The Molecular Structure of $[Mo(CO)_3H(\eta\text{-}C_5Me_5)]$† and its Conversion to $[Mo(CO)_3Cl(\eta\text{-}C_5Me_5)]$ and $[Li(Me_2NCH_2CH_2NMe_2)_2][Mo(CO)_3(\eta\text{-}C_5Me_5)]$

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Crystals of $[Mo(CO)_3H(\eta\text{-}C_5Me_5)]$ (**1**) suitable for an *X*-ray structural determination were obtained by reacting equimolar amounts of $[Mo(CO)_3(C_7H_8)]$ (C_7H_8 = cycloheptatriene) and C_5HMe_5 in methanol under hydrogen at room temperature. Complex (**1**) crystallizes in the monoclinic space group $P2_1$ in a unit cell of dimensions a = 8.003(2), b = 12.874(3), c = 7.087(2) Å, β = 103.06(2)°, and Z = 2; R' = 0.047 for 1 136 observed reflections. Complex (**1**) reacts at room temperature with CCl_4 to give $[Mo(CO)_3Cl(\eta\text{-}C_5Me_5)]$ (**2**), and with $LiBu^n$ in the presence of tetramethylethylenediamine (tmen) to give $[Li(tmen)_2][Mo(CO)_3(\eta\text{-}C_5Me_5)]$ (**3**). Complexes (**2**) and (**3**) were isolated in high yields and were analytically and spectroscopically characterized. Complex (**1**) does not react with CO (1 atm), CO_2 (1 atm), or with other CO_2-like molecules (CS_2, *p*-tolylcarbodi-imide).

The chemical properties of mono(pentamethylcyclopentadienyl) derivatives of molybdenum have been elucidated mainly with regard to the $[\{Mo(CO)_3(\eta\text{-}C_5Me_5)\}_2]$ and $[\{Mo(CO)_2(\eta\text{-}C_5Me_5)\}_2]$ dimers.[1] Few reports concern the reactivity of mononuclear analogues, namely the reaction of $[Mo(CO)_3H(\eta\text{-}C_5Me_5)]$ with elemental sulphur[2] and the reactions of $[Mo(CO)_3(\eta\text{-}C_5Me_5)]^+$, generated *in situ* from $[\{Mo(CO)_3(\eta\text{-}C_5Me_5)\}_2]$, with cyclopropanes[3] and cyclopropene carboxylates.[4] This is probably due to the lack of readily available mononuclear complexes containing the $Mo(\eta\text{-}C_5Me_5)$ unit.

This paper describes the first molecular structure of a $[MoL_3L'(\eta\text{-}C_5Me_5)]$ type compound, *i.e.* $[Mo(CO)_3H(\eta\text{-}C_5Me_5)]$. Structural determinations of complexes containing the $Mo(\eta\text{-}C_5Me_5)$ unit are rare;[2,5] to the best of our knowledge, an *X*-ray crystal structure determination has been reported for only one mononuclear complex, $[Mo(CO)_2(NO)(\eta\text{-}C_5Me_5)]$,[5d] and only for a few dimeric complexes.[2,5a–c]

Convenient syntheses and analytical and spectroscopic characterization of the useful derivatives $[Mo(CO)_3Cl(\eta\text{-}C_5Me_5)]$ and $[Li(tmen)_2][Mo(CO)_3(\eta\text{-}C_5Me_5)]$ (tmen = $Me_2NCH_2CH_2NMe_2$) are also reported.

Results and Discussion

Complex $[Mo(CO)_3H(\eta\text{-}C_5Me_5)]$ (**1**) was first synthesized by acidification of $Li[Mo(CO)_3(\eta\text{-}C_5Me_5)]$, generated *in situ* followed by sublimation under high vacuum.[2,6] We have found that by mixing equimolar amounts of $[Mo(CO)_3(C_7H_8)]$ (C_7H_8 = cycloheptatriene) and C_5HMe_5 in methanol under hydrogen (**1**) precipitates from the reaction mixture after 1 d at room temperature as a pale yellow crystalline solid which does not need further purification.‡

When (**1**) is dissolved in an excess of CCl_4 $[Mo(CO)_3Cl(\eta\text{-}C_5Me_5)]$ (**2**) precipitates in high yield as a crystalline red solid. If chloroform or methylene chloride are used instead of CCl_4 the reaction is much slower and considerable amounts of $[\{Mo(CO)_3(\eta\text{-}C_5Me_5)\}_2]$ and $[\{Mo(CO)_2(\eta\text{-}C_5Me_5)\}_2]$ form together with (**2**). Complex (**2**) was reported[8] to form by photolysis of $[\{Mo(CO)_3(\eta\text{-}C_5Me_5)\}_2]$ in CCl_4, but experimental details, analytical and spectroscopic characterizations were not given. The corresponding iodo derivative was formed by reacting either $[\{Mo(CO)_2(\eta\text{-}C_5Me_5)\}_2]$ or $[Mo(CO)_3Me(\eta\text{-}C_5Me_5)]$ with iodine in dichloromethane (yields 26 and 44% respectively).[9]

The reaction of (**1**) with n-butyl-lithium and tetramethylethylenediamine (tmen) (1:1:2 ratio) carried out in toluene gives $[Li(tmen)_2][Mo(CO)_3(\eta\text{-}C_5Me_5)]$ (**3**) in high yield as a yellow crystalline solid which is very sensitive to moisture.

Complex (**3**) has not been isolated previously although it was reported that a solution containing $Li[Mo(CO)_3(\eta\text{-}C_5Me_5)]$ can be obtained by refluxing $[Mo(CO)_6]$ in the presence of $Li(\eta\text{-}C_5Me_5)$ in tetrahydrofuran (thf),[6] while $Na[Mo(CO)_3(\eta\text{-}C_5Me_5)]$ can be obtained by reduction of $[\{Mo(CO)_3(\eta\text{-}C_5Me_5)\}_2]$ with sodium amalgam in thf and subsequently identified by reactions with electrophiles.[9]

Chloroform and toluene solutions of (**1**) have been treated with CO (1 atm), CO_2 (1 atm), CS_2 (strong excess), and *p*-tolylcarbodi-imide. No reaction with any of these ligands was observed, the only detectable reaction being a slow conversion of $[Mo(CO)_3H(\eta\text{-}C_5Me_5)]$ into the dimer $[\{Mo(CO)_3(\eta\text{-}C_5Me_5)\}_2]$.

Crystal Structure of $[Mo(CO)_3H(\eta\text{-}C_5Me_5)]$.—The geometry of the $Mo(CO)_3(\eta\text{-}C_5Me_5)$ moiety is shown in Figures 1 and 2. The H atom was not located, but its position can be inferred from the geometry of the remainder of the molecule.

The *trans* C(11)–Mo–C(13) angle is 101.7(6)° while the C(11)–Mo–C(12) and C(12)–Mo–C(13) angles are 83.1(8) and 85.7(7)° respectively (Table 1). These geometrical facts are characteristic of a 'four-legged piano stool' geometry[10] where the 'hole' in the co-ordination sphere around the molybdenum atom at a vertex of the square pyramid can be interpreted to be the result of the 'missing' H atom.

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† Tricarbonylhydrido(η-pentamethylcyclopentadienyl)molybdenum.

Supplementary data available (No. SUP 56462, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: atm = 101 325 Pa.

‡ While this study was being completed a synthesis[7] was reported which made use of $[Mo(CO)_3(C_6H_5Me)]$ and a strong excess of C_5HMe_5 in tetrahydrofuran; at the end of the work-up (**1**) was obtained by sublimation at 60 °C under high vacuum.

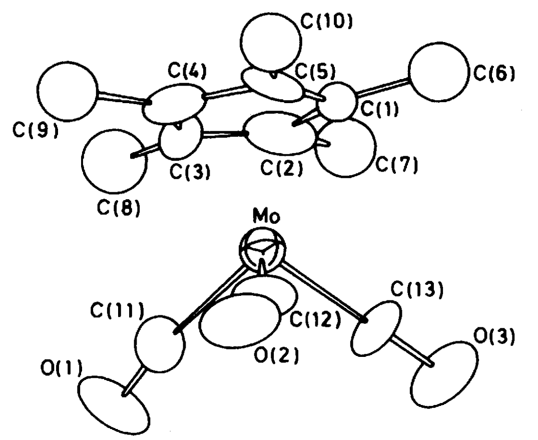

Figure 1. A perspective view of complex (**1**) with the atom-numbering scheme

Table 1. Bond distances (Å) and angles (°) for $[Mo(CO)_3H(\eta-C_5Me_5)]$ (**1**)

Mo–C(1)	2.370(13)	C(2)–C(3)	1.426(24)
Mo–C(2)	2.320(16)	C(2)–C(7)	1.599(22)
Mo–C(3)	2.301(15)	C(3)–C(4)	1.344(31)
Mo–C(4)	2.338(8)	C(3)–C(8)	1.627(25)
Mo–C(5)	2.351(19)	C(4)–C(5)	1.465(32)
Mo–C(11)	1.931(17)	C(4)–C(9)	1.526(15)
Mo–C(12)	1.981(22)	C(5)–C(10)	1.535(25)
Mo–C(13)	1.907(12)	C(11)–O(1)	1.097(24)
C(1)–C(2)	1.397(25)	C(12)–O(2)	1.201(28)
C(1)–C(5)	1.397(22)	C(13)–O(3)	1.150(15)
C(1)–C(6)	1.483(23)		

C(11)–Mo–C(12)	83.1(8)	C(4)–C(3)–C(8)	142.7(14)
C(11)–Mo–C(13)	101.7(6)	C(3)–C(4)–C(5)	107.8(12)
C(12)–Mo–C(13)	85.7(7)	C(3)–C(4)–C(9)	112.4(10)
C(2)–C(1)–C(5)	105.7(12)	C(5)–C(4)–C(9)	139.2(10)
C(2)–C(1)–C(6)	140.4(11)	C(1)–C(5)–C(4)	108.4(12)
C(5)–C(1)–C(6)	113.5(11)	C(1)–C(5)–C(10)	140.4(14)
C(1)–C(2)–C(3)	110.3(14)	C(4)–C(5)–C(10)	111.0(12)
C(1)–C(2)–C(7)	110.0(12)	Mo–C(11)–O(1)	166.6(16)
C(3)–C(2)–C(7)	139.6(14)	Mo–C(12)–O(2)	165.5(18)
C(2)–C(3)–C(4)	107.8(14)	Mo–C(13)–O(3)	175.4(10)
C(2)–C(3)–C(8)	108.8(14)		

In addition the Mo–C(1), Mo–C(4), and Mo–C(5) distances are longer than the other two distances from the metal to the pentamethylcyclopentadienyl ligand. Such a distortion can be explained by electronic effects exerted by the hydride ligand which is *trans* to C(4)–C(5)–C(1).[2] This observation seems to be consistent with the strong *trans* effect expected for a molybdenum-bonded H atom.

The distance of the Mo atom to the centroid of C_5Me_5 ring is the same (2.016 Å) as that found for $[Mo(CO)_2(NO)(\eta-C_5Me_5)]$.[5d] The Mo–C(12) and C(12)–O(2) distances [1.981(22) and 1.201(28) Å respectively] are greater than the Mo–C(11), C(11)–O(1), Mo–C(13), and C(13)–O(3) distances [1.931(17), 1.097(24), 1.907(12), and 1.150(15) Å respectively], while the Mo–C(11)–O(1) and Mo–C(12)–O(2) angles [166.6(16) and 165.5(18)° respectively] notably deviate from 180°. However the quality of the *X*-ray diffraction data (see standard deviations) prevents us from expressing any hypothesis about the non-equivalence of the molybdenum co-ordinated CO molecules.

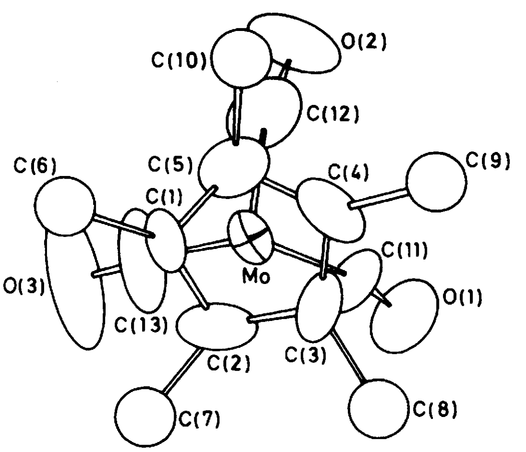

Figure 2. Projection of the molecule of (**1**) perpendicular to the C_5Me_5 ring

Table 2. Fractional atomic co-ordinates for $[Mo(CO)_3H(\eta-C_5Me_5)]$ (**1**) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.807 6(1)	0.0000	0.995 4(1)
C(1)	0.976 6(17)	0.054 9(16)	0.779 0(20)
C(2)	0.965 3(25)	−0.053 4(11)	0.775 5(24)
C(3)	0.791 6(26)	−0.085 2(14)	0.706 4(20)
C(4)	0.695 8(13)	0.000 8(24)	0.660 8(11)
C(5)	0.809 5(27)	0.090 8(17)	0.708 0(27)
C(6)	1.106 9(21)	0.138 8(14)	0.813 0(26)
C(7)	1.152 6(23)	−0.103 2(15)	0.838 9(26)
C(8)	0.786 1(24)	−0.211 0(14)	0.683 7(27)
C(9)	0.511 6(17)	−0.023 8(9)	0.556 4(18)
C(10)	0.710 9(21)	0.192 4(11)	0.649 9(21)
C(11)	0.661 3(26)	−0.100 3(13)	1.081 0(22)
C(12)	0.665 2(31)	0.100 9(19)	1.100 5(22)
C(13)	0.977 1(16)	0.024 3(29)	1.227 5(14)
O(1)	0.606 3(22)	−0.163 2(15)	1.520 0(22)
O(2)	0.549 8(23)	0.150 5(19)	1.137 9(26)
O(3)	1.085 7(15)	0.033 8(22)	1.363 6(14)

Experimental

All preparations were carried out under an atmosphere of purified nitrogen or hydrogen. Solvents were dried and purified by reflux over a suitable drying agent and distilled under nitrogen. I.r. spectra were recorded on a Perkin-Elmer 283 B double-beam spectrometer and n.m.r. on a Varian EM 360 instrument. The compounds $[Mo(CO)_3(C_7H_8)]$[11] and C_5HMe_5[12] were prepared as previously described.

$[Mo(CO)_3H(\eta-C_5Me_5)]$ (**1**).—$[Mo(CO)_3(C_7H_8)]$ (6.39 g, 23.6 mmol) and an equimolar amount of C_5HMe_5 were mixed under hydrogen in anhydrous methanol (150 cm^3). The solution was kept at room temperature in the dark* for 24 h. The solution was concentrated, cooled to −78 °C and the yellow crystalline solid filtered off and vacuum dried (60%). I.r. and n.m.r. spectra were identical to those described.[7]

$[Mo(CO)_3Cl(\eta-C_5Me_5)]$ (**2**).—Complex (**1**) (1.314 g, 4.16 mmol) was slowly added under stirring at −20 °C to CCl_4 (25

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* Keeping the reaction mixture in the dark under hydrogen avoids the formation of considerable amounts of $[\{Mo(CO)_3(\eta-C_5Me_5)\}_2]$ and $[\{Mo(CO)_2(\eta-C_5Me_5)\}_2]$.

cm^3). A red-orange crystalline solid precipitated in a few minutes from the red solution. The mixture was stirred for 1 h and then the product was filtered off and vacuum dried (80%) (Found: C, 44.60; H, 4.40; Cl, 10.05. Calc. for $C_{13}H_{15}ClMoO_3$: C, 44.55; H, 4.30; Cl, 10.0%). I.r.(Nujol): ν(CO) at 2 030s, 1 965s, and 1 945s cm^{-1}. ^1H N.m.r. ($CDCl_3$) ($SiMe_4$ standard): δ 1.9 (s, C_5Me_5).

$[Li(tmen)_2][Mo(CO)_3(\eta\text{-}C_5Me_5)]$ **(3)**.—A solution of $LiBu^n$ (0.6366 g, 9.94 mmol) and tmen (2.310 g, 19.88 mmol) was slowly added to a solution of **(1)** (3.144 g, 9.94 mmol) in toluene (50 cm^3). After a few minutes a yellow crystalline solid precipitated. The reaction mixture was kept overnight at room temperature and the product was filtered off and vacuum dried (70%) (Found: C, 54.00; H, 8.65; N, 10.25. Calc. for $C_{25}H_{47}LiMoN_4O_3$: C, 54.15; H, 8.55; N, 10.10%). I.r.(Nujol): ν(CO) at 1 885s, 1 755s, and 1 745s cm^{-1}. ^1H N.m.r., $[^2H_6]$benzene (standard $SiMe_4$): δ 2.3 (s, 24 H, NMe), 1.9 (s, 8 H, NCH_2), and 0.5 (s, 15 H, C_5Me_5).

Crystallography.—A crystal of size 0.15 × 0.20 × 0.15 mm was analysed on a computer-controlled Philips PW1100 single-crystal diffractometer, equipped with graphite-monochromatized Mo-K_α radiation. The cell parameters were obtained by least-squares refinement for the setting angles of 25 reflections.

Crystal data. $C_{13}H_{16}MoO_3$, $M = 316.21$, monoclinic, space-group $P2_1$, $a = 8.003(2)$, $b = 12.874(3)$, $c = 7.087(2)$ Å, $\beta = 103.06(2)^\circ$, $D_c = 1.471$ g cm^{-3}, $Z = 2$, $U = 711.29$ Å^3, $F(000) = 320$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 8.68$ cm^{-1}.

Intensities were collected up to $2\theta = 50^\circ$; the θ–2θ scan technique was employed, the scan range being 1.6°, and the speed 0.06° s^{-1}. A total of 1 339 reflections were measured of which 1 136 with $I > \sigma(I)$ were used in the subsequent refinement. No intensity decrease during measurements was observed. The data were corrected for Lorentz and polarization factors. No absorption or secondary-extinction correction was applied.

The structure was solved by Patterson methods and refined by full-matrix least-squares methods using SHELX-76.[13] Due to the unfavourable ratio of the number of reflections to the number of parameters, the Mo–C and C–O bond lengths were constrained to 1.91 ± 0.05 and 1.16 ± 0.04 Å respectively. The hydrogen atoms of the methyl groups were included at calculated positions (C–H = 1.08 Å) with an overall isotropic parameter, $U = 0.14$ Å^2. The Mo atom, O and C atoms, except the methyl C atoms, were refined with anistropic thermal parameters. The refinement converged at $R = 0.044$ and $R' = 0.047$ for 146 parameters and 1 136 observed reflections; $R' = \{[\Sigma w(|F_o| - |F_c|)]^2/(\Sigma w F_o{}^2)\}^{\frac{1}{2}}$, $w = [\sigma^2(F_o) + 0.020\,841 F_o{}^2]^{-1}$. A final difference Fourier map showed no significant features. The atomic scattering factors were taken from ref. 13 for O, N, C, and H and from ref. 14 for Mo; the correction for anomalous dispersion was included. The atomic positions are listed in Table 2.

Acknowledgements

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