundant, or did not meet the criterion of having  $I > 3\sigma(I)$ .

similar high quality. The discrepancies between the two determinations are given in the form of a BMFIT plot and BMFIT data.

## Experimental

The data were collected at room temperature, using standard techniques as described in detail elsewhere [4]. Complex II crystallizes in the triclinic system as

TABLE 2

ATOMIC COORDINATES FOR  $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Mo}]_2(\mu\text{-}\eta^2\text{-CNC}_6\text{H}_5)$ 

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Mo(1)	0.23060(7)	0.10170(6)	0.28296(5)
Mo(2)	0.43225(6)	0.29352(6)	0.26808(5)
O(1)	0.1014(6)	0.2216(6)	0.5462(5)
O(2)	0.6367(8)	0.0039(7)	0.3594(7)
O(3)	-0.1288(6)	0.2491(7)	0.3436(6)
O(4)	0.7357(8)	0.2272(10)	0.0484(7)
N(1)	0.2565(6)	0.2283(6)	0.1122(5)
C(5)	0.3370(7)	0.2528(7)	0.1625(6)
C(17)	0.1563(8)	0.1790(8)	0.4474(6)
C(18)	0.5540(10)	0.1124(10)	0.3271(8)
C(19)	0.0040(10)	0.1991(8)	0.3193(6)
C(20)	0.6240(10)	0.2493(10)	0.1295(9)
C(0)	0.2234(5)	-0.1052(6)	0.2282(5)
C(1)	0.2214(5)	-0.1148(8)	0.3531(5)
C(2)	0.3672(5)	-0.1180(6)	0.3544(5)
C(3)	0.4592(5)	-0.1103(6)	0.2302(5)
C(4)	0.3704(5)	-0.1024(6)	0.1523(5)
C(6)	0.1995(5)	0.2828(5)	0.0120(3)
C(7)	0.1311(5)	0.2109(5)	-0.0307(3)
C(8)	0.0819(5)	0.2618(5)	-0.1348(3)
C(9)	0.1011(5)	0.3847(5)	-0.1962(3)
C(10)	0.1694(5)	0.4567(5)	-0.1534(3)
C(11)	0.2187(5)	0.4057(5)	-0.0493(3)
C(12)	0.3404(7)	0.4053(6)	0.4586(5)
C(13)	0.4732(7)	0.4359(6)	0.3840(5)
C(14)	0.4365(7)	0.5174(6)	0.2799(5)
C(15)	0.2811(7)	0.5372(6)	0.2903(5)
C(16)	0.2217(7)	0.4679(6)	0.4008(5)
H(0)	0.1365(5)	-0.1011(6)	0.1989(5)
H(1)	0.1330(5)	-0.1186(6)	0.4272(5)
H(2)	0.3993(5)	-0.1244(6)	0.4295(5)
H(3)	0.5676(5)	-0.1104(6)	0.2026(5)
H(4)	0.4052(5)	-0.0960(6)	0.0601(5)
H(7)	0.1174(5)	0.1227(5)	0.0133(3)
H(8)	0.0329(5)	0.2102(5)	-0.1655(3)
H(9)	0.0658(5)	0.4212(5)	-0.2708(3)
H(10)	0.1832(5)	0.5448(5)	-0.1974(3)
H(11)	0.2677(5)	0.4573(5)	-0.0187(3)
H(12)	0.3320(7)	0.3495(6)	0.5381(5)
H(13)	0.5747(7)	0.4054(6)	0.4016(5)
H(14)	0.5077(7)	0.5544(6)	0.2114(5)
H(15)	0.2236(7)	0.5906(6)	0.2303(5)
H(16)	0.1150(7)	0.4639(6)	0.4322(5)

shown by the Niggli matrix:

$$\begin{bmatrix} S_{11} & S_{22} & S_{33} \\ S_{23} & S_{13} & S_{12} \end{bmatrix} = \begin{bmatrix} 95.7949 & 104.4358 & 132.3707 \\ 17.3017 & 37.8361 & 39.2636 \end{bmatrix}$$

which allows no transformation of the triclinic cell used here to any other crystal system.

The parameters used in programming data collection and those parameters derived from data collection and processing are summarized in Table 1. The structure was solved by the heavy atom method and the refined values of the atomic coordinates are given in Table 2. Tables of thermal parameters and structure factors may be obtained from the authors on request.

## Discussion

The molecular geometry of II is depicted in Fig. 1, showing the same *trans* arrangement of Cp rings as was present in the structure determined by Adams [2]. Figure 2 is a BMFIT [6] double stereo plot comparing II as determined here with the Adams coordinates. As can be seen, the fit is not exact, and in certain locations some of the deviations are fairly large. Table 3 gives a list of these deviations, the largest of which are associated with the most remote atoms of the phenyl ring. This is not too surprising since this ring has a large area over which packing forces can exert bending and torsional changes. The next largest deviations are associated with the Cp ring on the left of Fig. 2 (which was drawn in exactly the same orientation), but these deviations are smaller. What is, in fact, surprising is that there are relatively modest deviations overall and particularly that the torsional orientations of the two Cp rings remain virtually unchanged, since it is known from NMR data that in solution these rings are free to rotate. Thus, it seems that while packing forces clearly

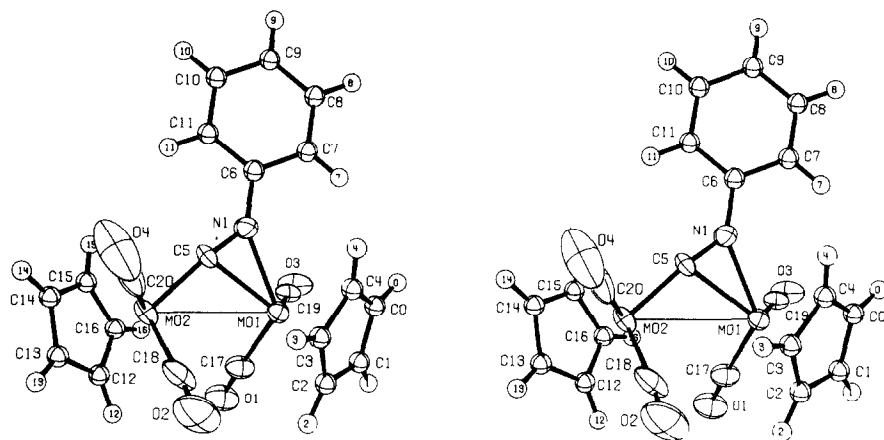


Fig. 1. Stereo representation of molecule II showing the numbering system used in the crystallographic study. The thermal ellipsoids are 50% equiprobability envelopes for the heavy atoms, hydrogens were drawn of convenient size for representational purposes and to minimize undesirable obscuration of the heavy atom framework. The hydrogen atoms are labelled according to the number of the carbon atoms to which they are attached.

TABLE 3

SELECTED BOND DISTANCES (Å) AND BOND ANGLES (Deg) FOR  $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Mo}]_2(\mu, \eta^2\text{-CNC}_6\text{H}_5)$

<i>Bond lengths</i>			
Mo(1)–Mo(2)	3.238(1)	Mo(2)–C(5)	1.932(8)
Mo(1)–N(1)	2.185(7)	Mo(2)–C(18)	1.937(12)
Mo(1)–C(5)	2.248(8)	Mo(2)–C(20)	1.952(11)
Mo(1)–C(17)	1.948(9)	Mo(2)–C(12)	2.351(7)
Mo(1)–C(19)	1.964(11)	Mo(2)–C(13)	2.333(8)
Mo(1)–C(0)	2.326(7)	Mo(2)–C(14)	2.329(7)
Mo(1)–C(1)	2.266(7)	Mo(2)–C(15)	2.345(7)
Mo(1)–C(2)	2.311(7)	Mo(2)–C(16)	2.359(8)
Mo(1)–C(3)	2.397(7)		
Mo(1)–C(4)	2.406(7)		
		O(1)–C(17)	1.15(1)
N(1)–C(5)	1.234(9)	O(2)–C(18)	1.82(2)
N(1)–C(6)	1.395(8)	O(3)–C(19)	1.14(2)
		O(4)–C(20)	1.14(1)
<i>Bond angles</i>			
Mo(2)–Mo(1)–N(1)	68.0(2)	Mo(1)–Mo(2)–C(5)	42.9(2)
Mo(2)–Mo(1)–C(5)	35.8(2)	Mo(1)–Mo(2)–C(18)	78.2(3)
N(1)–Mo(1)–C(5)	32.3(2)	Mo(1)–Mo(2)–C(20)	114.0(3)
Mo(2)–Mo(1)–C(17)	74.7(3)	C(5)–Mo(2)–C(18)	107.0(4)
Mo(2)–Mo(1)–C(19)	117.5(3)	C(5)–Mo(2)–C(20)	87.8(4)
N(1)–Mo(1)–C(17)	124.3(3)	C(18)–Mo(2)–C(20)	80.9(5)
C(5)–Mo(1)–C(17)	103.3(4)		
N(1)–Mo(1)–C(19)	87.7(3)	Mo(2)–C(5)–N(1)	169.7(7)
C(5)–Mo(1)–C(19)	106.1(3)	Mo(2)–C(18)–O(2)	175.8(1.2)
C(17)–Mo(1)–C(19)	74.3(4)	Mo(2)–C(20)–O(4)	178.1(1.2)
Mo(1)–C(5)–Mo(2)	101.3(3)		
Mo(1)–N(1)–C(5)	76.7(5)		
Mo(1)–N(1)–C(6)	145.2(5)		
Mo(1)–C(17)–O(1)	174.0(9)		
Mo(1)–C(19)–O(3)	176.3(9)		
C(5)–N(1)–C(6)	136.9(7)		



Fig. 2. BMFIT comparison of the stereochemistry of the molecules present in our crystalline polymorph(triclinic) vs. that of the ones present in the polymorph(monoclinic) studied by Adams et al. In order to generate this Figure, the least-squares fitting routine of BMFIT was asked to match as perfectly as possible Mo(1), Mo(2), C(5), and N. No effort was made to fit the other ones. Nonetheless, it should be noted that the conformation of the Cp ring on the lower right is almost perfect while that of the ring on the other side and the phenyl ring have slightly different orientations. For details of the numerical differences (in Å) of the two sets of atoms, see Tables 4 and 5.

TABLE 4

DIFFERENCES (Å) IN THE TWO FORMS OF  $[\text{C}_5\text{H}_5(\text{CO})_2\text{Mo}]_2(\mu, \eta^2\text{-CNC}_6\text{H}_5)$  EXPRESSED AS DISTANCES BETWEEN ATOMS

Atom 1	Atom 2 <sup>a</sup>	Distance	Atom 1	Atom 2	Distance
Mo(1)	Mo(1)	0.020	C(1)	C(P12)	0.080
Mo(2)	Mo(2)	0.017	C(2)	C(P11)	0.076
N(1)	N	0.021	C(3)	C(P15)	0.078
C(5)	C(31)	0.022	C(4)	C(P14)	0.079
C(6)	C(31)	0.229	C(7)	C(36)	0.314
O(1)	O(1)	0.239	C(8)	C(35)	0.568
O(2)	O(3)	0.414	C(9)	C(34)	0.777
O(3)	O(2)	0.196	C(10)	C(33)	0.726
O(4)	O(4)	0.431	C(11)	C(32)	0.445
C(17)	C(1)	0.135	C(13)	C(P24)	0.235
C(18)	C(3)	0.246	C(14)	C(P23)	0.214
C(19)	C(2)	0.116	C(15)	C(P22)	0.200
C(20)	C(4)	0.245	C(16)	C(P21)	0.212
C(0)	C(P13)	0.082			

<sup>a</sup> Atom labelling corresponds to ref. 2.

affect the details of the conformational orientations of the two crystalline forms of II, they do not completely determine the molecular conformation in this case. It is also interesting to note that despite the ability of molecule II to display crystal polymorphism it does so while retaining the Cp rings in the *trans* conformation.

TABLE 5

DIFFERENCES (Å) IN BOND LENGTHS AND BOND ANGLES (°) BETWEEN THE TWO FORMS OF  $[\text{C}_5\text{H}_5(\text{CO})_2\text{Mo}]_2(\mu, \eta^2\text{-CNC}_6\text{H}_5)$

<i>Bond lengths (<math>\Delta d</math>)</i>		
Molecule (this work)	Molecule (ref. 2)	$\Delta d$
Mo(1)–Mo(2)	Mo(1)–Mo(2)	0.026
Mo(1)–N(1)	Mo(1)–N	0.020
Mo(1)–C(5)	Mo(1)–C(5)	0.001
Mo(2)–N(1)	Mo(2)–N	0.012
Mo(2)–C(5)	Mo(2)–C(5)	0.009
N(1)–C(5)	N–C(5)	0.008
<i>Bond angles (<math>\Delta\omega</math>)</i>		
Molecule (this work)	Molecule (ref. 2)	$\Delta\omega$
Mo(2)–Mo(1)–N(1)	Mo(2)–Mo(1)–N	0.7
Mo(2)–Mo(1)–C(5)	Mo(2)–Mo(1)–C(5)	0.7
N(1)–Mo(1)–C(5)	N–Mo(1)–C(5)	0.1
Mo(1)–Mo(2)–N(1)	Mo(1)–Mo(2)–N	0.5
Mo(1)–Mo(2)–C(5)	Mo(1)–Mo(2)–C(5)	0.6
N(1)–Mo(2)–C(5)	N–Mo(2)–C(5)	0.7
Mo(1)–N(1)–Mo(2)	Mo(1)–N–Mo(2)	1.2
Mo(1)–N(1)–C(5)	Mo(1)–N–C(5)	1.0
Mo(2)–N(1)–C(5)	Mo(2)–N–C(5)	1.1
Mo(1)–C(5)–Mo(2)	Mo(1)–C(5)–Mo(2)	1.3
Mo(1)–C(5)–N(1)	Mo(1)–C(5)–N	0.9
Mo(2)–C(5)–N(1)	Mo(2)–C(5)–N	1.9

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