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The Crystal Structures of Bis(μ-ethoxycarbonylimido)-bis[(η-cyclopentadienyl)-oxomolybdenum](*Mo–Mo*), (η^5-C_5H_5)MoO(μ-$NCOOC_2H_5$)$_2$OMo(η^5-C_5H_5), and μ-Ethoxycarbonylimido-μ-oxo-bis[(η-cyclopentadienyl)oxomolybdenum](*Mo–Mo*), (η^5-C_5H_5)MoO(μ-$NCOOC_2H_5$)(μ-O)(η^5-C_5H_5)OMo

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Abstract

The structures of the two nitrene complexes [$Mo_2(C_5H_5)_2(C_3H_5NO_2)_2O_2$], $C_{16}H_{20}Mo_2N_2O_6$ (I) [triclinic, $C\bar{1}$, a = 6·819 (4), b = 8·115 (3), c = 10·095 (7) Å, α = 93·35 (4), β = 124·26 (4), γ = 92·62 (3)°], and [$Mo_2(C_5H_5)_2(C_3H_5NO_2)O_3$], $C_{13}H_{15}Mo_2NO_5$ (II) [monoclinic, $P2_1/c$, a = 8·439 (2), b = 26·218 (4), c = 6·789 (2) Å, β = 98·66 (2)°] have been determined. (I) and (II) are binuclear complexes, both having a Mo—Mo bond. In (I) the two Mo atoms are joined by two $NCOOC_2H_5$ groups, in (II) by a μ-$NCOOC_2H_5$ and a μ-O bridge. The structures have been refined to a final R of 0·029 (I) and 0·037 (II).

Introduction

The photolytic reaction between η^5-$C_5H_5Mo(CO)_3$-CH_3 (III) and $N_3COOC_2H_5$ (IV) in CH_2Cl_2 leads to the two nitrene complexes (η^5-C_5H_5MoO)$_2$(μ-$NCOOC_2H_5$)$_2$ (I) and (η^5-C_5H_5MoO)$_2$(μ-$NCOOC_2H_5$)(μ-O) (II). As byproducts, η^5-$C_5H_5Mo(CO)_3Cl$ (V), C_2Cl_4 and $H_2NCOOC_2H_5$ were formed, thus showing that the solvent takes part in the reaction. More interestingly, the formation of these other products can be best explained by supposing that free singlet nitrenes $|\bar{N}COOC_2H_5$ were present (Korswagen, Weidenhammer & Ziegler, 1979). Therefore, (I) and (II) can be seen as the reaction products of a free nitrene ($|\bar{N}COOC_2H_5$) with a metalloorganic substrate, a process not at all common in reactions of organic azides with metal complexes (Dekker & Knox, 1967; Edelblut, Haymore & Wentworth, 1978). Compounds like (I) and, especially, like (II) are of interest because of their similarity with the active site of the nitrogenase system (Moorehead, Weathers, Ufkes, Robinson & Schrauzer, 1977). In this paper the X-ray structural studies of (I) and (II) will be described.

Rotating-crystal and Weissenberg photographs (Cu $K\alpha$ radiation) showed the crystals to be triclinic (I) and monoclinic (II) and provided rough lattice constants. Exact lattice parameters for both compounds were calculated by least squares (Berdesinski & Nuber, 1966) from diffractometrically determined θ values of 60 (I) and 58 (II) selected reflections. Intensity measurements were performed on a computer-controlled diffractometer (AED-Siemens, Mo $K\alpha$, θ–2θ scans, five-value method) up to 2θ = 59·97 (I) and 61·98° (II). Reflections with $I < 2·568\sigma(I)$ were not considered. 2408 (I) and 3647 (II) independent intensities remained for calculation. These were corrected for Lorentz and polarization factors only. The crystal data for both compounds are listed in Table 1.

For (I), there is one molecule in the centrosymmetric cell ($C\bar{1}$) and therefore the molecule itself

Table 1. *Crystal data of* (I) *and* (II)

	(I)	(II)
a (Å)	6·819 (4)	8·439 (2)
b (Å)	8·115 (3)	26·218 (4)
c (Å)	10·095 (7)	6·789 (2)
α (°)	93·35 (4)	
β (°)	124·26 (4)	98·66 (2)
γ (°)	92·62 (3)	
d_o (Mg m^{-3})	2·01	1·95
d_c (Mg m^{-3})	1·91	2·04
Z, V (Å^3)	1, 458·8	4, 1485·03
FW, F(000)	528·2, 524	457·17, 896
Independent intensities	2408	3647
$2\theta_{max}$, $2\theta_{min}$	$59·97 \geq 2\theta \geq 4·91°$	$61·98 \geq 2\theta \geq 4·88°$
μ (Mo $K\alpha$) (mm^{-1})	1·3702	1·6677
Space group	$C\bar{1}$	$P2_1/c$
λ(Mo $K\alpha$) (Å)	0·7107	
Systematic absences	—	$0k0$: $k = 2n + 1$ $h0l$: $l = 2n + 1$
Crystal size (mm)	0·2 × 0·1 × 0·2	0·1 × 0·2 × 0·2
R_{iso}	0·087	0·098
R_{aniso}	0·029	0·037

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has to have a center of symmetry. The structure was solved by the heavy-atom method. Refinement with isotropic and anisotropic temperature factors resulted in $R = 0{\cdot}087$ and $0{\cdot}034$ respectively. A difference Fourier map allowed the location of the H atoms with one exception. Their coordinates were refined independently with one constant thermal parameter for all ($B = 5{\cdot}5$ Å^2). The final R was 0·029.* Tables 2 and 3 show the atomic coordinates and bond distances and angles, respectively.

(II) has four molecules in the unit cell. All non-hydrogen atoms were determined from Patterson and Fourier syntheses and refined with anisotropic parameters to $R = 0{\cdot}037$ ($R_{\rm iso} = 0{\cdot}098$) at which point a difference map enabled all the H atoms (except one) to be located, their coordinates being refined independently with $B = 5{\cdot}6$ Å^2. The final R was 0·037.* The atomic coordinates are listed in Table 4, bond distances and angles in Table 5.

Table 2. *Final atomic fractional coordinates of* (I) *for* Mo ($\times 10^5$), *the non-hydrogen atoms* ($\times 10^4$) *and the* H *atoms* ($\times 10^3$)

The numbering scheme of the H atoms corresponds to that of the C atoms.

	x	y	z
Mo	11085 (6)	1907 (4)	16272 (4)
O(1)	3845 (5)	1248 (4)	2603 (4)
O(2)	1604 (7)	−3879 (4)	−915 (4)
O(3)	3504 (5)	−3299 (3)	1758 (3)
N	1056 (6)	−1517 (4)	134 (4)
C(1)	2013 (7)	−2987 (5)	229 (5)
C(2)	4535 (9)	−4879 (5)	1989 (6)
C(3)	6591 (10)	−4782 (7)	3740 (7)
C(11)	−491 (10)	−2072 (6)	2329 (6)
C(12)	1610 (9)	−1314 (6)	3734 (5)
C(13)	1249 (12)	286 (7)	4030 (6)
C(14)	−1054 (14)	571 (7)	2781 (9)
C(15)	−2166 (9)	−928 (9)	1738 (7)
H(201)	325 (9)	−569 (8)	167 (9)
H(202)	510 (10)	−500 (9)	118 (9)
H(301)	798 (9)	−399 (8)	398 (9)
H(302)	610 (10)	−484 (9)	442 (8)
H(11)	−79 (9)	−320 (8)	183 (8)
H(12)	307 (10)	−182 (9)	439 (9)
H(13)	221 (10)	119 (10)	483 (9)
H(14)	−119 (9)	142 (8)	297 (8)
H(15)	−365 (10)	−113 (10)	72 (9)

Table 3. *Bond lengths* (Å) *and angles* (°) *of* (I)

Mo–Mo′	2·724 (1)	Mo–C(11)	2·429 (6)
Mo–O(1)	1·695 (3)	Mo–C(12)	2·379 (6)
Mo–N	1·971 (4)	Mo–C(13)	2·370 (8)
Mo–N′	1·978 (3)	Mo–C(14)	2·358 (12)
		Mo–C(15)	2·435 (7)
C(11)–C(12)	1·405 (6)	N–C(1)	1·369 (5)
C(12)–C(13)	1·379 (8)	C(1)–O(2)	1·207 (6)
C(13)–C(14)	1·395 (9)	C(1)–O(3)	1·335 (5)
C(14)–C(15)	1·424 (9)	O(3)–C(2)	1·459 (6)
C(15)–C(11)	1·385 (8)	C(2)–C(3)	1·510 (7)
N–Mo–Mo′	46·5 (1)	N–Mo–N′	92·7 (1)
N′–Mo–Mo′	46·3 (1)	Mo–N–Mo′	87·3 (1)
N–Mo–O(1)	104·9 (2)	Mo–N–C(1)	137·3 (3)
N′–Mo–O(1)	105·6 (2)	Mo′–N–C(1)	135·4 (4)
O(1)–Mo–Mo′	112·5 (1)		
O(2)–C(1)–O(3)	124·0 (4)	C(11)–C(12)–C(13)	109·0 (4)
N–C(1)–O(2)	124·7 (4)	C(12)–C(13)–C(14)	107·7 (5)
N–C(1)–O(3)	111·2 (3)	C(13)–C(14)–C(15)	108·0 (6)
C(1)–O(3)–C(2)	115·6 (4)	C(14)–C(15)–C(11)	107·2 (4)
O(3)–C(2)–C(3)	106·5 (6)	C(15)–C(11)–C(12)	108·0 (5)

Table 4. *Final atomic fractional coordinates of* (II) *for the* Mo *atoms* ($\times 10^5$), *the non-hydrogen atoms* ($\times 10^4$) *and the hydrogen atoms* ($\times 10^3$)

The numbering scheme for the H atoms corresponds to that of the C atoms.

	x	y	z
Mo(1)	21808 (5)	35341 (2)	53874 (7)
Mo(2)	−9645 (5)	33824 (2)	43254 (7)
O(1)	2992 (5)	3857 (2)	3621 (7)
O(2)	−1817 (5)	3041 (2)	6008 (7)
O(3)	929 (5)	3002 (1)	3922 (6)
O(4)	1052 (6)	4670 (2)	7513 (8)
O(5)	−1567 (5)	4469 (1)	6686 (6)
N	274 (5)	3930 (2)	5851 (7)
C(1)	−1 (7)	4386 (2)	6740 (8)
C(2)	−1993 (9)	4962 (3)	7460 (12)
C(3)	−3724 (9)	4926 (3)	7785 (13)
C(11)	4687 (7)	3565 (3)	7539 (10)
C(12)	4492 (7)	3063 (2)	6866 (9)
C(13)	3190 (7)	2846 (2)	7636 (10)
C(14)	2557 (8)	3199 (3)	8776 (9)
C(15)	3454 (9)	3673 (3)	8678 (9)
C(21)	−3320 (7)	3769 (3)	2583 (9)
C(22)	−2054 (8)	4052 (2)	2069 (9)
C(23)	−1181 (8)	3745 (3)	994 (9)
C(24)	−1825 (11)	3256 (3)	856 (9)
C(25)	−3204 (9)	3264 (3)	1790 (11)
H(201)	−187 (10)	520 (5)	639 (10)
H(301)	−422 (8)	483 (3)	679 (11)
H(302)	−380 (8)	469 (3)	869 (10)
H(303)	−404 (8)	520 (3)	805 (10)
H(11)	540 (8)	380 (3)	730 (10)
H(12)	515 (8)	288 (3)	616 (9)
H(13)	279 (8)	255 (3)	742 (10)
H(14)	199 (8)	311 (3)	919 (10)
H(15)	319 (8)	388 (3)	923 (10)
H(21)	−392 (8)	387 (3)	305 (10)
H(22)	−184 (8)	436 (3)	231 (9)
H(23)	−72 (8)	380 (2)	75 (10)
H(24)	−159 (4)	299 (1)	27 (5)
H(25)	−351 (4)	303 (1)	182 (5)

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* Lists of structure factors and anisotropic thermal parameters for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34554 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Bond lengths* (Å) *and angles* (°) *of* (II)

Mo(1)–Mo(2)	2·673 (1)	Mo(2)–O(2)	1·694 (5)
Mo(1)–O(1)	1·694 (5)	Mo(2)–O(3)	1·934 (5)
Mo(1)–O(3)	1·932 (4)	Mo(2)–N	1·975 (4)
Mo(1)–N	1·980 (5)	Mo(2)–C(21)	2·381 (6)
Mo(1)–C(11)	2·384 (6)	Mo(2)–C(22)	2·418 (6)
Mo(1)–C(12)	2·397 (6)	Mo(2)–C(23)	2·435 (6)
Mo(1)–C(13)	2·433 (7)	Mo(2)–C(24)	2·381 (6)
Mo(1)–C(14)	2·438 (6)	Mo(2)–C(25)	2·377 (7)
Mo(1)–C(15)	2·357 (6)		
C(11)–C(12)	1·393 (10)	C(21)–C(22)	1·387 (10)
C(12)–C(13)	1·407 (9)	C(22)–C(23)	1·373 (10)
C(13)–C(14)	1·365 (10)	C(23)–C(24)	1·388 (12)
C(14)–C(15)	1·464 (11)	C(24)–C(25)	1·407 (12)
C(15)–C(11)	1·416 (10)	C(25)–C(21)	1·439 (12)
N–C(1)	1·373 (7)	O(5)–C(2)	1·460 (8)
C(1)–O(4)	1·217 (7)	C(2)–C(3)	1·513 (11)
C(1)–O(5)	1·335 (7)		
N–Mo(1)–Mo(2)	47·4 (1)	N–Mo(2)–Mo(1)	47·6 (1)
N–Mo(1)–O(3)	93·8 (2)	N–Mo(2)–O(3)	93·8 (2)
N–Mo(1)–O(1)	106·0 (2)	N–Mo(2)–O(2)	106·0 (2)
Mo(1)–N–Mo(2)	85·0 (2)	Mo(1)–Mo(2)–O(3)	46·2 (1)
Mo(1)–O(3)–Mo(2)	87·4 (2)	Mo(1)–Mo(2)–O(2)	113·7 (1)
		O(3)–Mo(2)–O(2)	105·4 (2)
N–C(1)–O(4)	124·2 (5)	Mo(2)–Mo(1)–O(3)	46·4 (1)
N–C(1)–O(5)	111·2 (4)	Mo(2)–Mo(1)–O(1)	112·0 (1)
O(4)–C(1)–O(5)	124·5 (5)	O(3)–Mo(1)–O(1)	104·1 (2)
C(1)–O(5)–C(2)	115·6 (4)	Mo(1)–N–C(1)	136·1 (4)
O(5)–C(2)–C(3)	107·0 (5)	Mo(2)–N–C(1)	138·8 (4)
C(11)–C(12)–C(13)	108·7 (6)	C(21)–C(22)–C(23)	108·4 (6)
C(12)–C(13)–C(14)	109·3 (6)	C(22)–C(23)–C(24)	109·9 (7)
C(13)–C(14)–C(15)	107·5 (6)	C(23)–C(24)–C(25)	107·4 (7)
C(14)–C(15)–C(11)	106·3 (6)	C(24)–C(25)–C(21)	106·8 (7)
C(15)–C(11)–C(12)	108·0 (6)	C(25)–C(21)–C(22)	107·4 (6)

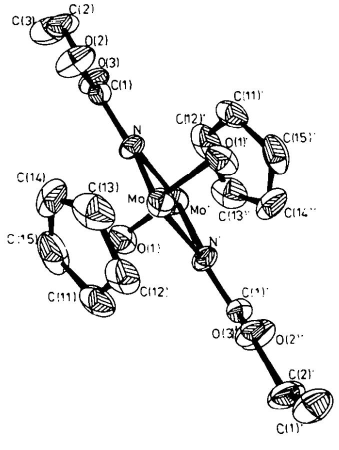

Fig. 1. *ORTEP* drawing of (I) with atom numbering. 50% probability ellipsoids are displayed.

All calculations were performed on computers Siemens 301 (Anorganisch-Chemisches Institut, Heidelberg) and IBM 370/168 (Universitätsrechenzentrum Heidelberg) with local versions of the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964). The atom numbering is given in the figures.

Discussion

The structures are shown in Figs. 1 and 2 (I) and in Figs. 3 and 4 (II). Both compounds are binuclear complexes in which two Mo atoms are joined by two μ-nitrene ligands ($NCOOC_2H_5$) in (I) and by one μ-nitrene and one μ-oxo ligand in (II). If the Mo–Mo bond is ignored and three coordination positions are assigned to the C_5H_5 ring, a distorted octahedral coordination results for each Mo atom in (I) and (II). This represents a major difference between (I) and (II) and other comparable compounds, such as di-μ-oxo-bis[diethyldithiocarbamatooxomolybdenum(V)] (VI) (Ricard, Martin, Wiest & Weiss, 1975),

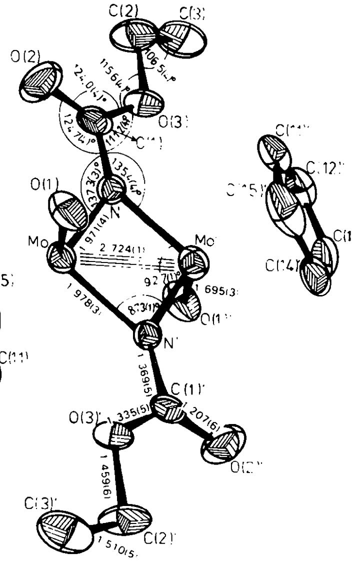

Fig. 2. *ORTEP* drawing of (I) with some bond lengths (Å) and angles (°) with view down to the four-membered Mo_2N_2 unit.

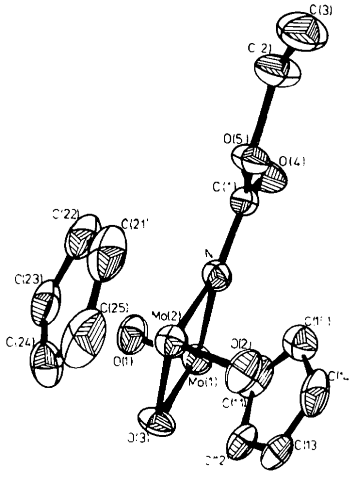

Fig. 3. *ORTEP* drawing of (II) with atom numbering. 50% probability ellipsoids are displayed.

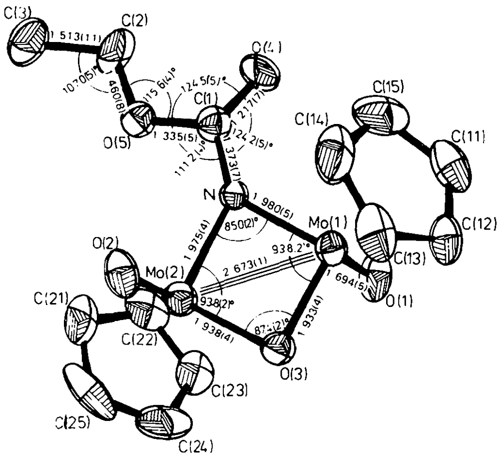

Fig. 4. *ORTEP* drawing of (II) with some bond lengths (Å) and angles (°) with view down to the four-membered Mo_2NO unit.

μ-oxo-μ-sulphido-bis[di-*n*-propyldithiocarbamatooxomolybdenum(V)] (VII) (Dirand-Colin, Ricard & Weiss, 1976) and the μ-O- and μ-NH-bridged complex $[S_2P(OC_2H_5)_2MoO]_2(\mu\text{-}O)(\mu\text{-}NH)$ (VIII) (Edelblut, Haymore & Wentworth, 1978). In these species the Mo atoms show square-pyramidal coordination, both pyramids sharing a common edge at the basal planes. Another difference between these new compounds and (VI), (VII) and (VIII) is the *trans* configuration of the two terminal O atoms and the planarity of the MoE_2Mo unit (E = O, NH, $NCOOC_2H_5$). For crystallographic reasons the four-membered ring is absolutely planar in (I); in (II) the deviations from planarity of the ring are within experimental error.

The Mo–Mo distances in (I) [2·724 (1) Å] and (II) [2·673 (1) Å] lie within the accepted values for a single bond, the values for (I) and (II) being comparable to those for (VI) [2·580 (1) Å], (VII) [2·673 (3) Å] and (VIII) [2·589 (1) Å]. In accordance with this are the Mo—O—Mo and Mo—N—Mo bond angles (Tables 3 and 5), which are significantly smaller than would be expected in the absence of Mo—Mo bonds (Edelblut, Haymore & Wentworth, 1978; Dahl, de Gil & Feltham, 1969). They are smaller than 90° and, correspondingly, the N—Mo—N and N—Mo—O angles are larger (Tables 3 and 5). The sum of the inner angles in the MoE_2Mo unit in (I) must be exactly 360° due to the center of symmetry. In (II) the sum is 360° too. The 18-electron rule also requires the presence of a Mo—Mo bond in (I) and (II), considering the isoelectronic μ-O and μ-NR (R = $COOC_2H_5$) ligands as four-electron donors.

The bond lengths in the Mo_2E_2 unit show (I) and (II) to be symmetrically bridged complexes. The Mo—N bonds in (I) and (II) have the same length within 1σ (Tables 3, 5); they are significantly longer than those in (VIII) but still smaller than the sum of the Slater radii (2·05 Å). This could be caused by the higher electronegativity of the $COOC_2H_5$ group and/or by the larger steric requirement of this group compared to the H atom of the NH ligand in (VIII). The Mo—O distances within the MoNMoO ring of (II) and in (VI), (VII) and (VIII) are all in good agreement. The sums of the bond angles around the bridging N atoms confirm their sp^2 hybridization [360·0 (I), 359·9° (II)]. This, together with the Mo—N lengths, shows the $NCOOC_2H_5$ groups to be correctly interpreted as bridging nitrenes.

The distances between the Mo atoms and the terminal O atoms in (I) and (II) agree well with comparable values reported. The sum of the Slater radii for Mo and O being 2·05 Å, the values found for the Mo—O_{term} bonds [1·695 (3) in (I) and 1·694 (5) Å in (II)] show that the bonds have at least partial double-bond character as in (VI), (VII) and (VIII).

The bond lengths and angles between the atoms in the $NCOOC_2H_5$ group are as expected. The N—C and C—O bonds are all shorter than normal single bonds (Tables 3 and 5); even the C—O distances in the carbonyl group [1·207 (6) in (I) and 1·217 (7) Å in (II)] are shorter than those usually found for esters. These shortened bond lengths, together with the fact that the NCOOC units of the $NCOOC_2H_5$ groups in (I) and (II) are almost coplanar with the Mo[μ-N(R)]$_2$Mo and Mo[μ-N(R)(μ-O)]Mo planes, show that the π electrons must be delocalized over almost the total region of the molecular framework [only the C atoms of the CH_3 groups are displaced from this plane: C(2) 0·07, C(3) 0·309 Å in (I), σ = 0·004 Å; C(2) 0·108, C(3) 0·294 Å in (II), σ = 0·005 Å]. This delocalization is an important factor in explaining the stability of (I) and (II).

The linkage of the Mo atoms to the C_5H_5 rings shows no peculiarities. The average Mo—C_{ring} distance is 2·394 (10) Å in (I) and 2·398 (6) Å in (II); the average C—C distance in the rings is 1·398 (9) Å in (I), 1·409 (10) and 1·399 (12) Å in (II). The rings are planar and the sum of the inner angles is 539·9 in (I) [$\overline{\angle}$ = 108·0 (5)] and 539·8 [$\overline{\angle}$ = 108·0 (6)] and 539·9° [$\overline{\angle}$ = 108·0 (7)] in (II).

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A Dehydromolybdenocene Dimer: Di-μ-(σ:η-cyclopentadienyl)-bis(η-cyclopentadienyl)dimolybdenum(*Mo–Mo*)

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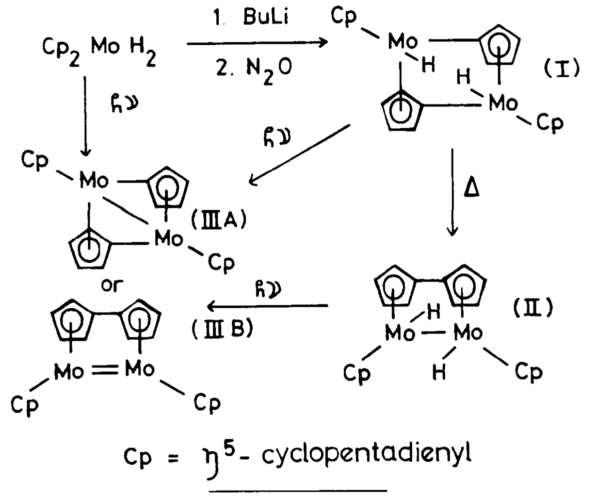
Abstract

$[Mo_2(C_5H_4)_2(C_5H_5)_2]$, $C_{20}H_{18}Mo_2$, $M_r = 450{\cdot}0$, orthorhombic, $a = 19{\cdot}061\,(3)$, $b = 12{\cdot}739\,(5)$, $c = 24{\cdot}850\,(7)$ Å, $U = 6034$ Å^3. Space group *Pbca*, $Z = 16$, $D_c = 1{\cdot}98$ Mg m^{-3}, Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å), $\mu = 1{\cdot}59$ mm^{-1}. The asymmetric unit contains two crystallographically independent dimeric molecules $C_{20}H_{18}Mo_2$ with the Mo atoms bridged by two σ:η^5-cyclopentadienyl ligands. The Mo–Mo distance is 2·885 Å (mean value).

Introduction

Two dimeric forms of molybdenocene, (I) and (II), have been isolated (Green & Simpson, 1978; Cooper, Green, Couldwell & Prout, 1977). The photochemical activation by UV light of each of these complexes leads to the same product (III) of formula $C_{20}H_{18}Mo_2$. This is called dehydromolybdenocene and may be prepared directly by irradiation of $(\eta\text{-}C_5H_5)_2MoH_2$ in benzene (Berry, Davies & Green, 1978).

Because (III) can also be prepared by irradiation of (II) (this reaction involves a C—C bond breaking), it is not possible to choose between (III*A*) and (III*B*) from spectroscopic data alone. The structure analysis by X-ray diffraction reveals that (III*A*) is the correct structure.



Experimental

The crystals were supplied by M. L. H. Green and S. Simpson. A small dark-red needle 0·10 × 0·15 × 0·70 mm was sealed under nitrogen in a glass capillary and mounted on a Nonius CAD-4 diffractometer. With Mo $K\alpha$ radiation from a graphite monochromator, the cell dimensions and orientation matrix were obtained by least squares from the setting angles of 25 reflexions. The intensities of reflexions with $\theta < 26°$ were measured by an $\omega/2\theta$ scan, with a variable scan rate and an ω-scan angle of $1{\cdot}00 + 0{\cdot}35\tan\theta$. 2315 reflexions with $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects but not for absorption and used in subsequent calculations. The structure was solved with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) from 205 reflexions with $1{\cdot}50 < E < 2{\cdot}90$. The *E* map corresponding to the solution with the best figure of merit revealed the positions of the Mo atoms. All the C atoms were located by Fourier synthesis. The structure was refined by least squares

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