Reactivity of Cationic Molybdenum(II) Complexes. Part 1. Hydride Reduction of the 18 Electron Complexes $[Mo(CO)_3(\eta\text{-}C_5Me_5)L]^+$ [L = PPh_3 or $P(OMe)_3$] and Isolation of the Thermally Stable Formyl Complex *cis*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CHO)]$. Crystal Structure of $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4\cdot 0.5MeOH$ †

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The compound $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ reacts with π acids, L [L = PPh_3, $P(OMe)_3$, CO, or *p*-MeC_6H_4NC], giving the 18 electron cations $[Mo(CO)_3(\eta\text{-}C_5Me_5)L]^+$. The complex $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4$ (**1**) has been characterized by a single-crystal *X*-ray diffraction study. The reaction of (**1**) with one equivalent of $Na[BH_4]$ gives the neutral metal formyl complex $[Mo(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)(CHO)]$, (**2**), which, in solution, converts to $[MoH(CO)_3(\eta\text{-}C_5Me_5)]$ above −40 °C. If $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$, (**3**), is used instead of (**1**), the reduction in methanol solution with $Na[BH_4]$ allows isolation of the thermally stable *cis*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CHO)]$, (**4**). Thermal decomposition of (**4**) in methanol solution at room temperature is slow and gives *cis*-$[MoH(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]$. This result emphasizes that the great difference observed in the thermal stability of complexes (**2**) and (**4**) is attributable to different decomposition pathways.

The Mo–H unit of 18 electron π cyclopentadienyl derivatives is a versatile moiety since hydrogen can be removed as H^+ or H^- giving access either to 18 electron anionic species[1] or to cationic co-ordinatively unsaturated species.[2] The compound $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$, which can be obtained by removing H^- from $[MoH(CO)_3(\eta\text{-}C_5Me_5)]$, behaves in solution as a 16 electron, co-ordinatively unsaturated species and easily adds a further ligand, giving 18 electron cationic complexes of general formula $[Mo(CO)_3(\eta\text{-}C_5Me_5)L]BF_4$. Both the cationic nature of the complexes $[Mo(CO)_x(\eta\text{-}C_5R_5)L_y]^+$ and the identity of L could influence the reactivity of co-ordinated carbon monoxide. We report the synthesis and isolation of neutral pentamethylcyclopentadienyl–molybdenum–formyl derivatives together with clear evidence of dependence of the thermal stability of the Mo–CHO unit upon the identity of L.

Results and Discussion

The compound $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ was obtained as a deep violet microcrystalline, thermally stable solid by hydride abstraction from $[MoH(CO)_3(\eta\text{-}C_5Me_5)]$[1] using $[CPh_3]BF_4$. The same reaction has been applied to the synthesis of the corresponding cyclopentadienyl derivative.[2]

$[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ easily undergoes co-ordinative addition reactions with π acceptors, equation (1), where

$$[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4 + L \xrightarrow{CH_2Cl_2} [Mo(CO)_3(\eta\text{-}C_5Me_5)L]BF_4 \quad (1)$$

L = PPh_3, $P(OMe)_3$, CO, or *p*-MeC_6H_4NC. The complexes $[Mo(CO)_3(\eta\text{-}C_5Me_5)L]BF_4$ are obtained quantitatively under ambient conditions as thermally stable, crystalline, diamagnetic solids; their spectroscopic properties (see Experimental section) and the *X*-ray crystal structure determination of one of them (L = PPh_3) confirm their nature as 18 electron cations. The attack of H^- upon co-ordinated CO has proved to be a general route to transition-metal–formyl complexes, and cationic carbonyl derivatives are the best substrates for the synthesis of neutral formyl complexes.[3] As far as Group 6B is concerned, the unique example of isolation of a stable formyl complex, $[Cr(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CHO)]$, was recently reported by some of us.[4]

The molybdenum–formyl complex *trans*-$[Mo(CO)_2(\eta\text{-}C_5H_5)(PPh_3)(CHO)]$ was also reported as being obtained by reduction of the cation $[Mo(CO)_3(\eta\text{-}C_5H_5)(PPh_3)]^+$ with $Li[BEt_3H]$,[5] $[NEt_4][BH_4]$, or $Na[BH_4]$;[6] however, *trans*-$[Mo(CO)_2(\eta\text{-}C_5H_5)(PPh_3)(CHO)]$ is labile in solution, rapidly converting to $[MoH(CO)_3(\eta\text{-}C_5H_5)]$ and PPh_3. Spectroscopic evidence of the formation in solution of a Mo–CHO unit was achieved by treating $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ with $Li[BEt_3H]$ at −60 °C.[7]

Use of the permethylated cyclopentadienyl ligand has been shown to stabilize the Re–CHO unit.[8] In the hope of observing the same effect with molybdenum, we attempted the reduction of $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4$ (**1**). Equimolar methanol solutions of (**1**) and $Na[BH_4]$ were mixed at −40 °C; a yellow powder precipitated within a few minutes and its i.r. spectrum [ν_{CO} (Nujol mull), 1 930s, 1 860vs, 1 610m, cm^{-1}] suggested formation of the neutral formyl complex $[Mo(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)(CHO)]$[6] (**2**). While, in the solid state, complex (**2**) is stable at room temperature (r.t.) for a few hours, it is labile in solution and its ^1H n.m.r. spectrum at r.t. could only show clean conversion to $[MoH(CO)_3(\eta\text{-}C_5Me_5)]$ and free PPh_3.

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† Tricarbonyl(η-pentamethylcyclopentadienyl)(triphenylphosphine)-molybdenum(II) tetrafluoroborate–methanol (2/1).

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

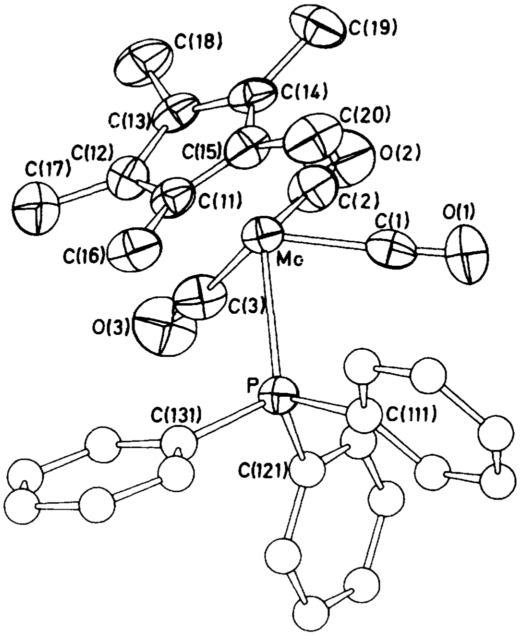

Figure. Molecular structure and labelling for the cation $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]^+$. Hydrogen atoms have been omitted for greater clarity

By performing the reaction at −40 °C and recording ^1H n.m.r. spectra, formyl proton signals were detected at δ 14.40 (d, $^3J_{PH}$ 14) and 14.54 (d, $^3J_{PH}$ 3 Hz) suggesting the presence of both the *cis* and *trans* isomers of (**2**).

Raising the temperature caused immediate disappearance of the signal at δ 14.54 while the signal at δ 14.40 completely disappeared at 0 °C; having observed that the formyl complex with a higher value of $^3J_{PH}$ is the more stable, we concluded that the isolated species was *cis*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)(CHO)]$.[4,9–12]

Our results, compared with those reported by Gibson *et al.*,[6] show that the permethylated ligand has no relevant effect upon the thermal stability of the Mo–CHO unit. However, we observed the reverse order of thermal stability of the two possible isomers, since in the case of the cyclopentadienyl system,[6] the *trans* formyl isomer was isolated as a pure product in high yield under the same experimental conditions in which we have isolated only the *cis* isomer.

By treating $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$, (**3**), instead of (**1**), with an equimolar amount of $Na[BH_4]$ in MeOH, yellow crystals of *cis*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CHO)]$, (**4**), were obtained. Complex (**4**) is sufficiently stable at room temperature, both in solution and in the solid state, for full analytical and spectroscopic characterization. The i.r. spectrum (Nujol mull) shows ν_{CO} absorptions at 1 950s, 1 870vs, and 1 600m cm^{-1} in addition to two peaks diagnostic for formyl complexes[13] in the ν_{CH} region (2 640w and 2 510w cm^{-1}). The ^1H n.m.r. spectrum (CD_3OD) of (**4**) shows the formyl proton at δ 14.67 (d, $^3J_{PH}$ 6 Hz) together with a doublet, δ 3.70 ($^3J_{PH}$ 12 Hz, 9 H), and a singlet, δ 2.00 (15 H). When the reaction between (**3**) and $Na[BH_4]$ is carried out at 0 °C, the ^1H n.m.r. spectrum of the solution shows, in addition to the signals reported above, a doublet at δ 14.62 ($^3J_{PH}$ 1.4 Hz), a doublet at δ 3.62 ($^3J_{PH}$ 12 Hz, 9 H), and a singlet at δ 1.98 (15 H) attributable to *trans*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CHO)]$. The greater thermal stability of the *cis* isomers of the formyl complexes (**2**) and (**4**), compared to that of the *trans* isomers, parallels the behaviour of the analogous chromium derivatives.[4]

Table 1. Selected bond lengths (Å) and angles (°) for $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4\cdot 0.5MeOH$ *

(*a*) Metal co-ordination sphere			
Mo–P	2.562(2)	MoC(14)	2.292(7)
Mo–C(1)	1.991(11)	Mo–C(15)	2.347(10)
Mo–C(2)	1.975(10)	Mo–cp	2.01
Mo–C(3)	1.995(10)		
Mo–C(11)	2.408(7)		
Mo–C(12)	2.333(8)		
Mo–C(13)	2.305(8)		
P–Mo–C(1)	76.4(2)	P–Mo–cp	124.2
P–Mo–C(2)	122.5(3)	C(1)–Mo–cp	120.2
P–Mo–C(3)	77.5(2)	C(2)–Mo–cp	113.3
C(1)–Mo–C(2)	76.9(4)	C(3)–Mo–cp	118.4
C(1)–Mo–C(3)	121.1(4)		
C(2)–Mo–C(3)	74.4(4)		
(*b*) η-C_5Me_5 ligand			
C(11)–C(12)	1.413(11)	C(11)–C(16)	1.508(11)
C(12)–C(13)	1.431(11)	C(12)–C(17)	1.509(14)
C(13)–C(14)	1.413(12)	C(13)–C(18)	1.516(12)
C(14)–C(15)	1.396(13)	C(14)–C(19)	1.508(13)
C(15)–C(11)	1.376(14)	C(15)–C(20)	1.550(16)
C(12)–C(11)–C(15)	106.5(8)	C(15)–C(11)–C(16)	128.3(9)
C(11)–C(12)–C(13)	108.7(7)	C(11)–C(12)–C(17)	125.4(8)
C(12)–C(13)–C(14)	106.5(7)	C(12)–C(13)–C(18)	125.8(9)
C(13)–C(14)–C(15)	107.3(8)	C(13)–C(14)–C(19)	125.7(8)
C(14)–C(15)–C(11)	111.0(9)	C(14)–C(15)–C(20)	122.7(10)
(*c*) Other ligands			
C(1)–O(1)	1.170(10)	P(1)–C(11)	1.812(5)
C(2)–O(2)	1.138(10)	P(1)–C(12)	1.821(5)
C(3)–O(3)	1.134(10)	P(1)–C(13)	1.819(5)
Mo–C(1)–O(1)	176.9(9)	Mo–P–C(11)	114.1(2)
Mo–C(2)–O(2)	176.5(8)	Mo–P–C(12)	115.2(2)
Mo–C(3)–O(3)	174.9(8)	Mo–P–C(13)	114.3(2)

* Cp indicates the centroid of the pentamethylcyclopentadienyl ring.

The new formyl complex *cis*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CHO)]$ shows remarkable thermal stability, as verified by ^1H n.m.r.; in polar, protic solvents like methanol or ethanol it can be handled for a number of days at r.t. while in apolar solvents, like benzene, decomposition is much faster ($\tau_{\frac{1}{2}}$ = 4 h for a 0.3 mol dm^{-3} solution) and clean conversion into *cis*-$[MoH(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]$ * is shown by the appearance of a new signal at −6.35 (d, $^2J_{PH}$ 70 Hz, Mo–H).

As mentioned above, the thermal decomposition of the formyl complex (**2**) occurs *via* loss of the PPh_3 ligand, while (**4**) decomposes through CO loss. The strengthening of the Mo–P bond in (**4**), achieved using $P(OMe)_3$ instead of PPh_3,[14] inhibits the decomposition route arising from Mo–P bond breaking and leaves, as an alternative, the CO-elimination pathway; the latter is evidently a higher energy process, as shown by the greater thermal stability of $[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CHO)]$ compared to that of $[Mo(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)(CHO)]$.[15]

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* When the thermal conversion of the formyl complex (**4**) to the corresponding hydride was complete, the deuteriated solvent was vacuum evaporated and the solid residue analyzed. The i.r. spectrum (Nujol) showed absorptions at 1 940vs and 1 860s cm^{-1}; the relative intensities of the terminal CO stretches (the higher frequency band being more intense), together with the large value of $^2J_{PH}$ for the Mo–H signal in the ^1H n.m.r. spectrum (70 Hz), agree with the hypothesis of a *cis* co-ordination of the CO molecules in $[MoH(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]$.[9,12]

Crystal Structure of $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4$.—*X*-Ray structures for a large number of neutral $[ML_4(\eta\text{-}C_5H_5)]$ complexes have been reported and their four-legged piano-stool geometry has been discussed in detail by Hoffmann and co-workers.[16]

$[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]^+$ also belongs to this class of compounds. Nevertheless it represents an uncommon example of structurally determined cationic four-legged piano-stool complexes. The molecular structure is shown in the Figure and bond lengths and angles are given in Table 1. The Mo–ring carbon atom distances range from 2.292(7) to 2.408(7) Å, closely resembling the analogous separations found in the complex $[Mo(CO)_2(\eta\text{-}C_5Me_5)\{\eta^4\text{-}C(CH_2)_3\}]$[17] and in several molybdenum complexes containing cyclopentadienyl groups.[18] Also the metal–ring centroid distance of 2.01 Å approaches the values observed so far in $Mo\text{–}(\eta\text{-}C_5H_5)$ complexes. The cyclopentadienyl ring is slightly tilted from the plane perpendicular to the Mo–centroid axis as indicated by an angle of 3.3° between the axis and the normal to the cyclopentadienyl plane. The cyclopentadienyl ring is almost planar and the metal groups are shifted 0.18—0.27 Å, with respect to the plane, away from the Mo atom. The Mo–P distance of 2.562(2) Å is somewhat elongated in comparison with that in $[Mo(CO)_2(\eta\text{-}C_5H_5)(PPh_3)I]$,[19] 2.481(5) Å, and in $[Mo(CO)_2(\eta\text{-}C_5H_5)(PPh_3)\{C(CN)_2C(CN)_2Me\}]$,[20] 2.518(1) Å, as a probable consequence of the cationic nature of $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]^+$.

The metal–carbonyl systems are approximately linear with normal C–O distances.

Experimental

All preparations were carried out under an atmosphere of purified nitrogen or carbon monoxide. Solvents were dried and purified by reflux over a suitable drying agent and distilled under nitrogen.

I.r. spectra were recorded with a Perkin-Elmer 283B double-beam spectrometer and n.m.r. spectra with either a Varian EM 360 or Bruker WM 250 spectrometer. The compounds $[MoH(CO)_3(\eta\text{-}C_5Me_5)]$[1] and $[CPh_3]BF_4$[21] were prepared as previously described.

$[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$.—$[CPh_3]BF_4$ (7.89 g, 23.9 mmol) was added in small portions to a solution of $[MoH(CO)_3(\eta\text{-}C_5Me_5)]$ (7.559 g, 23.9 mmol) in methylene chloride (70 cm^3), with stirring, at −30 °C. The solution turned deep violet and was stirred at −30 °C for 1 h. After addition of n-hexane (200 cm^3) the mixture was kept at −70 °C overnight, then the deep violet solid was filtered off, washed with n-hexane, and vacuum dried. Yield: 6.72 g, 16.7 mmol, 70% (Found: C, 39.2; H, 3.95. Calc. for $C_{13}H_{15}BF_4MoO_3$: C, 38.8; H, 3.75%). I.r. (Nujol): 2 050m, 1 970s, 1 945s cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 2.30 (s).

$[Mo(CO)_4(\eta\text{-}C_5Me_5)]BF_4$.—$[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ (0.691 g, 1.72 mmol) was dissolved in methylene chloride (20 cm^3) under CO and kept overnight at room temperature. The solution was then concentrated to half volume and n-hexane (20 cm^3) added. The yellow microcrystalline solid was filtered off, washed with n-hexane, and vacuum dried. Yield: 0.516 g, 1.2 mmol, 69.8% (Found: C, 39.0; H, 3.50. Calc. for $C_{14}H_{15}BF_4MoO_4$: C, 39.1; H, 3.50%). I.r. (Nujol): 2 100m, 1 995s cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 2.00 (s).

$[Mo(CO)_3(\eta\text{-}C_5Me_5)(p\text{-}MeC_6H_4NC)]BF_4$.—The compound $p\text{-}MeC_6H_4NC$ (0.224 g, 1.91 mmol) was added to a solution of $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ (0.768 g, 1.91 mmol) in methylene chloride (20 cm^3). The colour of the solution turned immediately from violet to red. The solution was kept overnight at room temperature, then the solvent was vacuum evaporated and the residue dissolved in tetrahydrofuran (thf) (15 cm^3). From the solution, a yellow microcrystalline solid precipitated after a few minutes and, after cooling for some hours at −70 °C, it was filtered off, washed with diethyl ether, and vacuum dried. Yield: 0.597 g, 1.15 mmol, 60.2% (Found: C, 48.9; H, 4.20. Calc. for $C_{21}H_{22}BF_4MoNO_3$: C, 48.6; H, 4.25%). I.r. (Nujol): 2 165m, 2 075m, 2 020m, 1 940s cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 2.2 (s, 15 H, C_5Me_5), 2.5 (s, 3 H, MeC_6H_4), 7.4—7.8 (q, AA′BB′, 4 H, C_6H_4).

$[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4$ (**1**).—Triphenylphosphine (0.768 g, 2.93 mmol) was added, with stirring at −30 °C, to a solution of $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ (1.179 g, 2.93 mmol) in methylene chloride (25 cm^3). The solution was kept for 1 h at −30 °C and during this time the colour slowly changed from violet to red-brown. The temperature was allowed to rise to room temperature. After 12 h the solution was concentrated to a volume of 5 cm^3 and diethyl ether was added (50 cm^3). A brown oil immediately precipitated and, after stirring for several hours at room temperature, gave a yellow solid which was filtered off, washed with diethyl ether, and vacuum dried. Yield: 1.58 g, 2.38 mmol, 81% (Found: C, 56.4; H, 4.70. Calc. for $C_{31}H_{30}BF_4MoO_3P$: C, 56.1; H, 4.55%). I.r. (Nujol): 2 050m, 1 990s, 1 960s cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 2.0 (s, 15 H, C_5Me_5), 7.0—7.8 (m, 15 H, PPh_3).

cis-$[Mo(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)(CHO)]$ (**2**).—A solution of $Na[BH_4]$ (0.0627 g, 1.5 mmol) in methanol (10 cm^3) was added dropwise at −60 °C to a stirred solution of $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4$ (0.996 g, 1.5 mmol) in methanol (20 cm^3). A yellow air-sensitive powder precipitated out and was filtered off and vacuum dried to yield 0.477 g (55%), of product. ^1H N.m.r. (CD_3OD, $T = -40$ °C): δ 14.40 (d, $^3J_{PH}$ 14.0 Hz, 1 H), 7.60—7.30 (m, 15 H), 1.82 (s, 15 H). I.r. (Nujol): 2 640vw, 2 510w, 1 930s, 1 860vs, 1 610m cm^{-1}.

Meaningful analytical data could not be obtained due to thermal decomposition.

$[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (**3**).—A methylene chloride solution (10 cm^3) of $P(OMe)_3$ (0.547 g, 4.41 mmol) was added dropwise at −30 °C into a stirred solution of $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ (1.774 g, 4.41 mmol) in methylene chloride (25 cm^3). The cooling bath was then removed and the solution left overnight at room temperature. After addition of diethyl ether (40 cm^3), the formation of a brown oil was initially observed. Solidification of this oil was obtained by vigorously stirring the mixture for several hours. The yellow powder was filtered off, washed with diethyl ether, and vacuum dried. Recrystallization from methanol–diethyl ether (1:1.5) yielded 1.523 g (66%) of product (Found: C. 36.95; H, 4.65. Calc. for $C_{16}H_{24}BF_4MoO_6P$: C, 36.55; H, 4.65%). I.r. (Nujol): ν_{CO} 2 040s, 1 995vs, 1 950vs cm^{-1}. ^1H N.m.r. (CD_3OD): δ 4.00 (d, $^3J_{PH}$ 12 Hz, 9 H), 2.15 (s, 15 H).

cis-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CHO)]$ (**4**).—A solution of $Na[BH_4]$ (55 mg, 1.39 mmol) in methanol (20 cm^3) was added, while cooling to −30 °C, to a stirred solution of (**3**) in methanol (30 cm^3). The solution was slowly warmed to 0 °C over the course of 1 h and the solvent was vacuum evaporated. The residue was extracted with diethyl ether–hexane (1:4) and the solution concentrated and stored overnight at −78 °C; during this time a yellow microcrystalline solid precipitated and was filtered off and vacuum dried to yield 0.398 g (65%) of product (Found: C, 44.10; H, 5.70. Calc. for $C_{16}H_{25}MoO_6P$: C, 43.65; H, 5.70%). I.r. (Nujol): 2 640w, 2 510m, 1 950s, 1 870vs, 1 600m cm^{-1}. ^1H N.m.r. (CD_3OD): δ 14.67 (d, $^3J_{PH}$ 6 Hz, 1 H), 3.70 (d, $^3J_{PH}$ 12 Hz, 9 H), 2.00 (s, 15 H).

Molecular Structure Determination.—Crystals of $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4\cdot 0.5MeOH$ suitable for the *X*-ray

Table 2. Positional parameters (× 10^4) for the non-hydrogen atoms of $[Mo(CO)_3(\eta^5\text{-}C_5Me_5)(PPh_3)]BF_4\cdot 0.5MeOH$ *

Atom	*x*	*y*	*z*
Mo	1 881(1)	2 562(1)	3 610(1)
P	3 302(2)	1 633(2)	4 304(2)
O(1)	835(6)	1 115(7)	5 354(8)
O(2)	919(7)	4 588(8)	5 469(8)
O(3)	3 573(6)	4 947(7)	4 685(8)
C(1)	1 247(7)	1 666(9)	4 732(9)
C(2)	1 286(8)	3 841(10)	4 820(9)
C(3)	2 993(8)	4 046(9)	4 299(9)
C(11)	1 855(7)	1 414(8)	1 388(8)
C(12)	2 032(7)	2 708(8)	1 584(8)
C(13)	1 171(7)	3 187(8)	2 063(8)
C(14)	484(7)	2 167(8)	2 203(8)
C(15)	922(9)	1 126(11)	1 779(10)
C(16)	2 486(9)	532(11)	653(9)
C(17)	2 900(10)	3 424(14)	1 126(13)
C(18)	973(11)	4 473(11)	2 188(12)
C(19)	−578(8)	2 180(14)	2 538(13)
C(20)	334(10)	−222(10)	1 603(11)
C(111)	2 883(5)	111(5)	4 471(4)
C(112)	2 305(5)	−823(5)	3 438(4)
C(113)	1 924(5)	−1 994(5)	3 535(4)
C(114)	2 121(5)	−2 231(5)	4 666(4)
C(115)	2 699(5)	−1 297(5)	5 699(4)
C(116)	3 080(5)	−126(5)	5 601(4)
C(121)	3 999(3)	2 549(5)	5 840(3)
C(122)	3 516(3)	3 265(5)	6 801(5)
C(123)	4 026(3)	3 879(5)	8 011(5)
C(124)	5 019(3)	3 777(5)	8 259(5)
C(125)	5 502(3)	3 060(5)	7 298(5)
C(126)	4 992(3)	2 446(5)	6 088(5)
C(131)	4 285(4)	1 432(4)	3 233(6)
C(132)	4 478(4)	257(4)	2 580(6)
C(133)	5 202(4)	143(4)	1 716(6)
C(134)	5 732(4)	1 204(4)	1 506(6)
C(135)	5 539(4)	2 379(4)	2 159(6)
C(136)	4 815(4)	2 493(4)	3 023(6)
B(1)	2 231(12)	6 682(15)	9 899(15)
F(1)	3 066(11)	7 682(13)	10 491(13)
F(2)	2 399(11)	5 842(13)	10 443(13)
F(3)	2 213(9)	6 156(13)	8 579(11)
F(4)	1 426(12)	7 182(16)	10 268(14)
F(1A)	2 987(26)	6 076(30)	10 067(31)
F(2A)	1 263(21)	6 203(29)	10 165(26)
F(3A)	2 349(27)	7 799(31)	10 152(31)
F(4A)	2 301(25)	6 981(36)	8 797(34)
O(4)	812(15)	3 260(20)	8 379(20)
C(4)	1 239(16)	3 747(20)	7 545(21)

* A denotes the fluorine atoms of the disordered $[BF_4]^-$ anion which were refined with population parameters 0.3; the remaining fluorine atoms have been refined with population parameters 0.7.

structural determination were obtained by recrystallization from a methanol–diethyl ether mixture. A yellow-orange plate-like crystal of dimensions 0.10 × 0.23 × 0.55 mm was sealed inside a Lindemann capillary under an atmosphere of dry nitrogen. All *X*-ray measurements from the crystal were performed on a Philips PW 1100 diffractometer using graphite-monochromated Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å).

Crystal data. $C_{31}H_{30}BF_4MoO_3P\cdot 0.5MeOH$, M = 680.32, triclinic, a = 13.548(3), b = 11.507(2), c = 11.141(2) Å, α = 108.34(1), β = 92.34(1), γ = 100.12(1)°, U = 1 614.4 Å^3, space group $P\bar{1}$ (no. 2), Z = 2, D_c = 1.40 g cm^{-3}, $F(000)$ = 694, μ(Mo-K_α) = 4.97 cm^{-1}.

Data collection. θ–2θ mode with ω scan width of 1°, ω scan speed 0.05° s^{-1}; 4 503 reflections measured ($2.5 \leqslant \theta \leqslant 23°$, $\pm h$, $\pm k$, l); 2 951 reflections with $I > 3\sigma(I)$ corrected for absorption using a ψ-scan method (max., min. transmission factors = 0.91, 0.84) were used in the subsequent calculations.

Structure analysis and refinement. The structure was solved by Patterson and Fourier techniques using the SHELX 76 program package.[22] Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms of the complex cation, except the phenyl carbon atoms, gave the final R 0.058 and R' 0.061. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The phenyl rings were treated as rigid bodies of D_{6h} symmetry with C–C distances fixed at 1.395 Å and calculated H-atom positions (C–H 1.0 Å).

All the hydrogen atoms of the methyl groups (except for those of the methanol solvent molecule) were located from a difference Fourier map. They were subsequently refined with the C–H distances kept fixed at 1.0 Å and isotropic thermal parameters. The $[BF_4]^-$ ion was found to be disordered between two orientations, refined with population parameters 0.7 and 0.3. At the final stage a difference Fourier map revealed two higher peaks attributed to a methanol solvent molecule. The high parameters indicated that the solvent positions were probably partially occupied with population parameters 0.5. The highest peak on the final difference map (0.8 e Å^{-3}) was located near one of the phenyl rings. The atomic positions are listed in Table 2.

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