Synthesis of Dicarbonyl and Halogeno Complexes of (η-Pentamethylcyclopentadienyl)(nitrosyl)-molybdenum and -tungsten. Crystal Structure of [{Mo(η^5-C_5Me_5)(NO)Br(μ-Br)}$_2$]†

Pilar Gomez-Sal, Ernesto de Jesús, Wilfried Michiels, Pascual Royo,* and Amelio Vâzquez de Miguel
Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, 28871 Alcalá de Henares, Madrid, Spain
Sagrario Martínez-Carrera
Departamento de Rayos X, Instituto Rocasolano, C.S.I.C., Madrid, Spain

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Under appropriate conditions the reaction of [M(η^5-C_5Me_5)(NO)$(CO)_2$] [M = Mo, (**1**); or W, (**2**)] with X_2 (X = Cl, Br, or I) gives [{M(η^5-C_5Me_5)(NO)X_2}$_n$] [M = Mo, (**3a**)—(**3c**); or W, (**4a**)—(**4c**); *n* = 1 or 2]. When M = W and X = Cl the new carbonylnitrosyl compound [W(η^5-C_5Me_5)(NO)Cl_2(CO)] (**5**) has been isolated and characterized; (**5**) is proposed to be an intermediate in the preparation of (**4a**) from (**2**). The compound (**3b**) or (**4b**) reacts with mono- or bi-dentate phosphines giving [M(η^5-C_5Me_5)(NO)Br_2L] [L = PPh_3, M = Mo, (**6b**); or W, (**7**); L = $OPPh_3$, M = Mo, (**8**); or W, (**9**)] or [Mo(η^5-C_5Me_5)(NO)Br(L–L)][Mo(η^5-C_5Me_5)(NO)Br_3] [L–L = $Ph_2PCH_2PPh_2$ (dppm), (**10**); or $Ph_2PCH_2CH_2PPh_2$ (dppe), (**11**)]. Complex (**11**) is in equilibrium with an isomer [Mo_2(η^5-C_5Me_5)$_2$$(NO)_2$$Br_4$(dppe)] (**12**). *X*-Ray structure analysis of [{Mo(η^5-C_5Me_5)(NO)-Br(μ-Br)}$_2$] (**3b**) shows space group *C*2/*c* with *a* = 15.102(4), *b* = 8.403(6), *c* =21.498(10) Å, β = 98.69(2)°, and *Z* = 4; *R* = 0.063 and *R'* = 0.055, based on 2 688 observed reflections. The molecule is dimeric with two bridging bromo atoms, in contrast with the monomeric nature of the recently reported structure of the parent (**4c**).

The nitrosyl compounds [M(η^5-C_5H_5)(NO)$(CO)_2$] (M = Mo or W) were first synthesized in 1955.[1] The best method for their synthesis is the nitrosylation of Na[M(η^5-C_5H_5)$(CO)_3$][2,3] or [M(η^5-C_5H_5)H$(CO)_3$][4,5] with *p*-$MeC_6H_4SO_2N(NO)Me$ (Diazald). Although, some derivatives have been obtained from the dicarbonyl compounds, the starting materials mostly employed for the preparation of (cyclopentadienyl)(nitrosyl)-molybdenum or -tungsten compounds are the halogeno derivatives [{M(η^5-C_5H_5)(NO)X_2}$_n$] (X = Cl, Br, or I) obtained by halogenation of the dicarbonyl compounds with X_2.[5,6]

The pentamethylcyclopentadienyl compounds [M(η^5-C_5Me_5)(NO)$(CO)_2$] [M = Mo, (**1**); or W, (**2**)] were obtained[7] in 1980 by a method similar to that used for the cyclopentadienyl analogues. We have studied the halogenation reaction[8] of (**1**) and (**2**) with the goal of extending our preparation of methyl derivatives [{M(η^5-C_5R_5)(NO)Me(X)}$_n$] from R = H[9] to R = Me.[10] Although a systematic study of the halogenation reaction has not been carried out (the reactivity of the chromium analogue has been studied[11]), the preparation and crystal structure of [W(η^5-C_5Me_5)(NO)I_2] (**4c**) have been reported during the preparation of this manuscript.[12] The derivative (**4c**) is a 16-electron monomeric compound[12a] whereas the bromo molybdenum compound (**3b**) reported here is an 18-electron dimeric species.

Results and Discussion

Preparative Results.—Compounds (**1**) and (**2**) have been obtained by reported methods.[7] The use of K(C_5Me_5) instead of Na(C_5Me_5) simplifies the preparation of (**1**) and increases the yield from 41 to 77% based on the metal (32 to 60% based on C_5Me_5H). The ^{13}C-{^1H} n.m.r. data for (**1**) and (**2**) are reported in the Experimental section.

The reaction between compound (**1**) or (**2**) with X_2 (X = Cl, Br, or I) [equation (1)] leads to the halogeno derivatives

$$\underset{(1),(2)}{[\mathrm{M}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{NO})(\mathrm{CO})_2]} + \mathrm{X_2} \longrightarrow \underset{(3),(4)}{[\{\mathrm{M}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{NO})\mathrm{X_2}\}_n]} + \mathrm{CO} \qquad (1)$$

[{M(η^5-C_5Me_5)(NO)X_2}$_n$] [M = Mo, (**3a**)—(**3c**); or W, (**4a**)—(**4c**); *n* = 1 or 2], similarly to their C_5H_5 analogues.[5,6] A titrated CCl_4 solution of chlorine was used in the case of X = Cl.

In the preparation of compound (**4a**), the presence (i.r. monitoring) of [W(η^5-C_5Me_5)(NO)Cl_2(CO)] (**5**) was observed; this compound can be isolated in low yields (7%) if the temperature is maintained below −10 °C. Carbonylnitrosyl intermediates [equation (2)] have been previously proposed,[6a]

$$[\mathrm{M}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{NO})(\mathrm{CO})_2] + \mathrm{X_2} \xrightarrow{-\mathrm{CO}} [\mathrm{M}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{NO})\mathrm{X_2}(\mathrm{CO})] \xrightarrow{-\mathrm{CO}} [\{\mathrm{M}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{NO})\mathrm{X_2}\}_n] \qquad (2)$$

or sometimes identified by i.r. spectroscopy.[6d,12a] To our knowledge, (**5**) is the first compound of this type stable enough to be isolated and characterized. We have not been able to obtain (**5**) by reaction of (**4a**) with CO (1 atm, *ca.* 105 Pa) nor (**4a**) from pure (**5**) by spontaneous loss of CO.

Bromo compounds (**3b**) and (**4b**) react with P- and O-donor ligands such as PPh_3 and $OPPh_3$ giving [equation (3)] monomeric [M(η^5-C_5Me_5)(NO)X_2L] [L = PPh_3, M =

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† Di-μ-bromo-bis[bromo(η-pentamethylcyclopentadienyl)nitrosylmolybdenum].

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

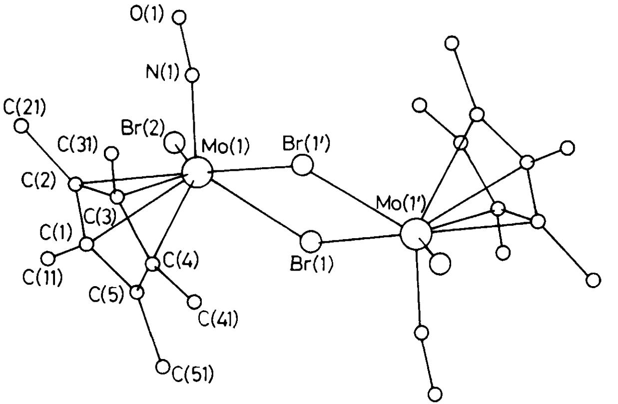

Figure. View of the structure of the complex [{Mo(η^5-C_5Me_5)(NO)Br(μ-Br)}$_2$] (**3b**) showing the atom numbering scheme

$$[\{M(\eta^5\text{-}C_5Me_5)(NO)X_2\}_n] + L \longrightarrow \underset{\textbf{(3),(4)}}{} \quad \underset{\textbf{(6)—(9)}}{[M(\eta^5\text{-}C_5Me_5)(NO)X_2L]} \quad (3)$$

Mo, (**6b**); or W, (**7**); L = $OPPh_3$, M = Mo, (**8**); or W, (**9**)]. Interestingly, whereas the iodomolybdenum compound (**3c**) reacts with PPh_3 giving (**6c**), the final product of reaction of (**4c**) with PPh_3 contains (^1H and ^{31}P n.m.r. evidence) major quantities of (**4c**) and free phosphine.

Analytical and physical data for compounds (**3**)—(**9**) are given in Table 1, and n.m.r. and i.r. data in Table 2. The C_5Me_5 compounds are more soluble and air stable than the C_5H_5 analogues. Their ν(NO) bands are shifted by 10—20 cm^{-1} to lower values with respect to the C_5H_5 analogues,[5,6,13,14] in agreement with the increasing basicity of the pentamethylated ring,[15] and are in the range[16] expected[17] for linear NO. The linear NO and the dimeric nature proposed for (**3b**) have been confirmed in the solid state by an *X*-ray analysis (see below).

The green-yellow toluene solutions of compound (**3b**) react with the diphosphines dppm ($Ph_2PCH_2PPh_2$) and dppe ($Ph_2PCH_2CH_2PPh_2$) to give initially orange-red solutions from which precipitate in 2 h the ionic complexes (**10**) and (**11**) respectively [equation (4)]. Their structures have been assigned

$$\underset{\textbf{(3b)}}{[\{Mo(\eta^5\text{-}C_5Me_5)(NO)Br_2\}_n]} + \text{L–L} \longrightarrow \quad (4)$$
$$[Mo(\eta^5\text{-}C_5Me_5)(NO)Br(\text{L–L})][Mo(\eta^5\text{-}C_5Me_5)(NO)Br_3]$$
$$\text{L–L} = \text{dppm}, \textbf{(10)}; \text{ or dppe},$$
$$\textbf{(11)} \rightleftharpoons \underset{\textbf{(12)}}{[Mo_2(\eta^5\text{-}C_5Me_5)_2(NO)_2Br_4(\text{dppe})]}$$

on the basis of their analytical and spectroscopic properties (see Tables 1 and 2). Each compound presents two ν(NO) bands as well as two ^1H n.m.r. C_5Me_5 signals, due to the cationic and anionic components. The two P atoms of each complex are not equivalent in the ^{31}P-{^1H} n.m.r. spectrum, in accord with a *cis* chelate co-ordination. Their shifts and $J(^{31}P-^{31}P)$ couplings are similar to those found for other molybdenum-chelated dppm and dppe complexes.[13b,18,19] We have estimated a ring contribution (Δ_R)[17] to the ^{31}P-{^1H} n.m.r. shift of −26.7 p.p.m. for (**10**) and 27.2 p.p.m. for (**11**), close to the typical molybdenum values of −20 p.p.m. for dppm and 25 p.p.m. for dppe.[18] In solution (CH_2Cl_2), complex (**11**) is in equilibrium with its isomer (**12**), (**12**) being the most stable at low temperature; a mixture of the two isomers is obtained in the solid. The molar conductivities of (**10**) and (**11**) (Table 1, footnotes *d* and *f*) in acetonitrile and nitromethane are consistent with 1:1 electrolytes.[20] A similar behaviour has been reported[21] for carbonyliron derivatives.

Crystal Structure of [{Mo(η^5-C_5Me_5)(NO)Br(μ-Br)}$_2$] (**3b**).—The molecular structure of compound (**3b**) based on the *X*-ray structural analysis is shown in the Figure with the numbering scheme employed. Atomic parameters for the non-hydrogen atoms are listed in Table 3, important bond distances and bond angles in Table 4. The structure contains discrete dimeric molecules, with crystallographically imposed C_i symmetry. The asymmetric unit in the unit cell contains half a molecule. The dimer is bridged by two bromine atoms. Then, the formal electron count for this complex is 18 electrons, in contrast with that (16 electrons) recently reported for monomeric (**4a**).[12a]

The co-ordination around atom Mo(1) is a 'four-legged piano-stool,' all the angles having the usual values for this kind of structure. The distances from Mo(1) to the ring plane and to the best N(1)–Br(1)–Br(1')–Br(2) plane are 2.012(1) and 0.814(1) Å, respectively. The angle between these two planes is 14.4(2)°. The Mo(1)–C(1—5) distances ranging from 2.258(8) to 2.438(10) Å indicate some ring tilt due to the *trans* effect of the NO ligand.[22] The Mo(1)–N(1) distance [1.773(2) Å] is shorter than those found (1.78—1.92 Å)[9,23] in other four-legged piano-stool complexes of the {Mo(NO)}^{4} type,[17] indicating important retrodonation. The Mo(1)–N(1)–O(1) angle [168.5(8)] is slightly bent but the NO group must be classified as linear.[17] The terminal Mo(1)–Br(2) bond length [2.557(2) Å] is also shorter than those found in related compounds (2.61—2.68 Å);[9,24] this shortening has also been found in the Mo–I(terminal) distance of the monomer (**4c**).[12a] The bromine bridges are quasi-symmetrical [2.614(1) and 2.685(1) Å]. The Mo(1)···Mo(1') distance [4.168(2) Å] indicates no metal–metal interaction.

Experimental

All reactions were carried out in dried Schlenk tubes under argon or nitrogen; the manipulations were carried out using syringes or canulae through Subaseals. The solvents were dried and distilled under an inert nitrogen atmosphere before use. I.r. spectra were recorded in Nujol mulls over the range 4 000—200 cm^{-1} on a Perkin-Elmer 599 spectrophotometer, ^1H, ^{13}C, and ^{31}P n.m.r. spectra on a Varian FT 80 A spectrometer. Melting points were determined with a Büchi SMP-20 instrument. The C, H, and N analyses were made with a Perkin-Elmer sigma 3B instrument fitted with Carbobax column and a flame ionization detector. The conductivity measurements were carried out in a WTW LF42 instrument. Microanalytical, melting point, i.r., n.m.r., and conductivity data for the new complexes are collected in Tables 1 and 2. The compounds C_5Me_5H[25] and dppm[26] were prepared according to literature methods. All other reagents were obtained from commercial sources, and used without further purification.

Preparations.—[Mo(η^5-C_5Me_5)(NO)(CO)$_2$] (**1**). A tetrahydrofuran (thf) solution (100 cm^3) containing C_5Me_5H (10.3 g, 76 mmol) and solid K (2.7 g, 69 mmol) was heated under reflux with vigorous stirring for 5 h. A white suspension of K(C_5Me_5) was obtained. Then [Mo(CO)$_6$] (15.4 g, 58 mmol) was added and the mixture heated under reflux. When evolution of CO had stopped (10 h) the solution was allowed to reach room temperature and a thf solution (50 cm^3) of *p*-$MeC_6H_4SO_2N$(NO)Me (Diazald) (13.4 g, 62.7 mmol) slowly added (30 min) with stirring. The solution was filtered through a Celite column and evaporated to dryness under reduced pressure. The residue was extracted with diethyl ether (2 × 100 cm^3), the solution filtered through a Celite column and evaporated to dryness. The

Table 1. Analytical, physical, and spectroscopic data for complexes (**3**)—(**12**)

Complex			Colour	M.p. (°C)	Analysis (%)[a] C	H	N	X[b]
$[\{Mo(\eta^5\text{-}C_5Me_5)(NO)X_2\}_n]$	(**3a**)	X = Cl	Orange	238	36.0	4.7	4.1	21.1
					(36.2)	(4.6)	(4.2)	(21.3)
	(**3b**)	X = Br	Brown-red	165	28.5	3.7	3.4	38.4
					(28.5)	(3.6)	(3.3)	(38.0)
	(**3c**)	X = I	Red-violet	262	23.2	2.9	2.7	
					(23.3)	(2.9)	(2.7)	
$[\{W(\eta^5\text{-}C_5Me_5)(NO)X_2\}_n]$	(**4a**)	X = Cl	Pale green	79[c]	29.0	3.6	3.3	15.7
					(28.6)	(3.6)	(3.3)	(16.9)
	(**4b**)	X = Br	Emerald green	106[c]	23.0	2.9	2.7	29.4
					(23.6)	(3.0)	(2.7)	(31.4)
	(**4c**)	X = I	Brown-green	142[c]	20.3	2.6	2.5	
					(19.9)	(2.5)	(2.3)	
$[W(\eta^5\text{-}C_5Me_5)(NO)Cl_2(CO)]$	(**5**)		Green		30.2	3.5	2.6	
					(29.5)	(3.4)	(3.1)	
$[Mo(\eta^5\text{-}C_5Me_5)(NO)X_2(PPh_3)]$	(**6a**)	X = Cl	Yellow	127[c]	56.3	5.2	2.2	11.6
					(56.6)	(5.1)	(2.3)	(11.9)
	(**6b**)	X = Br	Yellow	80[c]	49.2	4.6	2.2	23.2
					(49.2)	(4.4)	(2.0)	(23.4)
	(**6c**)	X = I	Yellow	98[c]	42.8	3.9	1.8	
					(43.3)	(3.9)	(1.8)	
$[W(\eta^5\text{-}C_5Me_5)(NO)Br_2(PPh_3)]$	(**7**)		Brown-yellow	82[c]	43.4	3.7	2.0	
					(43.6)	(3.9)	(1.8)	
$[Mo(\eta^5\text{-}C_5Me_5)(NO)Br_2(OPPh_3)]$	(**8**)		Yellow	175[c]	47.6	4.3	2.3	23.1
					(48.1)	(4.3)	(2.0)	(22.9)
$[W(\eta^5\text{-}C_5Me_5)(NO)Br_2(OPPh_3)]$	(**9**)		Brown	127[c]	42.5	4.2	1.9	
					(42.7)	(3.8)	(1.8)	
$[Mo(\eta^5\text{-}C_5Me_5)(NO)Br(L\text{–}L)]$ $[Mo(\eta^5\text{-}C_5Me_5)(NO)Br_3]$	(**10**)	L–L = dppm[d]	Yellow	118[c]	44.0	4.0	2.2	
					(44.1)	(4.3)	(2.3)	
	(**11**) + (**12**)[e]	L–L = dppe[f]	Yellow	250[c]	44.8	4.4	2.3	
					(44.5)	(4.4)	(2.3)	

[a] Required values given in parentheses. [b] Halogen; method used is no good for determining iodide. [c] With decomposition. [d] Molar conductivity (25 °C, 5×10^{-4} mol dm^{-3}): Λ_M 88.1 (MeCN), 59.8 ($MeNO_2$), and 14.7 (CH_2Cl_2) ohm^{-1} cm^2 mol^{-1}. [e] See text. [f] Λ_M (25 °C, 5×10^{-4} mol dm^{-3}): 124.3 (MeCN), 67.2 ($MeNO_2$), and 24.1 (CH_2Cl_2) ohm^{-1} cm^2 mol^{-1}.

Table 2. Selected n.m.r. and i.r. data for complexes (**3**)—(**12**)

Complex	$\delta_H(C_5Me_5)$[a]	δ_P[b]	ν(NO)[c]/cm^{-1}
(**3a**)	1.50 (s)		1 652
(**3b**)[d]	1.50 (s)		1 660
(**3c**)	1.55 (s)		1 658
(**4a**)	1.56 (s)		1 620
(**4b**)	1.60 (s)		1 630
(**4c**)	1.64 (s)		1 625
(**5**)[e]	1.55 (s)		1 636
(**6a**)	1.56 (s)	[f]	1 657
(**6b**)	1.51 (s)	[f]	1 658
(**6c**)	1.70 (s)	[f]	1 655
(**7**)	1.77 (s)	31.7 (s)[g]	1 625
(**8**)	1.73 (s)	33.0 (s)	1 646
(**9**)	1.77 (s)	25.3 (s)	1 625
(**10**)	1.79 (s)[h,i]	−3.6 (d), −19.1 (d)[c,h,j]	1 663[h]
	1.88 (s)[i,k]		1 645[k]
(**11**)	1.61 (s)[h,i]	64.8 (d), 44.6 (d)[c,h,l]	1 659 or 1 630
	1.91 (s)[i,k]		1 645[k]
(**12**)	1.68 (s)[i]	37.1 (m br)[c]	1 659 or 1 630

[a] 80 MHz, solvent C_6D_6, internal standard $SiMe_4$. [b] $^{31}P\text{-}\{^1H\}$, 32 MHz, solvent C_6H_6, external standard H_3PO_4. [c] In CH_2Cl_2. [d] $\delta_C(^{13}C\text{-}\{^1H\}$, 20 MHz, solvent CH_2Cl_2, external standard $SiMe_4$): 121.2 (C_5Me_5) and 11.9 p.p.m. (C_5Me_5). [e] ν(CO) 1 980 cm^{-1}. [f] Too insoluble in C_6H_6. [g] J(PW) 265 Hz. [h] Assigned to the cationic part. [i] In CD_2Cl_2. [j] J(PP) 78 Hz. [k] Assigned to the anionic part. [l] J(PP) 38 Hz.

residue was Soxhlet extracted with light petroleum (b.p. 40—60 °C) and sublimed at 60 °C and 5×10^{-3} mmHg (*ca.* 0.67 Pa). Orange crystals [14.3 g, 77% based on Mo, 60% based on C_5Me_5H] of compound (**1**) were obtained (Found: C, 45.5; H, 5.0; N, 4.3. Calc. for $C_{12}H_{15}MoNO_3$: C, 45.4; H, 4.8; N, 4.4%); $\nu_{max.}$ 2 010 and 1 929 (CO) and 1 648 cm^{-1} (NO) (CH_2Cl_2). δ_H(80 MHz, C_6D_6, internal standard $SiMe_4$): 1.64 (C_5Me_5, s). $\delta_C(^{13}C\text{-}\{^1H\}$, 20 MHz, CH_2Cl_2, external $SiMe_4$): 231.0 (CO, s), 106.5 (C_5Me_5, s), and 10.8 p.p.m. (C_5Me_5).

The tungsten compound (**2**) was obtained similarly (45% based on W, 42% based on C_5Me_5H) but in lower yields than those previously reported [68% based on W, 49% based on C_5Me_5H,[7] 81% based on $Li(C_5Me_5)$[12a]] (Found: C, 34.7; H, 3.5; N, 3.5. Calc. for $C_{12}H_{15}NO_3W$: C, 35.6; H, 3.7; N, 3.4%); ν(CO) 1 990 and 1 910 (CO) and 1 630 cm^{-1} (NO) (CH_2Cl_2). δ_H(80 MHz, C_6D_6, internal standard $SiMe_4$): 1.57 (C_5Me_5, s). $\delta_C(^{13}C\text{-}\{^1H\}$, 20 MHz, CH_2Cl_2, external $SiMe_4$): 195.3 (CO, s), 115.2 (C_5Me_5, s), and 11.1 p.p.m. (C_5Me_5).

$[\{Mo(\eta^5\text{-}C_5Me_5)(NO)Cl_2\}_n]$ (**3a**).—All operations should be carried out under a well ventilated hood. Chlorine was bubbled through a CCl_4 solution until saturation. The solution was diluted six times in CCl_4 and introduced in a burette with a sealed receiver. A fraction of the solution (0.5 cm^3) was titrated[27] by addition to a KI (0.5 g) solution in water (50 cm^3). Then, the chlorine solution (2.2 mmol) was slowly added over a stirred solution of compound (**1**) (0.71 g, 2.2 mmol) in CCl_4 (50 cm^3). Carbon monoxide was evolved and a brown solid precipitated. Stirring was continued for 15 min and then hexane (20 cm^3) was added. The solid was filtered off, washed with hexane, and dried *in vacuo*. The product should be purified by Soxhlet extraction with CH_2Cl_2. The orange solid (0.67 g, 90%) is soluble in CH_2Cl_2.

Compound (**4a**) was obtained by the same method (60%) and

Table 3. Crystal data for complex (**3b**)

Crystal data	
Formula	$C_{20}H_{30}Br_4Mo_2N_2O_2$
Crystal habit	Prismatic
Crystal size (mm)	0.2 × 0.15 × 0.02
Symmetry, space group	Monoclinic, $C2/c$
Unit-cell determination:	Least-squares fit from 25 reflections ($\theta < 30$)
Unit-cell dimensions/Å	$a = 15.102(4), b = 8.403(6), c = 21.498(10), \alpha = 90.0, \beta = 98.69(2), \gamma = 90.0$
U/Å^3, Z	2 696(2), 4
D_c/g cm^{-3}, M, F(000)	2.074, 841.96, 1 616
μ/cm^{-1}	67.99
Experimental data	
Technique	Bisecting geometry Graphite-oriented monochromator, Mo-K_α radiation ω—2θ scans, scan width 1.0° Detector apertures 1 × 1, up to $\theta_{max.}$ 30° 1 min per reflection
Number of reflections:	
Measured	8 345
Independent	3 924
Observed	2 688 [$I > 2\sigma(I)$]
Range of hkl	−21 to 21, 0—11, 0—30, $(\sin\theta/\lambda)_{max.}$ 0.70
Value of $R_{int.}$	0.014
Standard reflections:	Two every 90 min, no variation

Table 4. Important bond distances (Å) and angles (°) with estimated standard deviations for complex (**3b**)

(*i*) Involving the Mo atom			
Mo(1)–Br(1)	2.685(1)	Mo(1)–C(2)	2.261(9)
Mo(1)–Br(1′)	2.614(1)	Mo(1)–C(3)	2.258(8)
Mo(1)–Br(2)	2.557(2)	Mo(1)–C(4)	2.382(8)
Mo(1)–N(1)	1.773(2)	Mo(1)–C(5)	2.438(10)
Mo(1)–C(1)	2.414(10)	Mo(1)–cp	2.023
Mo(1)–Br(1)–Mo(1′)	103.75(4)	Br(1)–Mo(1)–cp	116.2
Br(1)–Mo(1)–Br(1′)	76.25(4)	Br(2)–Mo(1)–N(1)	85.2(2)
Br(1)–Mo(1)–Br(2)	79.63(5)	Br(2)–Mo(1)–cp	108.8
Br(1)–Mo(1)–N(1)	125.4(2)	N(1)–Mo(1)–cp	118.3
(*ii*) Involving the C_5Me_5 ligand			
C(1)–C(2)	1.398(12)	C(1)–C(11)	1.506(18)
C(2)–C(3)	1.401(15)	C(2)–C(21)	1.486(14)
C(3)–C(4)	1.436(12)	C(3)–C(31)	1.480(13)
C(4)–C(5)	1.404(12)	C(4)–C(41)	1.512(19)
C(5)–C(1)	1.406(16)	C(5)–C(51)	1.506(19)
(*iii*) Involving the NO group			
N(1)–O(1)	1.144(11)	Mo(1)–N(1)–O(1)	168.5(8)

cp = Centroid of the cyclopentadienyl ring, C(1)—C(5). Primed atoms at $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$.

Table 5. Atomic parameters for complex (**3b**)

Atom	x	y	z
Mo(1)	0.738 77(4)	0.275 19(8)	0.594 95(3)
Br(1)	0.642 02(6)	0.273 46(15)	0.479 39(4)
Br(2)	0.613 55(8)	0.468 51(13)	0.611 27(6)
N(1)	0.812 29(54)	0.429 43(96)	0.626 51(41)
O(1)	0.864 60(56)	0.510 68(118)	0.654 56(45)
C(1)	0.658 81(61)	0.118 50(124)	0.662 48(48)
C(11)	0.571 15(80)	0.153 80(195)	0.685 00(86)
C(2)	0.743 11(62)	0.168 47(100)	0.691 93(41)
C(21)	0.759 12(113)	0.263 51(148)	0.750 84(49)
C(3)	0.809 19(54)	0.090 65(101)	0.661 07(39)
C(31)	0.907 01(69)	0.090 42(169)	0.682 59(63)
C(4)	0.763 12(77)	−0.002 43(102)	0.612 39(45)
C(41)	0.808 77(129)	−0.118 10(153)	0.573 64(72)
C(5)	0.670 70(77)	0.018 89(123)	0.612 13(52)
C(51)	0.596 79(111)	−0.063 49(165)	0.569 09(83)

can be obtained as red or green crystals depending on the solvent. Red-brown (**3b**) (78%), red-violet (**3c**) (70%), green (**4b**) (83%), and green-brown (**4c**) (92%) were obtained similarly to their cyclopentadienyl analogues.[5,6]

[W(η^5-C_5Me_5)(NO)Cl_2(CO)] (**5**). The reaction was carried out from (**2**) (2.50 g, 6.2 mmol) in CCl_4 (25 cm^3) as described for (**4a**), but all operations were performed at low temperature (*ca.* −20 to −10 °C). The green-blue suspension was filtered at −10 °C, and the solution [the solid contains (**4a**)] evaporated to dryness, washed with hexane, and dried under reduced pressure (0.20 g, 7%).

[Mo(η^5-C_5Me_5)(NO)Br_2(PPh_3)] (**6b**). Triphenylphosphine (0.11 g, 0.42 mmol) was added to a solution of (**3b**) (0.18 g, 0.21 mmol) in toluene (10 cm^3). The mixture was stirred for 1 h and hexane (30 cm^3) added. The yellow precipitate (0.26 g, 89%) was separated by filtration and dried *in vacuo*. Solid compound (**6b**) is stable in the air but its solutions decompose readily in the air or by heating. Compounds (**6a**), (**6c**), and (**7**)—(**9**) were obtained similarly.

[Mo(η^5-C_5Me_5)(NO)Br(dppm)][Mo(C_5Me_5)(NO)Br_3] (**10**). The addition of dppm (0.16 g, 0.42 mmol) in toluene (10 cm^3) to a toluene (30 cm^3) solution of compound (**3b**) (0.35 g, 0.42 mmol) produces an orange solution. After stirring for 2—3 h a yellow precipitate was obtained and filtered off. The solid (84%) was recrystallized by dissolution in CH_2Cl_2 and precipitation with toluene. It is insoluble in hexane and toluene.

The similar reaction with dppe gives a mixture of the isomers (**11**) and (**12**) (total yield: 88%).

Crystal Structure of [{Mo(η^5-C_5Me_5)(NO)Br(μ-Br)}$_2$] (**3b**).—A suitably sized red crystal of (**3b**) was mounted in a Enraf-Nonius CAD-4 automatic four-circle diffractometer. The crystallographic data are summarized in Table 5. Data were collected at room temperature.

Intensities were corrected for Lorentz and polarization effects in the usual manner. A correction for absorption was applied (maximum and minimum transmission factors 1.419 and 0.755, respectively).[28] No extinction correction was made. The structure was solved by a combination of heavy-atom, direct methods, and Fourier synthesis.

The structure was refined on F by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. In the later stages of the refinement H atoms were included at fixed calculated positions, and with the thermal parameters of the atoms to which they are attached. Final R and R' values of 0.063 and 0.055, respectively (weighting scheme, empirical fit so as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and *vs.* $\langle\sin\theta/\lambda\rangle$), were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from ref. 29. Calculations were performed with SIR 88,[30] DIRDIF,[31] PESOS,[32] PARST,[33] and X-RAY 80,[34] on a VAX 11750 computer.

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