Synthesis of (Pentamethylcyclopentadienyl)nitrosylmolybdenum Complexes containing Halide, Methyl, or Cyclopentadienyl Ligands. Crystal Structures of $[MoMe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(NO)]$ and $[\{Mo(\eta\text{-}C_5Me_5)O(\mu\text{-}O)\}_2]$†

Ernesto de Jesús, Amelio Vázquez de Miguel, and Pascual Royo*
Departamento de Química Inorgánica, Campus Universitario, Universidad de Alcalá de Henares, 28871 Alcalá de Henares, Madrid, Spain
Anna Maria Manotti Lanfredi and Antonio Tiripicchio
Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

Treatment of the dihalogeno derivatives $[\{Mo(\eta\text{-}C_5Me_5)(NO)X(\mu\text{-}X)\}_2]$ [X = Cl, (**1a**); Br, (**1b**); or I, (**1c**)] or $[Mo(\eta\text{-}C_5Me_5)(NO)X_2(PPh_3)]$ [X = Cl, (**2a**); Br, (**2b**); or I, (**2c**)] with Al_2Me_6 gives the halogenomethyl complexes $[\{MoMe(\eta\text{-}C_5Me_5)(NO)(\mu\text{-}X)\}_2]$ (**3a**)—(**3c**) or $[MoMe(\eta\text{-}C_5Me_5)(NO)X(PPh_3)]$ (**4a**)—(**4c**) respectively. Dimers (**3**) react with PPh_3 to give monomers (**4**). Complex (**1b**) reacts with LiMe to give $[MoMe_2(\eta\text{-}C_5Me_5)(NO)]$ (**5**). Reactions of (**1**) or (**3b**) with $Tl(C_5H_5)$ give the '20-electron' mixed bis(cyclopentadienyl) complexes $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(NO)Y]$ [Y = Cl, (**6a**); Br, (**6b**); I, (**6c**); or Me, (**7**)]. The structure of complex (**7**) (crystal A) has been determined by *X*-ray diffraction methods. By accident, the structure of the first crystal examined (B) contained (**7**) and the oxo complex *trans*-$[\{Mo(\eta\text{-}C_5Me_5)O(\mu\text{-}O)\}_2]$ (**8**) in an ordered mixture with a 2:1 molar ratio. Crystal A is orthorhombic, space group $Pna2_1$ with $Z = 4$ in a unit cell of dimensions $a = 9.370(4)$, $b = 12.322(5)$, and $c = 13.301(5)$ Å. Crystal B is monoclinic, space group $P2_1/a$ with $Z = 4$, (**7**), and 2, (**8**), in a unit cell of dimensions $a = 32.569(9)$, $b = 8.535(4)$, $c = 9.482(5)$ Å, and $\beta = 93.33(3)°$.

A bonding situation involving one $\eta^5\text{-}C_5H_5$ and one $\eta^3\text{-}C_5H_5$ ring was proposed to account for the isolated '20-electron' complexes $[Mo(\eta\text{-}C_5H_5)_2(NO)Y]$ (Y = Me, I,[1] or $\sigma\text{-}C_5H_5$[2]). However, the crystal structure determination of these compounds[3,4] showed two approximately equivalent cyclopentadienyl ligands in which all 10 carbons have significant bonding interactions with molybdenum, but are unsymmetrically bonded with distances ranging from 2.3 to 2.6 Å, the carbons opposite to the NO being the most distant atoms. Some authors have tried to describe this metal–cyclopentadienyl bonding situation,[5–8] and conclusions drawn from theoretical analysis[9] or reactivity studies.[10]

We have previously described[11] the preparation of halogenomethyl complexes $[\{MoMe(\eta\text{-}C_5H_5)(NO)(\mu\text{-}X)\}_2]$ (X = Cl, Br, or I) using Al_2Me_6 as a selective methylating agent and have shown that they are good starting materials for the synthesis of $[MoMe(\eta\text{-}C_5H_5)_2(NO)]$.

Here we report the preparation and characterization of the new pentamethylcyclopentadienyl complexes $[\{MoMe(\eta\text{-}C_5Me_5)(NO)(\mu\text{-}X)\}_2]$ [X = Cl, (**3a**); Br, (**3b**); or I, (**3c**)], their phosphine adducts $[MoMe(\eta\text{-}C_5Me_5)(NO)X(PPh_3)]$ (**4a**)—(**4c**), and the '20-electron' mixed bis(cyclopentadienyl) derivatives $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(NO)Y]$ [Y = Cl, (**6a**); Br, (**6b**); I, (**6c**); or Me, (**7**)].

Results and Discussion

Preparative Results.—Treatment of the dimers (**1**) with Al_2Me_6 leads to the halogenomethyl complexes (**3**) [see Scheme, (*i*)] under experimental conditions identical to those for the homologous C_5H_5 derivatives.[11] Analytically pure (**3**) are only isolated if the halogenomethylaluminium derivatives are previously separated[11] by addition of $[PPh_4]Br$ which easily forms insoluble ionic aluminium species but reacts slowly with the molybdenum compounds. This procedure, which was not suitable for the most acidic C_5H_5 compound[11] (the chloro complex) is however useful for all the C_5Me_5 compounds due to the decreased acidity caused by the pentamethylated ring.

Nevertheless, the excess of $[PPh_4]Br$ will react with complexes (**3**) decreasing their yields. The smaller are the Al:Mo and Br:Al ratios used to produce total methylation of molybdenum and total precipitation of aluminates, the higher are the yields of (**3**). We have carried out g.c. studies on the evolved CH_4 by hydrolysis of the reaction mixture obtained at different Al:Mo ratios, and determined that the three aluminium methyls can be interchanged by the molybdenum halogen. A 2:1:1.5 Mo:Al:Br ratio gives almost stoicheiometric yields (>90%), in comparison with the previously reported 1:1:1 ratio (*ca.* 70%).[11]

The adducts (**4**) were prepared by addition of PPh_3 to the solution containing the methyl complexes (**3**) [Scheme, (*i*) and (*ii*)], or by direct reaction with Al_2Me_6 of the previously isolated adducts (**2**) [Scheme, (*iii*) and (*iv*)]. In both cases, addition of methanol to form insoluble methoxyaluminium species[12] is the necessary last step for providing good yields of the three adducts.

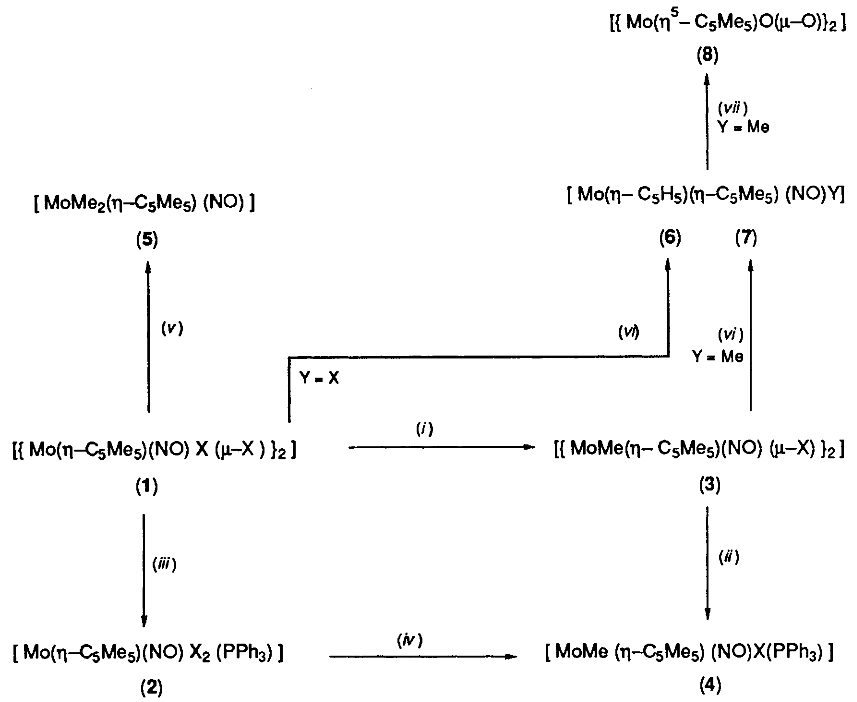
Reaction of the bromo complex (**1b**) with methyl-lithium [Scheme, (*v*)] affords a very insoluble product which is easily hydrolyzed by wet acetone and was characterized as $[MoMe_2(\eta\text{-}C_5Me_5)(NO)]$ (**5**), a thermally stable dialkyl 16-electron species similar to other previously reported complexes.[13]

The compound $Tl(C_5H_5)$ reacts with (**1**) and (**3b**) to give respectively the expected $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(NO)Y]$ [(**6**) and (**7**)] complexes [Scheme, (*vi*)].

---

† (η-Cyclopentadienyl)methylnitrosyl(η-pentamethylcyclopentadienyl)-molybdenum and di-μ-oxo-bis[oxo(η-pentamethylcyclopentadienyl)-molybdenum] (*Mo–Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme. (*i*) Al_2Me_6, $[PPh_4]Br$; (*ii*) from reaction mixture of (3), PPh_3, and methanol; (*iii*) PPh_3; (*iv*) Al_2Me_6, methanol; (*v*) LiMe; (*vi*) $Tl(C_5H_5)$; (*vii*) see text.

Table 1. Analytical and physical data for the new complexes

			Analysis (%)[a]			
Complex	Colour	M.p. (°C)	C	H	N	X[b]
$[\{MoMe(\eta\text{-}C_5Me_5)(NO)(\mu\text{-}X)\}_2]$						
(**3a**) X = Cl	Yellow	185[c]	42.6	5.9	4.2	11.8
			(42.4)	(5.8)	(4.5)	(11.4)
(**3b**) X = Br	Yellow-orange	125	37.2	5.7	3.6	22.1
			(37.1)	(5.1)	(3.9)	(22.4)
(**3c**) X = I	Orange	96[c]	32.3	4.4	3.7	
			(32.8)	(3.8)	(3.5)	
$[\{MoMe(\eta\text{-}C_5Me_5)(NO)X(PPh_3)]$						
(**4a**) X = Cl	Yellow	94[c]	60.0	5.9	2.6	6.4
			(60.7)	(5.8)	(2.4)	(6.2)
(**4b**) X = Br	Yellow	89[c]	56.3	5.5	2.6	12.7
			(56.3)	(5.4)	(2.3)	(12.9)
(**4c**) X = I	Yellow	64[c]	52.0	5.1	2.1	
			(52.3)	(5.0)	(2.1)	
$[MoMe_2(\eta\text{-}C_5Me_5)(NO)]$[d]						
(**5**)	Red-violet		49.8	7.3	4.4	
			(49.5)	(7.3)	(4.8)	
$[\{Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(NO)Y]$						
(**6a**) Y = Cl	Green	179[c]	49.6	5.9	3.9	9.9
			(49.8)	(5.6)	(3.9)	(9.8)
(**6b**) Y = Br	Green	118	44.3	5.1	3.7	19.9
			(44.3)	(5.0)	(3.5)	(19.7)
(**6c**) Y = I	Green	156	39.7	4.7	3.4	
			(39.7)	(4.4)	(3.1)	
(**7**) Y = Me	Red	94	56.7	6.5	4.4	
			(56.3)	(6.8)	(4.1)	

[a] Required values given in parentheses. [b] Halogen; method used is not good for determining iodide. [c] With decomposition. [d] See text.

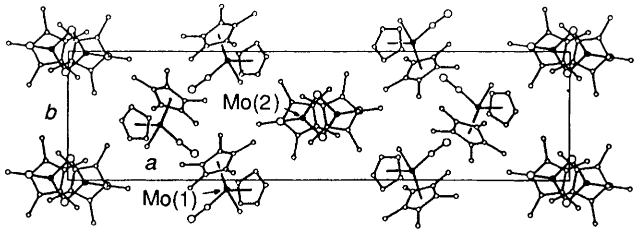


Figure 1. View along *c* of the packing in crystal B

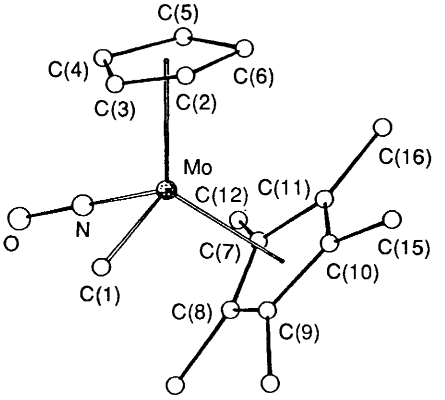


Figure 2. View of the structure of the complex $[MoMe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(NO)]$ (**7**) in crystal A. The structure of (**7**) in crystal B is practically identical

The μ-oxo compound (**8**) was formed by accident in the low-temperature crystallization of a CH_2Cl_2 solution of pure (**7**) and its nature was fully elucidated by *X*-ray structure determination of this crystallized sample. Probably the first step of the oxidation was the hydrolysis of a Mo–C_5H_5[10b] or/and a

Table 2. Proton, ^{31}P n.m.r., and i.r. data for the new complexes

Complex	$\delta(^1H)^a$			
	C_5R_5	CH_3	$\delta(^{31}P)^b$	$\nu(NO)^c/cm^{-1}$
(3a)	1.51 (15 H, s)	1.00 (3 H, s)		1 611
(3b)	1.47 (15 H, s)	1.01 (3 H, s)		1 622
(3c)	1.50 (15 H, s)	1.01 (3 H, s)		1 615
(4a)	1.50 (15 H, s)	1.17 (3 H, s)	25.25 (s)	1 610
(4b)	1.52 (15 H, s)	1.31 (3 H, s)	24.41 (s)	1 612
(4c)	1.60 (15 H, s)	1.15 (3 H, s)	25.87 (s)	1 608
$(5)^d$	1.58 (15 H, s)	1.52 (6 H, s)		1 582
(6a)	1.57 (15 H, s) 5.63 (5 H, s)			1 635
(6b)	1.59 (15 H, s) 5.65 (5 H, s)			1 630
(6c)	1.61 (15 H, s) 5.55 (5 H, s)			1 635
(7)	1.48 (15 H, s) 5.39 (5 H, s)	0.72 (3 H, s)		1 585

[a] 80 MHz, solvent C_6D_6, standard $SiMe_4$. [b] 32 MHz, solvent C_6H_6, external standard H_3PO_4. [c] In CH_2Cl_2. [d] See text.

Table 3. Carbon-13 n.m.r. data for selected complexes[a]

Complex	δ			
	C_5Me_5	$C_5\mathit{Me}_5$	C_5H_5	CH_3
(3b)	113.89 (s)	9.52 (s)		28.33 (s)
(4b)	111.51 (s)	9.52 (s)		26.98 (s)
(6a)	123.62 (s)	11.49 (s)	109.96 (s)	
(6b)	121.85 (s)	11.71 (s)	107.78 (s)	
(6c)	121.77 (s)	11.50 (s)	106.37 (s)	
(7)	117.90 (s)	10.55 (s)	106.70 (s)	5.95 (s)
$[J(C-H)]^b$	[117.46]	[126.92]	[174.82]	[134.85]

[a] $^{13}C-\{^1H\}$, 20 MHz, solvent CH_2Cl_2, standard $SiMe_4$. [b] In Hz, from ^{13}C; same conditions as for $^{13}C-\{^1H\}$.

Mo–Me[11] bond as suggested[14] by the formation of $[\{Mo(\eta^5-C_5Me_5)O_2\}_2(\mu-O)]$ from **(8)**.

Properties.—The C_5Me_5 complexes are more soluble and air stable than the C_5H_5 analogues.[11] This behaviour seems to be quite general.[15] However, they are more thermally sensitive and must be stored at low temperature.

Analytical, Physical, and Spectroscopic Data.—All the proposed stoicheiometries are in agreement with analytical data (Table 1). The spectroscopic properties of complexes (3) and (4) (Tables 2 and 3) are similar to those reported for the C_5H_5 analogues,[11] indicating analogous molecular structures and hypothetical formation of isomers. The only important differences are due to the nature of the ring, so that ν(NO) is 20—40 cm^{-1} lower for the C_5Me_5 derivatives, in agreement with the increased electron-donating capacity of the pentamethylated ring. The ν(NO) values are in the range expected for linear nitrosyls.[16]

Crystal Structures of Complexes (7) *and* (**8**).—Two crystals obtained from different crystallizations of complex (7) were analyzed. Crystal A contained only molecules of (7) while B was found to contain an ordered mixture of (7) and (**8**). Crystal B is centrosymmetrical and its unit cell contains four monomeric molecules of (7) (enantiomers two by two) and two dimeric molecules of (**8**), lying on the crystallographic inversion centre (molar ratio 2:1). The crystal packing is shown in Figure 1.

The structure of complex (7) (in crystal A) is represented in Figure 2 together with the atomic numbering scheme. Selected bond distances and angles for both determinations of (7) (in crystals A and B respectively) are given in Table 4. The Mo–C(1), Mo–N, and N–O bonds and the Mo–N–O angles in crystals A and B are compared in Table 5 with those found in the related $[Mo(\eta-C_5H_5)_2(NO)Y]$ (Y = Me[3] or σ-C_5H_5[4]) compounds. Table 6 shows a set of dimensions concerning the $M(C_5H_5)_2$ moiety,[17] considering a planar and regular C_5H_5 ring. The parameter X measures the ring slippage. The values of these dimensions for $[Mo(\eta-C_5H_5)_2(NO)Y]$[3,4] and representative $[Mo(\eta-C_5H_5)_2L_2]$ complexes[17,18] are also given in Table 6. Only the X value is clearly different for the nitrosyl derivatives ($X \approx 0.3$—0.4 Å compared with <0.15 Å), so that these compounds can be described as showing a $Mo(C_5H_5)_2L_2$ structure with both cyclopentadienyl rings moved back from their natural position. Both structures of complex (7) show a

Table 4. Relevant bond distances (Å) and angles (°) for complex (7) with estimated standard deviations (e.s.d.s) in parentheses *

	Crystal A	Crystal B
(*a*) Involving the Mo atoms		
Mo–N	1.92(3)	1.73(2)
Mo–C(1)	2.03(3)	2.20(3)
Mo–C(2)	2.46(3)	2.39(3)
Mo–C(3)	2.45(3)	2.28(3)
Mo–C(4)	2.36(2)	2.42(2)
Mo–C(5)	2.48(2)	2.65(3)
Mo–C(6)	2.59(2)	2.70(3)
Mo–C(7)	2.50(3)	2.50(2)
Mo–C(8)	2.34(2)	2.31(2)
Mo–C(9)	2.38(2)	2.31(2)
Mo–C(10)	2.62(3)	2.56(2)
Mo–C(11)	2.58(2)	2.67(2)
Mo–cp_1	2.16(2)	2.20(3)
Mo–cp_2	2.17(2)	2.16(2)
N–Mo–C(1)	88.9(11)	87.6(9)
cp_1–Mo–cp_2	122.9(8)	123.0(9)
N–Mo–cp_1	103.2(12)	114.2(9)
N–Mo–cp_2	114.4(11)	114.9(7)
C(1)–Mo–cp_2	112.5(11)	100.8(10)
C(1)–Mo–cp_2	109.5(11)	108.3(8)
(*b*) Involving the C_5H_5 ligand		
C(2)–C(3)	1.43(4)	1.42(4)
C(3)–C(4)	1.44(4)	1.33(4)
C(4)–C(5)	1.41(3)	1.32(4)
C(5)–C(6)	1.42(3)	1.29(4)
C(6)–C(2)	1.39(3)	1.51(4)
(*c*) Involving the C_5Me_5 ligand		
C(7)–C(8)	1.44(4)	1.46(2)
C(8)–C(9)	1.43(4)	1.39(2)
C(9)–C(10)	1.48(4)	1.46(2)
C(10)–C(11)	1.39(4)	1.35(2)
C(11)–C(7)	1.32(4)	1.45(2)
C(7)–C(12)	1.49(5)	1.46(3)
C(8)–C(13)	1.57(3)	1.51(3)
C(9)–C(14)	1.63(4)	1.53(3)
C(10)–C(15)	1.53(4)	1.54(3)
C(11)–C(16)	1.48(4)	1.50(3)
(*d*) Involving the NO group		
N–O	1.12(4)	1.27(3)
Mo–N–O	172.9(27)	175.1(16)

* cp_1 = Centroid of the cyclopentadienyl ring C(2)—C(6), cp_2 = centroid of the cyclopentadienyl ring C(7)—C(11).

Table 5. Comparison of selected bond distances (Å) and angles (°) between complex (7) and the related compounds

	Mo–C(1)	Mo–N	N–O	Mo–N–O
[MoMe(C_5H_5)(C_5Me_5)(NO)] (7)				
In crystal A	2.03(3)	1.92(3)	1.12(4)	173(3)
In crystal B	2.20(3)	1.73(2)	1.27(3)	175(2)
[MoMe(C_5H_5)$_2$(NO)][a]				
At Mo(1)	2.20(1)	1.75(1)	1.23(1)	178(2)
At Mo(2)	2.20(1)	1.76(1)	1.21(1)	178(1)
[Mo(C_5H_5)$_2$(σ-C_5H_5)(NO)][b]	2.29(1)	1.75(1)	1.21(1)	179(1)

[a] Ref. 3. [b] Ref. 4.

Table 6. Dimensions (distances in Å, angles in °) of the bis(cyclopentadienyl)molybdenum moiety in some representative systems[a]

Complex	a	b	θ	X_a	X_b	Φ[b]
[Mo(η-C_5H_5)$_2$$Cl_2$][c]						
At Mo(1)	1.98	1.97	130.9	0.15	0.06	s
At Mo(2)	1.97	1.98	130.2	0.08	0.15	e
[MoEt(η-C_5H_5)$_2$Cl][c]	1.97	1.98	133.9	0.13	0.04	s
[Mo(η-C_5H_5)$_2$H(CO)]$^+$[d]	1.96	1.95	144.9	0.02	0.05	e
[MoMe(η-C_5H_5)$_2$(NO)][e]						
At Mo(1)	2.18	2.11	139			27
At Mo(2)	2.13	2.14	136			2
[Mo(η-C_5H_5)$_2$(σ-C_5H_5)(NO)][f]	2.14	2.15	137.6	0.34	0.43	9
[MoMe(η-C_5H_5)(η-C_5Me_5)(NO)][g]						
In crystal A	2.15	2.15	136.3	0.23	0.32	42
In crystal B	2.15	2.12	141.2	0.48	0.42	26

[a] As defined in ref. 18; a, b = distances from metal to the ring plane, θ = angle between normals to the ring planes, X_a, X_b = distances from the ring centroid to the ring normals passing through the metal, and Φ = eclipsing angle between rings (0° for eclipsed, 36° for staggered rings). [b] s for staggered and e for eclipsed when value has not been calculated. [c] See ref. 17. [d] See ref. 18. [e] See ref. 3. [f] See ref. 4. [g] C_5H_5 = ring a, C_5Me_5 = ring b.

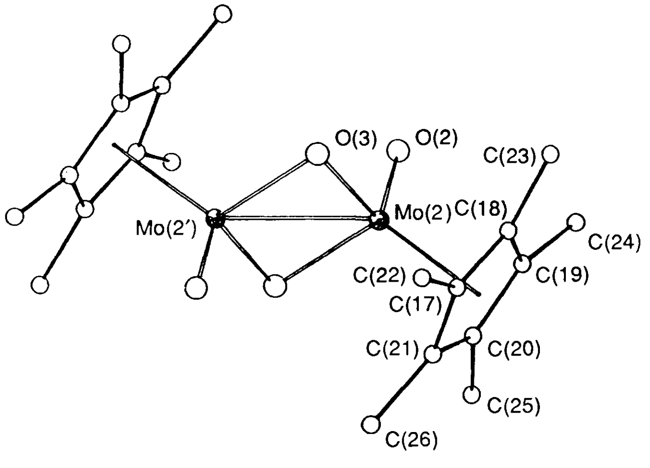


Figure 3. View of the structure of the complex [{Mo(η-C_5Me_5)O(μ-O)}$_2$] (8)

Table 7. Relevant bond distances (Å) and angles (°) for complex (**8**) with e.s.d.s in parentheses *

(*a*) Involving the Mo atoms

Mo(2)–Mo(2′)	2.647(3)	Mo(2)–C(19)	2.39(2)
Mo(2)–O(2)	1.72(1)	Mo(2)–C(20)	2.35(2)
Mo(2)–O(3)	1.94(1)	Mo(2)–C(21)	2.45(2)
Mo(2)–C(17)	2.44(2)	Mo(2)–cp_3	2.08(2)
Mo(2)–C(18)	2.36(2)		
O(2)–Mo(2)–O(3)	106.3(5)	Mo(2)–O(3)–Mo(2′)	85.5(4)
O(2)–Mo(2)–cp_3	117.4(6)	O(3)–Mo(2)–O(3′)	94.5(4)
O(3)–Mo(2)–cp_3	114.1(5)		

(*b*) Involving the C_5Me_5 ligand

C(17)–C(18)	1.38(2)	C(17)–C(22)	1.50(3)
C(18)–C(19)	1.41(2)	C(18)–C(23)	1.52(3)
C(19)–C(20)	1.41(2)	C(19)–C(24)	1.48(3)
C(20)–C(21)	1.38(2)	C(20)–C(25)	1.52(3)
C(21)–C(17)	1.44(2)	C(21)–C(26)	1.49(3)

* cp_3 = Centroid of the cyclopentadienyl ring C(17)—C(21). The primed atoms are related to the unprimed ones by the transformation $1 - x, 1 - y, -z$.

staggered ring configuration with the metal located on the line passing through the C(8) atom of the C_5Me_5 ring and the middle of the C(3)–C(4) bond of the C_5H_5 ring [C(3)–cp_1–cp_2–C(8) torsion angle = 42° for A and 26° for B]. In contrast, [Mo(η-C_5H_5)$_2$(σ-C_5H_5)(NO)] and [MoMe(η-C_5H_5)$_2$(NO)] show an eclipsed configuration at molybdenum [for Mo(2) in the latter complex].

The structure complex of complex (**8**) is represented in Figure 3 together with the atomic numbering scheme. Selected bond distances and angles are given in Table 7. The molecule lies on an inversion centre so that the Mo_2O_2 four-membered ring is planar. Each Mo atom completes the distorted tetrahedral co-ordination through a terminal oxo ligand and the centroid of a η^5-pentamethylcyclopentadienyl ring. The two C_5Me_5 rings and the terminal oxo ligands are arranged *trans* to each other. It should be noted that only *cis* isomers are known so far for structurally similar dinuclear complexes of molybdenum [{Mo(η^5-C_5R_5)O(μ-O)}$_2$] (R = H [19] or Me [20]) but the analogous *trans* isomer of chromium is known.[21] The Mo–Mo distance of 2.647(3) Å is consistent with a metal–metal single bond. This and the terminal and bridged Mo–O distances are close to those found in related μ-oxo complexes of molybdenum.[14,21–23]

Experimental

General Procedures.—For instrumentation and general manipulation see ref 11. The complexes [{Mo(η-C_5Me_5)(NO)X(μ-X)}$_2$] (1) and [Mo(η-C_5Me_5)(NO)X_2(PPh_3)] (2) were prepared similarly to C_5H_5 analogues,[24] with some variations.[25] Crystal A was obtained by Soxhlet extraction of complex (7) in pentane and slow cooling of the saturated solution. Crystal B was obtained by crystallization at −20 °C of a pure sample of (7) in a concentrated solution of dichloromethane for 2 months.

Preparations.—[{MoMe(η-C_5Me_5)(NO)(μ-X)}$_2$] (3). *Preparation of complex* (**3b**). A freshly prepared 10% toluene solution of Al_2Me_6 (1.80 cm^3, 0.90 mmol) was injected dropwise into a suspension of complex (**1b**) (1.50 g, 1.80 mmol) in toluene (20 cm^3) at −68 °C. The resultant mixture was allowed to warm up while stirring. The solid dissolved (between −45 and

Table 8. Experimental data for the *X*-ray diffraction studies *

	Crystal A	Crystal B
Molecular formula	$C_{16}H_{23}MoNO$	$C_{16}H_{23}MoNO\cdot0.5C_{20}H_{30}Mo_2O_4$
M	341.30	604.47
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/a$
a/Å	9.370(4)	32.569(9)
b/Å	12.322(5)	8.535(4)
c/Å	13.301(5)	9.482(5)
β/°		93.33(3)
U/Å^3	1 535(1)	2 631(2)
D_c/g cm^{-3}	1.476	1.526
F(000)	704	1 236
Crystal dimensions/mm	0.13 × 0.20 × 0.25	0.15 × 0.25 × 0.34
μ/cm^{-1}	8.26	9.55
2θ range/°	6—50	6—52
Reflections measured	*h,k,l*	±*h,k,l*
Unique total data	1 945	5 207
Unique observed data $[I > 2\sigma(I)]$	887	3 160
R	0.0654	0.1166
R′	0.1039	0.1666

* Details in common: niobium-filtered Mo-K_α radiation (λ = 0.710 73 Å), $Z = 4$; Siemens AED diffractometer; scan type θ—2θ; scan speed 3—12 °θ min^{-1}; scan range $(\theta - 0.6) - (\theta + 0.6 + 0.346 \tan \theta)$; one standard reflection measured every 50.

Table 9. Fractional atomic co-ordinates (× 10^4), with e.s.d.s in parentheses, for the non-hydrogen atoms of crystal A

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	1 134(1)	322(1)	0
N	1 552(35)	1 411(22)	−986(20)
O	1 913(27)	1 984(18)	−1 586(18)
C(1)	1 656(33)	1 402(22)	1 091(28)
C(2)	−984(32)	−184(18)	−989(21)
C(3)	−1 175(33)	913(23)	−667(24)
C(4)	−1 201(23)	881(16)	412(20)
C(5)	−1 212(24)	−220(14)	706(18)
C(6)	−1 125(18)	−875(14)	−167(15)
C(7)	2 795(27)	−929(20)	900(22)
C(8)	3 484(16)	−294(11)	133(23)
C(9)	2 966(21)	−687(16)	−812(17)
C(10)	2 010(32)	−1 601(23)	−568(24)
C(11)	1 906(27)	−1 618(18)	472(20)
C(12)	3 525(36)	−549(23)	1 831(27)
C(13)	4 682(21)	505(14)	−234(15)
C(14)	3 160(31)	−646(22)	−2 027(25)
C(15)	1 311(22)	−2 353(20)	−1 335(22)
C(16)	1 060(28)	−2 399(23)	1 078(23)

Table 10. Fractional atomic co-ordinates (× 10^4), with e.s.d.s in parentheses, for the non-hydrogen atoms of crystal B

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	3 164(1)	−715(2)	7 762(2)
Mo(2)	4 659(1)	4 840(2)	680(1)
O(1)	2 471(7)	−2 951(26)	8 144(20)
O(2)	4 218(3)	4 574(15)	−371(12)
O(3)	5 056(3)	3 336(13)	39(10)
N	2 777(5)	−2 058(20)	7 994(18)
C(1)	3 424(7)	−2 395(29)	6 295(25)
C(2)	3 384(9)	−179(33)	10 164(31)
C(3)	3 437(7)	−1 776(30)	9 813(24)
C(4)	3 766(8)	−1 780(30)	9 044(24)
C(5)	3 927(10)	−387(39)	8 850(34)
C(6)	3 735(8)	673(32)	9 523(27)
C(7)	3 144(5)	847(19)	5 535(16)
C(8)	2 740(5)	437(19)	6 021(17)
C(9)	2 675(5)	1 199(19)	7 281(16)
C(10)	3 029(5)	2 229(18)	7 555(15)
C(11)	3 292(6)	2 043(19)	6 523(16)
C(12)	3 304(6)	560(23)	4 135(21)
C(13)	2 442(7)	−598(27)	5 176(24)
C(14)	2 278(8)	1 205(30)	8 070(25)
C(15)	3 033(7)	3 476(25)	8 723(21)
C(16)	3 688(7)	2 929(28)	6 398(23)
C(17)	4 852(5)	5 857(19)	3 029(16)
C(18)	4 438(5)	6 087(19)	2 721(16)
C(19)	4 240(5)	4 614(20)	2 661(17)
C(20)	4 559(5)	3 497(19)	2 795(16)
C(21)	4 937(5)	4 198(21)	3 066(18)
C(22)	5 185(7)	7 071(30)	3 188(24)
C(23)	4 217(6)	7 652(24)	2 725(20)
C(24)	3 793(6)	4 376(24)	2 389(21)
C(25)	4 479(8)	1 745(31)	2 849(25)
C(26)	5 354(7)	3 492(29)	3 291(21)

−30 °C) and the resultant solution was stirred until it reached room temperature; $[PPh_4]Br$ (1.00 g, 2.40 mmol) was then added. After stirring for *ca.* 20 min the insoluble organoaluminate was filtered off and the solvent removed *in vacuo* leaving a residue, which was washed with hexane to give complex (**3b**) (yield 1.18 g, 93%) as a yellow solid. The chloro, (**3a**), and iodo, (**3c**), complexes were obtained from (**1a**) or (**1c**) by essentially identical procedures to those described for (**3b**) (yields 78 and 76% respectively).

$[MoMe(\eta\text{-}C_5Me_5)(NO)X(PPh_3)]$ (**4**). (*a*) *From complex* (**1**). The chloro complex (**4a**) was obtained by addition at −68 °C of triphenylphosphine (0.13 g, 0.50 mmol) to a red solution obtained as described above from complex (**1a**) (0.25 mmol) and a 10% solution of Al_2Me_6 (0.50 cm^3, 0.25 mmol) in toluene. The resultant yellow solution was evaporated to dryness and methanol (1 cm^3) was added dropwise at −68 °C. The mixture was allowed to warm up while stirring. When gas evolution had stopped the volatile components were removed and the residue extracted with toluene until a colourless solution was obtained. The solvent was removed *in vacuo* and the resultant yellow solid washed with hexane to give pure complex (**4a**) (yield 0.16 g, 56%). The preparation of the corresponding bromo, (**4b**), and iodo, (**4c**), complexes was carried out from (**1b**) or (**1c**) by the same method (yields 61 and 68% respectively).

(*b*) *From complex* (**2**). Complex (**4a**) was prepared by dropwise addition of a 10% toluene solution of Al_2Me_6 (0.17 cm^3, 0.085 mmol) to a stirred suspension of (**2**) (0.10 g, 0.17 mmol) in toluene (10 cm^3). Treatment of the resultant yellow solution continued as in (*a*) (yield 62%). Complexes (**4b**) and (**4c**) were prepared from (**2b**) and (**2c**) by the same method (yields 70 and 72% respectively).

$[MoMe_2(\eta\text{-}C_5Me_5)(NO)]$ (**5**). A 1.6 mol dm^{-3} solution of LiMe in diethyl ether (2.1 cm^3, 3.4 mmol) was slowly added to a solution of complex (**1b**) (0.71 g, 0.85 mmol) in toluene (*ca.* 15 cm^3) at −68 °C. The mixture was stirred and slowly (2 h) allowed to warm to room temperature. Stirring was continued for 1 h. The mixture was filtered and the insoluble residue treated with acetone to give a red solution. The solvent was removed under reduced pressure, the residue extracted into pentane (80 cm^3) and evaporated to dryness to give complex (**5**) (yield 56%) as a crystalline red-violet solid.

$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(NO)X]$ (**6**). The chloro complex (**6a**) was obtained by reaction in the dark of (**1a**) (0.40 g, 0.60 mmol) in toluene (*ca.* 60 cm^3) and $Tl(C_5H_5)$ (0.32 g, 1.2 mmol). After stirring for 10 h the TlCl formed was eliminated by gravity filtration through Celite. Solvent was removed under vacuum and the green solid was washed with hexane (10 cm^3) to give complex (**6a**) (yield 0.34 g, 79%). The corresponding bromo, (**6b**), and iodo, (**6c**), complexes were similarly prepared from (**1b**) and (**1c**) (yields 86 and 73% respectively).

[MoMe(η-C_5H_5)(η-C_5Me_5)(NO)] (**7**). This complex was obtained from (**3b**) by the same method used for (**6**) except that the product was extracted with pentane until colourless. The pentane solution was evaporated to dryness *in vacuo* and the residue was chromatographed over a 4 × 1 cm column using alumina as support and toluene as eluant. Red crystals of complex (**7**) were obtained (yield 47%).

X-Ray Collection, Structure Determinantion, and Refinement of Crystals A *and* B.—Both crystals A and B were of very poor quality, so that accurate determinations of the structures were prevented. The crystallographic data are collected in Table 8. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 (A) and 25 (B) carefully centred reflections. Data were collected at room temperature, the individual profiles being analyzed following Lehmann and Larsen.[26] No correction for absorption effects was made.

Both structures were solved by standard Patterson and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters only for the Mo, O, N, and C(1) (methyl group) atoms. The hydrogen atoms in both structures were placed at calculated positions and introduced in the final structure-factor calculations with fixed isotropic thermal parameters. The SHELX system of computer programs was used.[27] In the last cycles of refinement a weighting scheme was used, $w = [\sigma^2(F_o) + gF_o^2]^{-1}$, with $g = 0.0443$ for A and 0.0291 for B. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 28. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Universitario dell'Italia Nord-Orientale, Bologna. Final atomic co-ordinates for the non-hydrogen atoms of A and B are given in Tables 9 and 10 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Acknowledgements

We gratefully acknowledge the Comision Asesora de Investigacion Cientifica y Técnica for financial support (ref. 2001/83).

References

1 R. B. King, *Inorg. Chem.*, 1968, **7**, 90; J. L. Calderon and F. A. Cotton, *J. Organomet. Chem.*, 1968, **30**, 377.
2 F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, 1968, **90**, 6232.
3 F. A. Cotton and G. A. Rusholme, *J. Am. Chem. Soc.*, 1972, **94**, 402.
4 J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, 1969, **91**, 2528.
5 F. A. Cotton, *Discuss. Faraday. Soc.*, 1969, **47**, 79.
6 R. B. King, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 901.
7 J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307.
8 F. A. Cotton, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975.
9 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
10 (*a*) M. M. Hunt, W. G. Kita, B. E. Mann, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1978, 467; (*b*) M. M. Hunt, W. G. Kita, and J. A. McCleverty, *ibid.*, p. 474; (*c*) M. M. Hunt and J. A. McCleverty, *ibid.*, p. 480.
11 B. Alegre, E. de Jesús, A. Vázquez de Miguel, P. Royo, A. M. M. Lanfredi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1988, 819.
12 V. J. Shiner, jun., D. Whittaker, and V. P. Fernandez, *J. Am. Chem. Soc.*, 1963, **85**, 2318.
13 P. Legzdins, S. J. Rettig, L. Sánchez, B. E. Bursten, and M. G. Gatter, *J. Am. Chem. Soc.*, 1985, **107**, 1411; P. Legzdins, S. J. Rettig, and L. Sánchez, *Organometallics*, 1988, **7**, 2394.
14 P. Gomez-Sal, E. de Jesús, P. Royo, A. Vázquez de Miguel, S. Martinez-Carrera, and S. Garcia-Blanco, *J. Organomet. Chem.*, 1988, **353**, 191.
15 See for example, G. Parkin and J. E. Bercaw, *Polyhedron*, 1988, **7**, 2053 and refs. therein; A. H. Liu, R. C. Murray, J. C. Dewan, B. D. Santarsiero, and R. R. Schrock, *J. Am. Chem. Soc.*, 1987, **109**, 4282; P. Legzdins and C. R. Nurse *Inorg. Chem.*, 1985, **24**, 327 and refs. therein.
16 A. P. Gaugham, B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, and D. W. Meek, *J. Am. Chem. Soc.*, 1973, **95**, 6859; B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3060; R. D. Feltham and J. H. Enemark, *Top. Stereochem.*, 1981, **12**, 155.
17 K. Prout, T. S. Cameron, R. A. Forder, and, in parts, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290.
18 M. A. Adams, K. Folting, J. C. Huffman, and K. G. Caulton, *Inorg. Chem.*, 1979, **18**, 3020.
19 C. Coudwell and K. Prout, *Acta Crystallogr., Sect. B*, 1978, **34**, 933.
20 H. Arzoumanian, A. Badly, M. Pierrot, and J-F. Petrignani, *J. Organomet. Chem.*, 1985, **294**, 327.
21 M. Herberhold, W. Kremmitz, A. Razavi, H. Schöllhorm, and U. Thewald, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 601.
22 M. H. Chisholm, K. Folting, J. C. Huffman, and C. C. Kirkpatrick, *Inorg. Chem.*, 1984, **23**, 1021.
23 P. Leoni, M. Pasquali, L. Salsini, C. di Bugno, D. Braga, and P. Sabatino, *J. Chem. Soc., Dalton. Trans.*, 1989, 155; J. W. Faller and Y. Ma, *J. Organomet. Chem.*, 1988, **340**, 59.
24 R. King, *Inorg. Chem.*, 1967, **6**, 30; T. A. James and J. A. McCleverty, *J. Chem. Soc. A*, 1971, 1068; *ibid.*, p. 1596; J. A. McCleverty and D. Seddon, *J. Chem. Soc., Dalton Trans.*, 1972, 2526.
25 W. Michiels, E. de Jesús, A. Vázquez de Miguel, and P. Royo, *J. Chem. Soc., Dalton Trans.*, 1990, 2445.
26 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect A*, 1974, **30**, 580.
27 G. M. Sheldrick SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
28 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 20*th November* 1989; *Paper* 9/04940A