

# The Synthesis, using Hexamethyldialuminium, and Reactivity of New (1—5- $\eta$ -Cyclopentadienyl)methyl(nitrosyl)molybdenum Complexes. Crystal Structure of Bromo( $\eta^5$ -cyclopentadienyl)methyl(nitrosyl)(triphenylphosphine)-molybdenum†

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Under appropriate conditions the reaction of  $[\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{X}\}_2(\mu\text{-X})_2]$  [ $\text{X} = \text{Cl}$  (1), Br (2), or I (3)] with  $\text{Al}_2\text{Me}_6$ , gives the new (probably dimeric) methyl complexes  $[\{\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\}_2(\mu\text{-X})_2]$  (4)—(6) which react with an equimolar amount of different ligands to give the monomeric neutral complexes  $[\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{XL}]$  [ $\text{L} = \text{tetrahydrothiophene (tht)}$ ,  $\text{X} = \text{Br}$  (7);  $\text{L} = \text{PPh}_3$ ,  $\text{X} = \text{Cl}$  (8), Br (9), or I (10);  $\text{L} = \text{OPPh}_3$ ,  $\text{X} = \text{Cl}$  (11) or Br (12)] and the anionic complex  $[\text{PPh}_4][\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Br}_2]$  (13). One of the routes to prepare complexes (7)—(12) gives instead of (12) a solid, (14), which contains a cation of variable composition and the same anion as in (13). The complexes (5) and (9) react with  $\text{Ti}(\text{C}_5\text{H}_5)_n$  to give the known  $[\text{MoMe}(\eta^n\text{-C}_5\text{H}_5)_2(\text{NO})]$  (the value of  $n$  is unknown). The molybdenum-carbon bond in (9) suffers cleavage only by addition of highly concentrated solutions of strong protonic acids to give the neutral complex  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Br}_2(\text{PPh}_3)]$  with  $\text{HBr}$ , or the dicationic complex  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)_2\text{L}]^{2+}$  [ $\text{L} = \text{Me}_2\text{CO}$  (15)] with  $\text{HBF}_4$ . The same compound (9) reacts with  $\text{LiR}$  to give dialkyl complexes  $[\text{MoMe}(\text{R})(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)]$  [ $\text{R} = \text{Me}$  (16),  $\text{C}_2\text{Ph}$  (17), or  $\text{C}_6\text{F}_5$  (18)]. The structure of complex (9) has been determined by  $X$ -ray diffraction methods. Crystals are monoclinic, space group  $P2_1/a$  with  $a = 18.778(5)$ ,  $b = 14.713(5)$ ,  $c = 8.354(3)$  Å,  $\beta = 102.77(2)^\circ$ , and  $Z = 4$ . The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares methods to  $R = 0.036$  for 2 532 observed reflections. The structure is of the 'four-legged piano stool' type with the  $\text{PPh}_3$  and  $\text{Me}$  ligands in *trans* positions. The Mo-N and N-O bond distances [1.814(6) and 1.115(8) Å respectively] indicate considerable Mo-NO back-bonding. The Mo-N-O group is nearly linear [171.3(6)°].

Very many reports on the well-developed chemistry of cyclopentadienyl(nitrosyl)molybdenum have been published in the last 20 years. However, the alkyl derivatives are poorly represented; only two methyl complexes of this type are known,  $[\text{MoMe}(\eta^n\text{-C}_5\text{H}_5)_2(\text{NO})]$  ( $n$  is unknown) and  $[\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})_2]$ .<sup>2</sup> More recently, during the course of our work, the dialkyl derivative  $[\text{MoR}_2(\eta^5\text{-C}_5\text{H}_5)(\text{NO})]$  ( $\text{R} = \text{CH}_2\text{SiMe}_3$ ) has been reported.<sup>3</sup>

Here we report the synthesis of new methyl complexes, and the chemical behaviour of the products obtained. The starting compounds for the preparation of these complexes were the dimers  $[\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{X}\}_2(\mu\text{-X})_2]$  (1)—(3)<sup>4</sup> or their adducts with  $\text{PPh}_3$  and  $\text{OPPh}_3$ .<sup>5</sup> Hexamethyldialuminium was employed as methylating agent. Interaction of the alkylaluminiums with transition metals has been little studied.<sup>6</sup>

## Results and Discussion

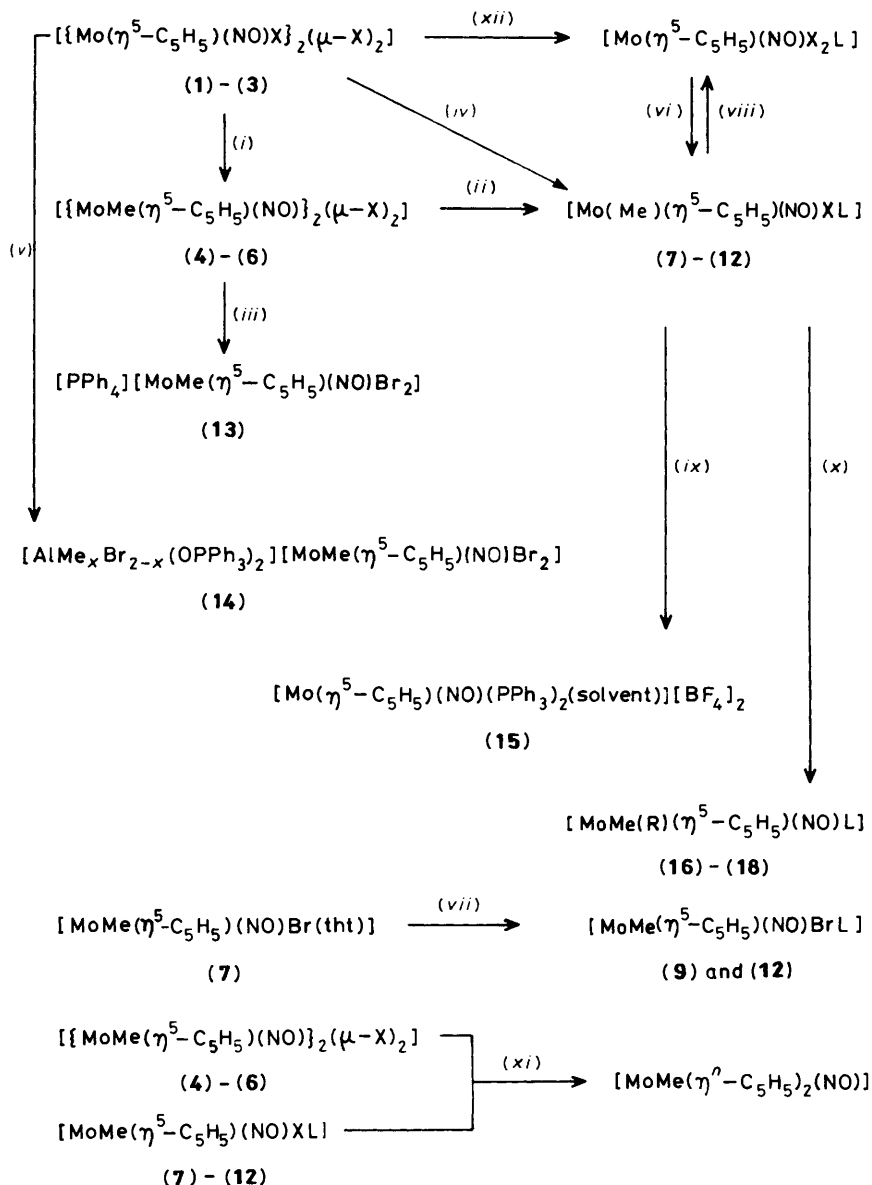
**Preparative Results.**—The selective methylation of only one of the halides bonded to each molybdenum atom in dimeric complexes of the type  $[\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{X}\}_2(\mu\text{-X})_2]$ <sup>4</sup> [ $\text{X} = \text{Cl}$  (1), Br (2), or I (3)] is not obtained in either reactions with lithium alkyls or Grignard reagents. We have studied reactions with hexamethyldialuminium [Scheme, reaction (i)] which are able to produce the monoalkylated derivatives (4)—

(6). Analytically pure products are isolated in good yields if the halogenomethylaluminium derivatives are previously eliminated. In fact, the direct reactions with (1)—(3) give the alkylated chloro, bromo, and iodo compounds (4)—(6) only in low yields, as pyrophoric powders. On the other hand, if the aluminium products are removed by precipitation as adduct complexes with a phosphonium halide, compounds (5) and (6), but not (4) (see below), are obtained as pure and non-pyrophoric microcrystals. Quantitative gas chromatography of the methane evolved by hydrolysis of the phosphonium halogenomethylaluminates, when a deficient amount of hexamethyldialuminium is employed, shows that at least two methyl groups can be redistributed from the aluminium to the molybdenum complex. The temperature of the reaction increases and its rate decreases, as expected, when the halogen electronegativity decreases:  $\text{X} = \text{Cl}$  (ca.  $-50^\circ\text{C}$ ) <  $\text{Br}$  (ca.  $-40^\circ\text{C}$ ) <  $\text{I}$  (ca.  $-20^\circ\text{C}$ ).

We propose (4)—(6) as dimers but the monomeric or dimeric nature of these complexes cannot be confirmed. However, complexes (4)—(6) have acidic properties and react with ligands to form neutral, (7)—(12) [Scheme, reaction (ii)], as well as anionic, (13) [Scheme, reaction (iii)], monomeric complexes.

There are two processes that appear to be in competition with each other. One is the selective separation of the halogenomethylaluminium products from the reaction mixture with (5) and (6) [Scheme, reaction (i)] by precipitation with  $[\text{PPh}_4]\text{Br}$ . The other is the reaction of (5) with  $[\text{PPh}_4]\text{Br}$  [Scheme, reaction (iii)]. This competition does not interfere when the Lewis acid strength of (5) and (6) is lower than that of the

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



**Scheme.** (i)  $\text{Al}_2\text{Me}_6$ ,  $[\text{PPh}_4]\text{Br}$ ; (ii) ligand, (L); (iii)  $[\text{PPh}_4]\text{X}$  (X = Br); (iv) (a)  $\text{Al}_2\text{Me}_6$ , ligand ( $\text{PPh}_3$  or tht) (1:4); (b)  $\text{Al}_2\text{Me}_6$ , ligand (1:2), methanol; (v)  $\text{Al}_2\text{Me}_6$ ,  $\text{PPh}_3\text{O}$  (1:4); (vi)  $\text{Al}_2\text{Me}_6$ , methanol; (vii) ligand ( $\text{PPh}_3\text{O}$  or  $\text{PPh}_3$ ); (viii)  $\text{HX}$  (X = Br); (ix)  $\text{PPh}_3 + \text{HBF}_4 \cdot \text{OEt}_2$  (solvent =  $\text{Me}_2\text{CO}$  or  $\text{Et}_2\text{O}$ ); (x)  $\text{LiR}$  (R = Me,  $\text{C}_2\text{Ph}$ , or  $\text{C}_6\text{F}_5$ ); (xi)  $\text{Tl}(\text{C}_5\text{H}_5)$ ; (xii) ligand (L =  $\text{PPh}_3$  or  $\text{PPh}_3\text{O}$ ); see ref. 5

aluminium species. So, the complete reaction between (5) and  $[\text{PPh}_4]\text{Br}$  in toluene takes more than 4 h whereas the same reaction with  $\text{Al}_2\text{Me}_6$  is almost instantaneous. However, the expected greater acid strength of dimer (4) makes the isolation of pure samples of this complex impossible. N.m.r. signals assigned to the anion  $[\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{ClBr}]^-$  were found in the precipitated phosphonium salt.

An alternative route to prepare adducts (7)–(12) [Scheme, reaction (iv)] is the addition of ligands (L) to the solution obtained from the preparation of the methyl complexes (4)–(6) without previous isolation of these compounds. In this case, the more acidic alkylaluminium product also competes in the formation of the adduct. This problem was successfully solved in two different ways: (a) by addition of an excess of the ligand (molar ratio L:Mo = 2:1) in order to form simultaneously the aluminium adduct; (b) by addition of methanol in order to obtain insoluble methoxoaluminium species, co-ordinatively saturated by formation of strong methoxo bridges.<sup>7</sup>

When L =  $\text{OPPh}_3$  and X = Br, method (a) affords an ionic complex [Scheme, reaction (v)] which has a variable composition, established by n.m.r. and microanalysis. A formulation such as  $[\text{AlMe}_x\text{Br}_{4-x}][\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{OPPh}_3)_2]$  could be proposed on the basis of the known tendency of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{X}_2\text{L}]$  to dissociate one halide in the presence of excess of ligand,<sup>5</sup> and of the aluminium derivatives to form halogenoaluminates,<sup>6b</sup> but  $\text{OPPh}_3$  gives very stable aluminium complexes,<sup>6b</sup> and prefers to be co-ordinated to the aluminium atom. For this reason the formulation (14), incorporating the uncommon cation  $[\text{AlMe}_x\text{Br}_{2-x}(\text{OPPh}_3)_2]^+$  and the same anion as (13), is proposed; n.m.r. and i.r. data are also in accord with this.

A third route to complexes (7)–(12) is the direct reaction of hexamethyldialuminium with the previously isolated adducts<sup>5</sup> of (1)–(3) followed by addition of methanol (Scheme, reaction (vi)).

We isolated complex (7) containing the labile ligand

**Table 1.** Analytical and physical data for the new complexes

Complex	Colour	M.p. (°C) <sup>a</sup>	Analysis (%) <sup>b</sup>			
			C	H	N	X <sup>c</sup>
[MoMe(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(NO)] <sub>2</sub> (μ-X) <sub>2</sub>						
(4) X = Cl <sup>d</sup>	Yellow		32.1 (29.8)	4.2 (3.3)	4.2 (5.8)	14.7 (14.9)
(5) X = Br	Reddish orange	> 210	25.7 (25.5)	3.0 (2.8)	5.0 (4.9)	27.4 (27.9)
(6) X = I	Brownish orange	> 250	22.0 (21.6)	2.4 (2.4)	3.8 (4.2)	
[MoMe(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(NO)XL]						
(7) L = tht, X = Br	Yellow	74	31.7 (32.1)	4.4 (4.3)	3.7 (3.7)	22.1 (22.4)
(8) L = PPh <sub>3</sub> , X = Cl	Yellow	165	56.6 (57.2)	4.9 (4.6)	2.9 (2.8)	7.8 (7.0)
(9) L = PPh <sub>3</sub> , X = Br	Yellow	134	52.3 (52.6)	4.3 (4.2)	2.5 (2.55)	14.2 (14.6)
(10) L = PPh <sub>3</sub> , X = I	Yellow	140	48.5 (48.4)	4.0 (3.9)	2.2 (2.35)	
(11) L = OPPh <sub>3</sub> , X = Cl	Yellow	170	55.3 (55.45)	4.8 (4.5)	3.0 (2.7)	
(12) L = OPPh <sub>3</sub> , X = Br	Yellow	93	51.2 (51.1)	4.3 (4.1)	2.6 (2.5)	14.4 (14.2)
[Q][MoMe(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(NO)Br <sub>2</sub> ]						
(13) Q = PPh <sub>4</sub> <sup>e</sup>	Yellow	140	51.1 (51.1)	4.1 (4.1)	1.7 (2.0)	22.4 (22.7)
(14) Q = AlMe <sub>x</sub> Br <sub>2-x</sub> (OPPh <sub>3</sub> ) <sub>2</sub> <sup>f</sup>	Yellow		52—54 (50—54)	4.5—5.0 (4.0—4.5)	1.2—1.7 (1.3—1.4)	
[Mo(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(NO)(PPh <sub>3</sub> ) <sub>2</sub> (Me <sub>2</sub> CO)][BF <sub>4</sub> ] <sub>2</sub>						
(15) <sup>g</sup>	Orange	84	55.6 (55.8)	4.3 (4.4)	1.6 (1.5)	
[MoMe(R)(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(NO)(PPh <sub>3</sub> )]						
(16) R = Me	Yellow	97	61.7 (62.1)	5.5 (5.4)	2.2 (2.2)	
(17) R = C <sub>2</sub> Ph	Orange	118	67.5 (67.5)	5.0 (5.0)	2.4 (2.5)	
(18) R = C <sub>6</sub> F <sub>5</sub>	Orange	127	56.0 (56.7)	3.9 (3.65)	2.4 (2.2)	

<sup>a</sup> With decomposition. <sup>b</sup> Required values given in parentheses. <sup>c</sup> Halogen; method used is not good for determining iodide. <sup>d</sup> Compound not obtained analytically pure; see Results and Discussion. <sup>e</sup>  $\Lambda_M = 136 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in acetone solution ( $5 \times 10^{-4} \text{ mol dm}^{-3}$ ). <sup>f</sup>  $x = 1$  or 2. <sup>g</sup>  $\Lambda_M = 186 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in acetone solution ( $5 \times 10^{-4} \text{ mol dm}^{-3}$ ).

tetrahydrothiophene (tht), to avoid the difficulty of handling the very unstable and sensitive starting complexes (4)–(6). Although (7) is almost as sensitive as the starting complexes, we isolated complexes (9) and (12) by substituting tht by PPh<sub>3</sub> and OPPh<sub>3</sub> respectively [Scheme, reaction (vii)].

The reactivity of selected complexes [(5) and (9)] was studied in reactions with protonating, alkylating, and reducing agents.

The Mo–CH<sub>3</sub> bond in compound (9) is cleaved only by addition of highly concentrated solutions of strong protonic acids, illustrating its stability. If the anion of the protonating agent has co-ordinative capacity [e.g., HBr, Scheme, reaction (viii)] the starting dihalogeno complex is produced. With non-co-ordinative anions [e.g., HBF<sub>4</sub>·OEt<sub>2</sub>, Scheme, reaction (ix)] in the presence of an excess of PPh<sub>3</sub>, the formation of [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)Br(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sup>9</sup> should be expected. However, HBr is also formed in this reaction and the solvent (Me<sub>2</sub>CO) is co-ordinated to give (15).

We also tried to reduce compounds (5) and (9) in order to isolate species of the type [{MoMe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)]<sub>2</sub> and [{MoMe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)(PPh<sub>3</sub>)<sub>2</sub>] under conditions similar to those recently reported for reductions of (3),<sup>10</sup> but only decomposition products were obtained.

Reaction of the halogenomethyl complex (9) with different alkyl lithium derivatives afforded the saturated mononuclear dialkyls (16)–(18) [Scheme, reaction (x)]. In spite of the proposed stability for 16-electron complexes [MoR<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)],<sup>3</sup> we were not able to isolate these species with R = Me from (4)–(6).

Finally, we also studied the reaction of dimer (5) and its PPh<sub>3</sub> adduct (9) with cyclopentadienylthallium(I) [Scheme, reaction (xi)]. Both (5) and (9) react to give the previously reported [MoMe(η<sup>n</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(NO)]<sup>1</sup> (*n* is unknown) which contains unusually distorted cyclopentadienyl rings. We have observed the preferred formation of the Mo(η<sup>n</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (value of *n* is

unknown) unit, with elimination of PPh<sub>3</sub> instead of formation of a σ-C<sub>5</sub>H<sub>5</sub> bond as observed for other ligands.<sup>11</sup> Steric effects cannot be the cause of the elimination of phosphine since C<sub>6</sub>F<sub>5</sub>, being bulkier than C<sub>5</sub>H<sub>5</sub> is co-ordinated together with triphenylphosphine in (18). The reaction of (5) with Li(C<sub>5</sub>Me<sub>5</sub>) or K(C<sub>5</sub>Me<sub>5</sub>) does not lead to the isolation of [MoMe(η<sup>n</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>n</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)], probably because of the strongly reducing and basic properties of the alkaline cyclopentadienides.<sup>1</sup> This mixed bis-cyclopentadienyl derivative has been obtained by a different route.<sup>12</sup>

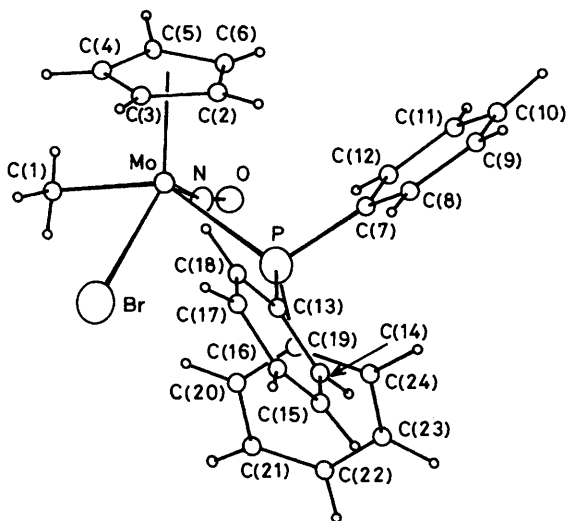
**Properties.**—Dimers (4)–(6) are extremely sensitive to air in solution to give green unidentified species, but stable under an inert atmosphere in the solid state. Adducts (7)–(12) are less sensitive, their stability varying with the ligands in the sequence X<sup>-</sup> > PPh<sub>3</sub> > OPPh<sub>3</sub> > tht, but their thermal stability is low, decomposing in solution by heating at 40–60 °C or at 80–120 °C for the solids. All the complexes are soluble in acetone and dichloromethane, and complexes (4)–(12) also in toluene, but slightly soluble [(15)–(18)] or insoluble in hydrocarbons.

**Structures.**—Physical and spectroscopic data shown in Tables 1 and 2 are consistent with the ‘four-legged piano stool’ structure previously reported<sup>13</sup> for similar complexes and established by our X-ray diffraction study of complex (9). This arrangement implies the possible formation of isomers when at least three of the four ligands (excluding the cyclopentadienyl) are non-equivalent. The complexes (7)–(12) show only one singlet for each cyclopentadienyl and methyl group in the <sup>1</sup>H n.m.r. spectrum (Table 2). This observation is in agreement with the existence of only one isomer in solution, or alternatively with a rapid interconversion between isomers. We did not observe any change of signals in the <sup>1</sup>H n.m.r. spectrum down to –100 °C. On the other hand, δ<sub>H</sub>(Mo–CH<sub>3</sub>) in complexes (7)–

**Table 2.** Spectroscopic data for the new complexes

Complex	$\delta_{\text{H}}(\text{C}_5\text{H}_5)^a$	$\delta_{\text{H}}(\text{CH}_3)^a$	$\delta_{\text{P}}^b$	$\nu(\text{NO})/\text{cm}^{-1c}$	$\nu(\text{C}_5\text{H}_5)/\text{cm}^{-1d}$
$[\{\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\}_2(\mu\text{-X})_2]$					
(4) X = Cl	4.96 (5 H, s)	1.39 (3 H, s)		1 640	825
(5) X = Br	4.93 (5 H, s)	1.31 (3 H, s)		1 650	820
(6) X = I	4.88 (5 H, s)	1.30 (3 H, s)		1 660	815
$[\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{XL}]$					
(7) L = tht, X = Br <sup>e</sup>	4.91 (5 H, s)	1.55 (3 H, s)		1 625	822
(8) L = PPh <sub>3</sub> , X = Cl	4.90 (5 H, s)	1.73 (3 H, s)	34.07 (s)	1 630	835
(9) L = PPh <sub>3</sub> , X = Br <sup>f</sup>	4.88 (5 H, s)	1.85 (3 H, s)	29.43 (s)	1 632	830
(10) L = PPh <sub>3</sub> , X = I	4.87 (5 H, s)	1.89 (3 H, s)	19.60 (s)	1 635	829
(11) L = OPPh <sub>3</sub> , X = Cl	4.98 (5 H, s)	1.32 (3 H, s)	29.16 (s)	1 638	825
(12) L = OPPh <sub>3</sub> , X = Br	5.04 (5 H, s)	1.32 (3 H, s)	30.34 (s)	1 637	816
$[\text{Q}][\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Br}_2]$					
(13) Q = PPh <sub>4</sub>	5.49 (5 H, s) <sup>g</sup>	1.06 (3 H, s) <sup>g</sup>		1 610	815
(14) Q = AlMe <sub>2</sub> Br <sub>2-x</sub> (OPPh <sub>3</sub> ) <sub>2</sub>	5.51 (5 H, s) <sup>g</sup>	1.08 (3 H, s) <sup>g</sup>		1 608	816
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)_2(\text{Me}_2\text{CO})][\text{BF}_4]_2$					
(15) <sup>h</sup>	5.76 (5 H, t) <sup>i</sup>		31.34 (s) <sup>i</sup>	1 690	845
$[\text{MoMe}(\text{R})(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)_3]$					
(16) R = Me	4.96 (5 H, s)	1.13 (6 H, s)	50.44 (s)	1 598	818
(17) R = C <sub>2</sub> Ph <sup>j</sup>	4.97 (5 H, s)	1.50 (3 H, s)	40.94 (s)	1 603	817
(18) R = C <sub>6</sub> F <sub>5</sub> <sup>k</sup>	5.01 (5 H, s)	0.84 (3 H, s)	35.84 (s)	1 622	821

<sup>a</sup> 60 MHz; solvent C<sub>6</sub>D<sub>6</sub>; standard SiMe<sub>4</sub>. <sup>b</sup> 80 MHz; solvent C<sub>6</sub>H<sub>6</sub>; external standard H<sub>3</sub>PO<sub>4</sub>. <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> In Nujol mull. <sup>e</sup>  $\delta_{\text{H}}(\text{C}_4\text{H}_8\text{S})$ : 2.62 (4 H, t), 1.43 (4 H, m). <sup>f</sup>  $\delta_{\text{C}}(^{13}\text{C}\{-^1\text{H}\})$ , 80 MHz, solvent CD<sub>2</sub>Cl<sub>2</sub>, standard SiMe<sub>4</sub>: 102.38 (s, C<sub>5</sub>H<sub>5</sub>), 15.48 (s, CH<sub>3</sub>). <sup>g</sup> In CD<sub>2</sub>Cl<sub>2</sub>. <sup>h</sup>  $\delta_{\text{H}}[\text{OC}(\text{CD}_3)_2]$  2.12 (6 H, s) in CD<sub>2</sub>Cl<sub>2</sub>. <sup>i</sup> In OC(CD<sub>3</sub>)<sub>2</sub>; J(PH) 2 Hz. <sup>j</sup>  $\delta_{\text{C}}(^{13}\text{C}\{-^1\text{H}\})$ , 80 MHz, solvent C<sub>6</sub>D<sub>6</sub>, standard SiMe<sub>4</sub>: 101.14 (s, C<sub>5</sub>H<sub>5</sub>), 98.81 (s, Mo-CCPh), 66.19 (s, Mo-CCPh), 9.10 (s, CH<sub>3</sub>). <sup>k</sup>  $\delta_{\text{F}}$  (80 MHz, solvent C<sub>6</sub>D<sub>6</sub>, external standard CFCl<sub>3</sub>): -106.00 (2 F, m), -162.90 (2 F, m), -166.18 (1 F, m).



**Figure.** View of the structure of the complex  $[\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Br}(\text{PPh}_3)]$  (9) with the atomic numbering scheme

(12) (Table 2) is weakly affected by the nature of the halogen, and considerably by the type of ligand L, in agreement with the structure found for (9) in which the PPh<sub>3</sub> ligand and the methyl group are *trans* to each other. This behaviour confirms that only one isomer is present in the solutions of (7)–(12), and probably it has the stereochemistry determined for (9) in the solid.

The same observations can be made for complexes (4)–(6). However, whether these complexes are monomeric or dimeric could not be confirmed. It has been reported<sup>3</sup> that the 16-electron species  $[\text{MoR}_2(\eta^5\text{-C}_5\text{H}_5)(\text{NO})]$  are stable as the

bonding character of the lowest unoccupied molecular orbital (l.u.m.o.) is very low. We have shown that the acidity of our dialkyl complexes is sufficient to stabilize the 18-electron species (16)–(18). Moreover, the higher electronegativity of X in relation to R stabilizes the l.u.m.o. and increases the acidity of the metal atom favouring the formation of the bridge in (4)–(6). We believe that complexes (4)–(6) are dimers in the solid state, but we cannot exclude the existence in solution of an equilibrium between dimeric and monomeric species.

**Crystal Structure of  $[\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Br}(\text{PPh}_3)]$  (9).**—The structure of (9) is represented in the Figure together with the atomic numbering system. Selected bond distances and angles are given in Table 3. The complex has a four-legged piano stool geometry. By considering the centroid of the cyclopentadienyl ring as a co-ordination site, the Mo atom is in a square-pyramidal environment with PPh<sub>3</sub> and Me ligands occupying *trans* positions of the base whose remaining positions are occupied by one Br atom and by one N atom from a nitrosyl group nearly linearly bonded to the metal. The Mo–N and N–O bond lengths [1.814(6) and 1.115(8) Å respectively] suggest considerable Mo–N back-bonding.

The Mo–C<sub>5</sub>H<sub>5</sub> distances are in the range 2.281(9)–2.398(9) Å, as for complexes having conventional Mo( $\eta^5\text{-C}_5\text{H}_5$ ) groups.<sup>14</sup> The cyclopentadienyl ring is planar [maximum deviation from the mean plane passing through the five carbon atoms being 0.003(9) Å for C(4)] with C–C bond lengths in agreement with the values found in normal  $\eta^5\text{-C}_5\text{H}_5$  rings in other complexes.<sup>15</sup> The distance of the Mo atom to the C<sub>5</sub> plane [2.020(9) Å] is close to the values found for previously reported<sup>16</sup> Mo( $\eta^5\text{-C}_5\text{H}_5$ ) complexes.

Metal nitrosyl complexes have been conveniently classified as  $\{\text{M}(\text{NO})_m\}^n$  species<sup>17</sup> and ca. 200 complexes have been considered<sup>13</sup> on this basis. According to this classification complex

**Table 3.** Relevant bond distances (Å) and angles (°)\*

(i) Involving the Mo atom			
Mo-N	1.814(6)	Mo-C(1)	2.235(10)
Mo-Br	2.630(2)	Mo-cp	2.020(9)
Mo-P	2.558(3)		
N-Mo-C(1)	84.1(3)	N-Mo-cp	120.8(3)
C(1)-Mo-Br	76.8(3)	C(1)-Mo-cp	104.4(4)
Br-Mo-P	78.1(1)	Br-Mo-cp	121.5(3)
N-Mo-P	83.2(2)	P-Mo-cp	112.4(3)
P-Mo-C(1)	142.5(3)	Br-Mo-N	117.5(2)
(ii) Involving the C <sub>5</sub> H <sub>5</sub> ligand			
C(2)-C(3)	1.379(12)	C(5)-C(6)	1.386(15)
C(3)-C(4)	1.365(14)	C(2)-C(6)	1.405(12)
C(4)-C(5)	1.396(12)		
C(3)-C(2)-C(6)	106.6(8)	C(4)-C(5)-C(6)	106.8(8)
C(2)-C(3)-C(4)	109.4(8)	C(5)-C(6)-C(2)	108.6(8)
C(3)-C(4)-C(5)	108.6(9)		
(iii) Involving the PPh <sub>3</sub> ligand			
P-C(7)	1.829(6)	P-C(19)	1.825(7)
P-C(13)	1.825(6)		
C(7)-P-C(13)	104.1(3)	C(13)-P-C(19)	105.0(3)
C(7)-P-C(19)	102.8(3)	C(13)-P-Mo	120.0(2)
C(7)-P-Mo	110.0(2)	C(19)-P-Mo	113.3(2)
(iv) Involving the NO group			
N-O	1.115(8)	Mo-N-O	171.3(6)

\* cp = Centroid of the cyclopentadienyl ring, C(2)-C(6).

(9) is expected to contain a nearly linear NO group, in agreement with the experimentally found angle of 171.3(6)°.

Taking into account the covalent radii for Br, P, and C (1.14, 1.10, and 0.77 Å)<sup>18</sup> a single-bond radius of ca. 1.48 Å can be estimated for the Mo atom in (9), comparable to the value of 1.52 Å estimated in [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>(NO)],<sup>19</sup> implying a formal oxidation state of Mo in (9) of 3+. The same value is calculated if the NO group is treated as a neutral ligand as proposed by Cotton and co-workers.<sup>19</sup>

The Mo-CH<sub>3</sub> bond [2.235(10) Å] is much shorter than that observed in [MoR(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>] [R = Me, 2.38(1); R = Et, 2.40(2); R = CH<sub>2</sub>CO<sub>2</sub>H, 2.36(1)],<sup>20</sup> in agreement with the higher formal oxidation state and the different co-ordination environment.

The Mo-Br bond length [2.630(2) Å] is close to the values found in [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Br(PPh<sub>3</sub>)]<sup>21</sup> and [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Br(SnBr<sub>3</sub>)].<sup>22</sup> Also the Mo-P bond length [2.558(3) Å] in (9) is close to the values found in other arylphosphine complexes.<sup>23,24</sup>

The pattern of valency angles at the Mo atom in [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)XYZL] complexes is almost insensitive to changes in the ligands. For instance, the *trans*-angles P-Mo-C(1) [142.5(3)°] and Br-Mo-N [117.5(2)°] in complex (9) are close to the *trans*-angles at the central Mo atom in [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)XYL<sub>2</sub>] (L = CO, X = COMe, Y = PPh<sub>3</sub>; L = PPh<sub>3</sub>, X = NCO, Y = CO) and [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)XL<sub>3</sub>] (L = CO, X = C<sub>3</sub>F<sub>7</sub>)<sup>23</sup> (ca. 132 and 108° respectively). The *cis*-angles N-Mo-C(1), C(1)-Mo-Br, Br-Mo-P, and N-Mo-P in (9) lie in the range 76–84°, slightly higher than in the above complexes<sup>23</sup> (73–80°).

The distance O...H(12) [2.56(7) Å] and the angle C(12)-H(12)-O [151(6)°] suggest intramolecular 'bent-bridge hydrogen bonding'.

## Experimental

All the reactions were carried out in dried Schlenk tubes under argon or nitrogen; the manipulations were carried out using syringes or canulae through Subaseals. The solutions of hexamethylaluminium (Ethyl Corporation; 10% in toluene) were made up in this way. The solvents were dried and distilled under an inert N<sub>2</sub> atmosphere before use. The i.r. spectra were recorded over the range 4 000–200 cm<sup>-1</sup> on a Perkin-Elmer 599 spectrophotometer using Nujol mulls or CH<sub>2</sub>Cl<sub>2</sub> solutions. The n.m.r. spectra were run on Bruker WP-60CW (<sup>1</sup>H, 60 MHz) or Varian FT 80A (<sup>13</sup>C, <sup>19</sup>F, or <sup>31</sup>P) spectrometers. The conductivities were measured at 20 °C in acetone using a WTW-LF42 conductimeter. The melting points were determined with a Büchi SMP-20 instrument. The C, H, and N analyses were made with a Perkin-Elmer 240B microanalyzer. The halogen analyses were performed according to ref. 25. Methane was determined by gas chromatography using a Perkin-Elmer sigma 3B instrument fitted with a Carboxax column and a flame ionization detector. [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)X]<sub>2</sub>(μ-X)<sub>2</sub> (1)–(3) and [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)X<sub>2</sub>L]<sub>2</sub> (L = PPh<sub>3</sub>, X = Cl, Br, or I; L = OPPh<sub>3</sub>, X = Cl or Br) were prepared as previously reported; recrystallization of (1) before use is essential. The microanalytical, melting point, i.r. and n.m.r. (<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>31</sup>P) data for the new complexes are collected in Tables 1 and 2.

*Preparation of [MoMe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)]<sub>2</sub>(μ-X)<sub>2</sub> (4)–(6).*—(a) *Compound (4).* The method employed was similar to that described below for (5). However an oil was obtained which after being repeatedly washed with hexane gave (4) as a yellow powder (yield: 62%) always contaminated with aluminium products.

(b) *Compound (5).* A freshly prepared 10% solution of Al<sub>2</sub>Me<sub>6</sub> in toluene (3.0 cm<sup>3</sup>, 1.5 mmol) was injected dropwise into a suspension of (2) (1.5 mmol) in toluene (25 cm<sup>3</sup>) at –78 °C. The resultant mixture was allowed to warm up with stirring. The solid dissolved (at ca. –20 °C) to give a pale orange solution and the stirring was continued until it reached 20 °C, when it became red. The solution was cooled again to –10 °C; tetraphenylphosphonium bromide (1.25 g, 3.0 mmol) was then added. After stirring for 20 min, the insoluble organoaluminum was filtered off and the solvent removed *in vacuo* to give (5) (yield: 0.62 g, 72%) as an orange solid.

(c) *Compound (6).* The method was identical to that described for (5) except that, in this case, stirring was continued at 20 °C for at least 1 h further to complete the reaction (yield: 68%).

*Preparation of [MoMe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)XL] (7)–(12).*—From pure (5) or (6). (i) Complex (7) was prepared as follows. Tetrahydrothiophene (0.15 cm<sup>3</sup>, 1.6 mmol) was injected into a red solution containing (5) (0.46 g, 0.8 mmol) in toluene (25 cm<sup>3</sup>). The colour changed to yellow-orange. The solvent was removed *in vacuo* to leave a yellow oil and the complex was precipitated with hexane to give (7) as a yellow solid (0.32 g, 53%). (ii) The preparation of (9) was carried out by the same method (yield: 94%). (iii) The preparation of (13) was also similar but the product was toluene insoluble and was recrystallized from dichloromethane–hexane (yield: 78%).

(b) From (1)–(3). (i) Complex (8) was prepared as follows. Triphenylphosphine (0.26 g, 1.0 mmol) dissolved in toluene (2 cm<sup>3</sup>) was added to a red solution obtained as described above from complex (1) (0.50 mmol) and 10% Al<sub>2</sub>Me<sub>6</sub> (1.0 cm<sup>3</sup>, 0.50 mmol) in toluene. The solution was evaporated to dryness and methanol (1 cm<sup>3</sup>) was added to the yellow oil at –78 °C and the mixture warmed up to 20 °C. When gas evolution stopped, a yellow crystalline solid was formed which was dried and recrystallized from benzene–hexane to give yellow crystals of (8) (yield: 0.30 g, 60%). (ii) The preparation of (9)–(12) was similarly carried out (yields: 82, 55, 28, 71% respectively).

**Table 4.** Fractional atomic co-ordinates ( $\times 10^4$ ), with e.s.d.s in parentheses, for the non-hydrogen atoms

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Mo	2 601(1)	2 973(1)	-23(1)	C(11)	-31(4)	2 417(6)	-3 308(10)
Br	3 137(1)	2 825(1)	3 152(1)	C(12)	488(4)	2 708(5)	-1 975(10)
P	1 474(1)	2 505(1)	1 026(2)	C(13)	1 541(4)	1 599(4)	2 544(8)
O	1 709(3)	4 537(4)	-1 369(8)	C(14)	1 066(4)	1 510(5)	3 577(9)
N	2 057(3)	3 972(4)	-740(7)	C(15)	1 131(5)	810(6)	4 685(11)
C(1)	3 535(6)	3 951(7)	430(16)	C(16)	1 674(5)	198(6)	4 791(11)
C(2)	2 418(5)	1 542(6)	-1 324(11)	C(17)	2 143(5)	255(5)	3 782(10)
C(3)	3 153(5)	1 577(6)	-604(12)	C(18)	2 081(4)	950(5)	2 672(9)
C(4)	3 468(5)	2 274(6)	-1 275(11)	C(19)	1 044(4)	3 451(4)	1 864(8)
C(5)	2 932(6)	2 698(6)	-2 465(11)	C(20)	1 450(6)	4 172(6)	2 591(12)
C(6)	2 282(6)	2 246(6)	-2 489(11)	C(21)	1 111(7)	4 889(7)	3 251(14)
C(7)	752(3)	2 121(4)	-686(8)	C(22)	396(6)	4 890(8)	3 130(13)
C(8)	488(4)	1 238(5)	-774(9)	C(23)	-4(7)	4 187(10)	2 431(15)
C(9)	-40(4)	968(6)	-2 145(10)	C(24)	304(5)	3 454(9)	1 779(13)
C(10)	-298(4)	1 554(6)	-3 373(10)				

Complex (9) was also obtained from (2) by this method on a six times larger scale for preparative purposes.

(c) From  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{X}_2\text{L}]$ . (i) Complex (10) was prepared as follows. A 10% solution of  $\text{Al}_2\text{Me}_6$  in toluene (0.50  $\text{cm}^3$ , 0.25 mmol) was injected dropwise into a stirred suspension of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}_2(\text{PPh}_3)]$  (0.50 mmol) at  $-45^\circ\text{C}$ . The resultant suspension was allowed to warm up to  $-30^\circ\text{C}$  and stirred for ca. 1 h at that temperature; the solution was then evaporated to dryness and methanol (5  $\text{cm}^3$ ) was added. The mixture was stirred for 5 min at  $-30^\circ\text{C}$ . The solvent was removed *in vacuo* and the residue crystallized from benzene to give (10) (yield: 0.21 g, 71%). (ii) Compounds (8) and (9) were similarly obtained (yields: 93, 62% respectively).

(d) From (7). (i) Complex (9) was prepared as follows. The addition of triphenylphosphine (0.07 g, 0.63 mmol) to a yellow-orange solution of (7) (0.10 g, 0.27 mmol) in toluene (20  $\text{cm}^3$ ) gave a yellow solution. This solution was evaporated to dryness and the resultant oil precipitated with hexane to give (9) as a yellow solid (yield: 0.118 g, 81%). (ii) Complex (12) was similarly obtained (yield: 72%).

*Reaction of (2) with  $\text{Al}_2\text{Me}_6$ .*—(a) And  $\text{PPh}_3$ . When the preparation of (9) from (2) was carried out as above, using an additional 0.5 mmol of  $\text{PPh}_3$ , and without addition of methanol, complex (9) was also obtained (yield: 67%).

(b) And  $\text{PPh}_3\text{O}$ . A similar reaction with  $\text{PPh}_3\text{O}$  gave a toluene-insoluble oil which was decanted and crystallized from hexane to afford a yellow solid characterized as (14) (yield: 70%).

*Reaction of (5) or (9) with Thallium Cyclopentadienyl.*—A mixture of (5) (0.45 g, 0.80 mmol) and  $\text{Tl}(\text{C}_5\text{H}_5)$  (0.43 g, 1.58 mmol) in benzene (30  $\text{cm}^3$ ) was stirred for 2 h. The precipitated  $\text{TlBr}$  was filtered off and the resultant red solution evaporated to dryness. The residue was extracted with pentane and the solvent removed under vacuum to give brown-purple crystals of  $[\text{MoMe}(\eta^5\text{-C}_5\text{H}_5)_2(\text{NO})]$  (0.31 g, 73%), m.p.  $60^\circ\text{C}$  (Found: C, 48.25; H, 5.10; N, 5.10. Calc. for  $\text{C}_{11}\text{H}_{13}\text{MoNO}$ : C, 48.7; H, 4.85; N, 5.15%;  $\nu(\text{NO})$  1 599  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ );  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  5.23 (10 H, s,  $\text{C}_5\text{H}_5$ ), 1.05 (3 H, s,  $\text{CH}_3$ ). Compound (9) reacts in the same way with  $\text{Tl}(\text{C}_5\text{H}_5)$  to produce the same bis(cyclopentadienyl) complex.

*Reactions of (9) with Acids.*—(a) *Hydrobromic acid.* Concentrated hydrobromic acid (0.5  $\text{cm}^3$ , ca. 9 mol  $\text{dm}^{-3}$ ) was added to a stirred solution of complex (9) (0.20 g, 0.36 mmol) in toluene (5  $\text{cm}^3$ ). Methane was evolved. The stirring was continued for a further 2 h and reaction took place to give a yellow precipitate which was filtered off and vacuum dried to give

$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Br}_2(\text{PPh}_3)]$  (yield: 0.10 g, 81%), m.p.  $178^\circ\text{C}$  (Found: C, 44.9; H, 3.55; N, 2.50. Calc. for  $\text{C}_{23}\text{H}_{20}\text{Br}_2\text{MoNOP}$ : C, 45.05; H, 3.30; N, 2.30%;  $\nu(\text{NO})$  1 660  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ );  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  5.88 [5 H, d,  $J(\text{PH})$  3 Hz,  $\text{C}_5\text{H}_5$ ].

(b) *Ethereal tetrafluoroboric acid.*  $\text{HBF}_4\cdot\text{OEt}_2$  (Ega-Chemie) (1  $\text{cm}^3$ ) was added to a mixture of solid complex (9) (0.33 g, 0.60 mmol) and  $\text{PPh}_3$  (0.16 g, 0.60 mmol) and the mixture stirred for 2 h. Methane was evolved. Diethyl ether (2  $\text{cm}^3$ ) was then added and the solid obtained was filtered off, washed with diethyl ether and crystallized from acetone to give (15) (yield: 70%).

*Reactions of (9) with Alkyl-lithiums.*—(a) *Preparation of (16).* Methyl-lithium (1.6 mol  $\text{dm}^{-3}$ ) in diethyl ether (0.6  $\text{cm}^3$ , 1 mmol) was added to a stirred suspension of complex (9) (0.55 g, 1 mmol) in toluene (25  $\text{cm}^3$ ) at  $-78^\circ\text{C}$ . The temperature was allowed to increase to ambient giving an orange solution. The solvent was removed *in vacuo* to leave an oil which was treated with methanol (2  $\text{cm}^3$ ), evaporated to dryness and the residue crystallized from toluene-pentane to give orange (16) (yield: 0.33 g, 69%).

(b) *Preparation of (17).* The compound  $\text{LiC}_2\text{Ph}$  was prepared by reacting a solution of  $\text{LiBu}^n$  in hexane (1.6 mol  $\text{dm}^{-3}$ , 0.5  $\text{cm}^3$ , 0.80 mmol) with  $\text{HC}_2\text{Ph}$  (0.08  $\text{cm}^3$ , 0.80 mmol) in diethyl ether (30  $\text{cm}^3$ ). The mixture was stirred for 4 h, the solvent was removed *in vacuo*, and the residue washed with hexane and dried *in vacuo*. Ether (30  $\text{cm}^3$ ) was injected and then complex (9) (0.33 g, 0.60 mmol) was added. After stirring for 30 min the red solution which formed was evaporated to dryness, the residue extracted with benzene (20  $\text{cm}^3$ ), and the solvent removed under vacuum. The resultant orange solid was washed with cold hexane (2  $\times$  15  $\text{cm}^3$ ) (0.20 g, 58%).

(c) *Preparation of (18).* The compound  $\text{Li}(\text{C}_6\text{F}_5)$  was prepared<sup>26</sup> by treating a solution of  $\text{LiBu}^n$  in hexane (1.6 mol  $\text{dm}^{-3}$ , 0.40  $\text{cm}^3$ , 0.66 mmol) with  $\text{C}_6\text{F}_5\text{Br}$  (0.08  $\text{cm}^3$ , 0.66 mmol) in diethyl ether (40  $\text{cm}^3$ ) at  $-78^\circ\text{C}$ . After stirring for 30 min, compound (9) (0.33 g, 0.60 mmol) was added and the temperature allowed to increase to ambient. An orange solution was formed. The solvent was removed under vacuum to leave an oil which was treated with methanol (1  $\text{cm}^3$ ), extracted with benzene, washed with pentane and dried *in vacuo* to give (18) as an orange solid (yield: 0.20 g, 53%).

*Crystal Structure Determination of (9).*—*Crystal data.*  $\text{C}_{24}\text{H}_{23}\text{BrMoNOP}$ ,  $M = 548.27$ , monoclinic,  $a = 18.778(5)$ ,  $b = 14.713(5)$ ,  $c = 8.354(3)$  Å,  $\beta = 102.77(2)^\circ$ ,  $U = 2 251(1)$  Å<sup>3</sup> (by least-squares refinement from the  $\theta$  values of 27 reflections accurately measured), space group  $P2_1/a$ ,  $Z = 4$ ,  $D_c = 1.618$  g  $\text{cm}^{-3}$ ,  $F(000) = 1 096$ . A yellow prismatic crystal of approximate

dimensions  $0.20 \times 0.25 \times 0.25$  mm, sealed in a glass capillary, was used for the structural analysis,  $\mu(\text{Mo-K}\alpha) = 24.12 \text{ cm}^{-1}$ . No correction for absorption effects was applied in view of the low absorbance of the sample.

**Data collection and processing.** Siemens AED diffractometer,  $\theta/2\theta$  mode, using the Nb-filtered Mo- $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ); all the reflections in the range  $3\text{--}27^\circ$  were measured. Of 5351 independent reflections, 2532, having  $I \geq 2\sigma(I)$ , were considered observed and used in the analysis.

**Structure analysis and refinement.** Patterson and Fourier methods, full-matrix least-square refinement with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. The hydrogen atoms were clearly localized in the final difference Fourier map and refined isotropically. The weighting scheme used in the last cycles of refinement was  $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$  with  $K = 0.7374$  and  $g = 0.0049$ . Final  $R$  and  $R'$  values were 0.036 and 0.046 respectively. Final atomic coordinates for the non-hydrogen atoms are given in Table 4. Additional data available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

The SHELX system of computer programs was used.<sup>27</sup> Atomic scattering factors, corrected for the anomalous dispersion of Mo, P, and Br, were taken from ref. 28. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Parma, Italy.

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