Mono-η-cyclopentadienylmolybdenum Chemistry: 1,2-Bis(dimethylphosphino)ethane-hydrido, -halogeno, -alkyne, and -oxo Derivatives

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The new compounds $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_3]$, $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$, $[Mo(\eta\text{-}C_5H_5)(dmpe)H_4][PF_6]$, $[Mo(\eta\text{-}C_5H_5)(dmpe)O][PF_6]$, $[Mo(\eta\text{-}C_5H_5)(dmpe)(PhC{\equiv}CPh)][PF_6]$, $[Mo(\eta\text{-}C_5H_5)(dmpe)(MeC{\equiv}CMe)][PF_6]$, and $[Mo(\eta\text{-}C_5H_5)_2(dmpe)][PF_6]$ [dmpe = 1,2-bis(dimethylphosphino)ethane] have been prepared and characterised by i.r., ^1H n.m.r., and mass spectra.

THE compounds $[M(\eta\text{-}C_5H_5)_2H_2]$, M = Mo or W, and $[M'(\eta\text{-}C_5H_5)_2H_3]$, M' = Nb or Ta, have been shown to lose dihydrogen either photochemically [1,2] or thermally [3] and the resulting compounds will activate aromatic or even saturated carbon–hydrogen bonds.[1,4] The system $[Mo(\eta\text{-}C_5H_5)(R_2PCH_2CH_2PR_2)H_3]$ is isoelectronic with the above compounds and the d^n electrons would be expected to have similar energies to those of $[Nb(\eta\text{-}C_5H_5)_2H]$ or $[W(\eta\text{-}C_5H_5)_2]$. Therefore, we were interested to discover whether such compounds would likewise react with carbon–hydrogen bonds. In pursuit of this objective we recently prepared the compound $[Mo(\eta\text{-}C_5H_5)(Ph_2PCH_2CH_2PPh_2)H_3]$ [5] but found no evidence for thermally or photochemically induced reaction between this compound or its derivatives and deuteriobenzene. The ligand 1,2-bis(dimethylphosphino)ethane (dmpe) is more electron releasing than 1,2-bis(diphenylphosphino)-ethane and so we set out to explore the chemistry of the $[Mo(\eta\text{-}C_5H_5)(dmpe)]$ system, as described below.

RESULTS

Chemical Studies.—The di-iodide $[Mo(\eta\text{-}C_5H_5)_2I_2]$ reacts slowly with dmpe and after addition of hexafluorophosphate the compound $[Mo(\eta\text{-}C_5H_5)_2(dmpe)][PF_6]_2$, (1), may be isolated in excellent yield. Treatment of (1) with sodium tetrahydroborate gives an orange-yellow compound and toluene solutions of this product react readily with hydrogen chloride forming the trichloride $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_3]$, (2), and an insoluble purple solid (1—2%). When cold dichloromethane is used as the solvent instead of toluene then apart from (2) and the insoluble purple solid there is also formed in 5—10% yield the dichlorohydrido-compound $[Mo(\eta\text{-}C_5H_5)(dmpe)HCl_2]$, (3). Compound (3) in chloroform at room temperature reacted over a period of two months forming the trichloro-derivative (2).

The ^1H n.m.r. spectrum of (2) shows a double doublet assignable to the $\eta\text{-}C_5H_5$ hydrogens arising from coupling between the $\eta\text{-}C_5H_5$ hydrogens and two inequivalent ^{31}P nuclei. Compound (3) is rather insoluble and the ^1H n.m.r. spectrum had a poor intensity; the η-cyclopentadienyl resonance was a triplet of triplets which may be assigned to coupling with two equivalent ^{31}P nuclei and a Mo–hydrogen bond. The i.r. spectrum of (3) shows a band at 1 820 cm^{-1} assignable to a Mo–H stretching frequency. However, there was no evidence for a Mo–H bond in the ^1H n.m.r. spectrum. Such a resonance would be very broad due to coupling with the five equivalent hydrogens of the $\eta\text{-}C_5H_5$ ring as well as with the two ^{31}P nuclei. We conclude that either the resonance due to Mo–H is lost in the noise, or that the molecule is fluxional and the Mo–H resonance is further broadened by exchange processes, or, less probably, that the Mo-H resonance lies under the bands assignable to the dmpe hydrogens. The reaction of (3) with chloroform giving (2) is strong circumstantial evidence in support of the given formulation for (3). Also, the mass spectrum of (2) shows a highest envelope with *m/e* values corresponding to the various isotopic components of the parent ion whereas the mass spectrum of (3) showed only highest bands assignable to $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_2]^+$ species.

The insoluble purple solid analyses, within experimental error, for the stoicheiometry $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_3]_n$ *i.e.* identical to (2) and the i.r. spectrum is similar to that of (2). In view of the small and irreproducible yields obtained for the insoluble solid (1—2%) we have not pursued its characterisation.

Treatment of (2) with $Na[Al(OCH_2CH_2OMe)_2H_2]$ gave a yellow air-sensitive compound $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$, (4). Compound (4) sublimes readily *in vacuo* at 120 °C and is soluble in benzene and slightly soluble in light petroleum. The ^1H n.m.r. spectrum shows a single triplet for the MoH_3 hydrogen showing the molecule to be fluxional.

Compound (4) in chloroform reacts slowly and when the solution is monitored by ^1H n.m.r. spectroscopy then *inter alia* the spectrum of (3) could be detected and, after about two weeks, the spectrum of (2) was also present. The photoelectron spectrum of (4) shows a first ionisation potential for the d^2 electrons at 6.4 eV.† Thus compound (4) is a true high-energy (electron-rich) compound. Full assignment of the photoelectron spectrum will be published elsewhere. Since the d^2 pair of electrons are clearly accessible it was possible that they would protonate. Indeed, it was found that (4) readily dissolved in dilute hydrochloric acid giving, after addition of hexafluorophosphate, the colourless tetrahydrido-compound $[Mo(\eta\text{-}C_5H_5)(dmpe)H_4][PF_6]$, (5). Addition of sodium hydroxide to a suspension of (5) in water reforms the parent trihydrido-compound (4). The ^1H n.m.r. spectrum of (4) shows the MoH_4 system as a single triplet which indicates the molecular ion to be fluxional. The ^{31}P n.m.r. showed only a broad singlet for the two ^{31}P nuclei.

A solution of (4) in acetonitrile was treated with diphenylacetylene giving dark green crystalline $[Mo(\eta\text{-}C_5H_5)(dmpe)(PhC{\equiv}CPh)][PF_6]$, (6). Compound (6) is soluble in acetone and nitromethane and the solutions are steadily decomposed in air. The ^{13}C n.m.r. spectrum of (6) shows resonances due to only one type of phenyl group. This, together with the 270 MHz ^1H n.m.r. data given in the

† Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J; 1 Torr = (101 325/760) Pa.

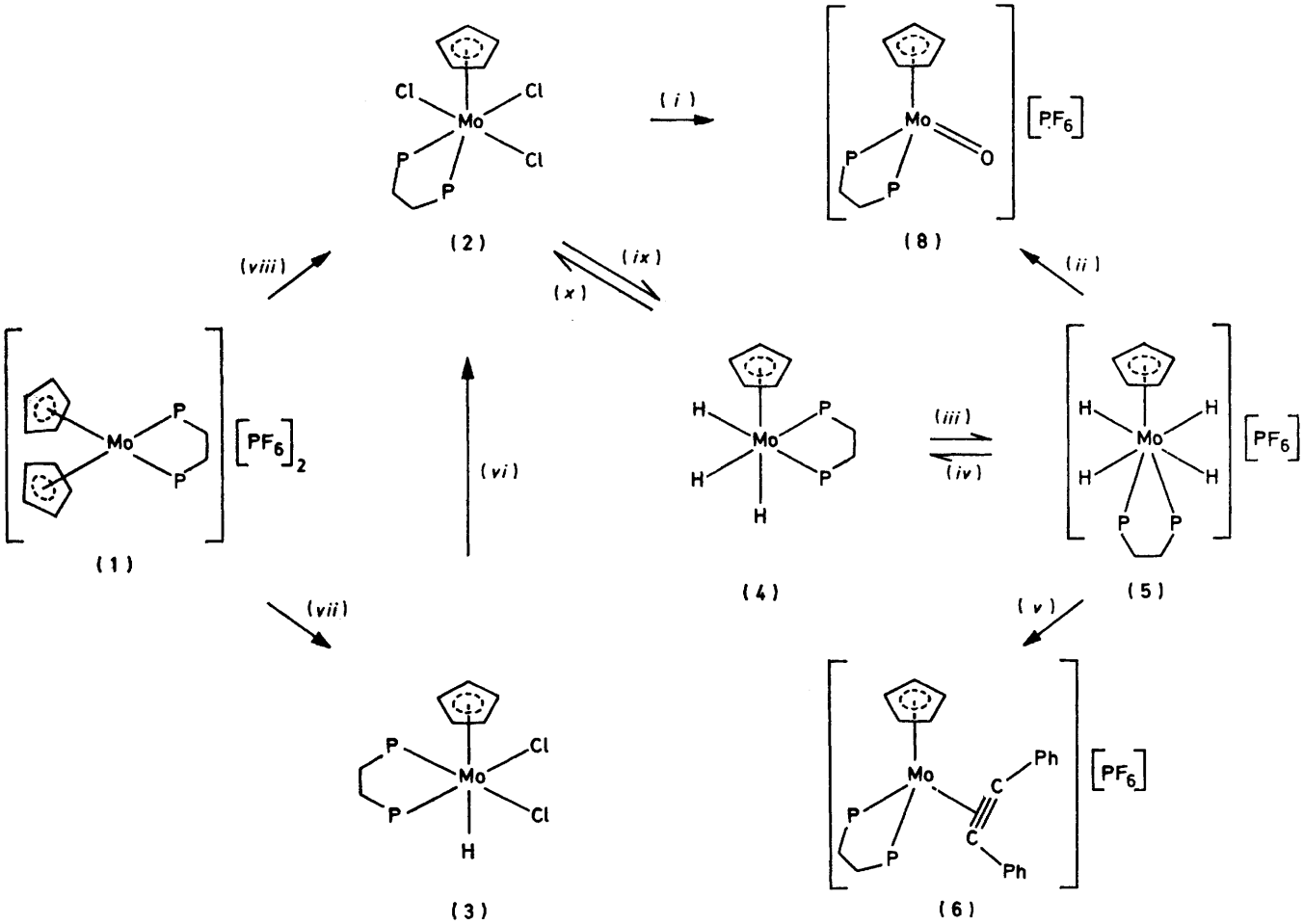
Analytical and spectroscopic data

Compound	Colour	Analysis (%) [a] C	H	^{1}H n.m.r. data [b]
(1) $[Mo(\eta\text{-}C_5H_5)_2(dmpe)][PF_6]_2$	Yellow	29.1 (28.8)	4.0 (3.9)	4.30, **5**, *t* [*J*(P–H) 2], η-C_5H_5; 7.84, **4**, *d* (*J* CH_2CH_2; 8.25, **12**, *d* [*J*(P–H) 12], 4Me [c]
(2) $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_2]$	Red-purple	32.4 (31.6)	5.2 [d] (5.1)	4.98, **6**, *d of d* [*J*(P–H) 3 and 1], η-C_5H_5; 8.20, **6**, *d* [*J*(P–H) 12]; 8.58, **6**, *d* [*J*(P–H) 9], 4Me [e]
(3) $[Mo(\eta\text{-}C_5H_5)(dmpe)HCl_2]$	Red	*f*		5.18, **5**, *d of t* [*J*(P–H) 10; *J*(H–H) 1], η-C_5H_5; 8.20, **6**, *d* [*J*(P–H) 10], 2Me; 8.3—8.6, **4**, *c broad*, CH_2CH_2; 8.74, **6**, *d* [*J*(P–H) 9], 2Me [d]
(4) $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$	Yellow	41.5 (42.1)	8.0 [g] (8.0)	5.43, **5**, *s*, *broad*, η-C_5H_5; 8.71, **16**, *c*, dmpe; 16.12, **3**, *t* [*J*(P–H) 27], H_3 [h]
(5) $[Mo(\eta\text{-}C_5H_5)(dmpe)H_4][PF_6]$	White	28.7 (28.6)	5.5 (5.5)	4.55, **5**, *s*, η-C_5H_5; 8.24, **16**, *d superimposed on a broad complex band* [*J*(P–H) 11], dmpe; 14.85, **4**, *t* [*J*(PH) 38], H_4 [i]
(6) $[Mo(\eta\text{-}C_5H_5)(dmpe)(PhC{\equiv}CPh)][PF_6]$	Green	47.3 (47.3)	5.0 (4.9)	2.66, **10**, *c*, Ph_2; 4.47, **5**, *t* [*J*(P–H) 1.5], η-C_5H_5; 8.52, **16**, '*t*' (peak separation 9 Hz), dmpe [j]
(7) $[Mo(\eta\text{-}C_5H_5)(dmpe)(MeC{\equiv}CMe)][PF_6]$	Blue-green	32.6 (35.3)	5.1 (5.3)	4.58, **5**, *t* [*J*(P–H) 1.5], η-C_5H_5; 7.18, **6**, *s*, Me_2; 8.64, **6**, *d* [*J*(P–H) 10.2], Me_2; 8.65, **6**, *d* [*J*(P–H) 9.0], Me_2; 7.6—8, **4**, *c broad*, $(CH_2)_2$ [j]
(8) $[Mo(\eta\text{-}C_5H_5)(dmpe)O][PF_6]$	Red	27.4 (27.9)	4.3 (4.4)	4.51, **5**, *t* [*J*(P–H) 7], η-C_5H_5; 8.04, **16**, *d* [*J*(P–H) 15]; 8.33, *d superimposed on a broad complex band* [*J*(P–H) 11], dmpe [k]

[a] Calculated values are given in parentheses. [b] Given as: chemical shift, **relative intensity**, *multiplicity* (*J* in Hz), assignment, *etc.* [c] In $(CD_3)_2SO$. [d] Mass spectrum, *m/e* at 420, P^+(^{96}Mo, ^{37}Cl). [e] In CD_2Cl_2. [f] Mass spectrum, *m/e* at 384, (P^+ – H) (^{96}Mo, ^{37}Cl). [g] Mass spectrum, *m/e* at 316, P^+(^{96}Mo), ν(Mo–H)$_{str.}$ at 1 800m, 1 705 cm^{-1}. [h] In $CD_3C_6D_5$. [i] In CD_3CN, ν(Mo–H) at 1 855w, 1 805m cm^{-1}. [j] In CD_3NO_2. [k] In $(CD_3)_2CO$.

Table, shows that either compound (6) is fluxional or that it has the static structure shown in the Scheme.

Treatment of acetonitrile solutions of (4) with but-2-yne gives a dark blue solid whose ^{1}H n.m.r. spectrum is con-



SCHEME (*i*) Dissolve in water, then $[NH_4][PF_6]$ (aq), 80%; (*ii*) dissolve in aqueous acetone, then $[NH_4][PF_6]$, 15%; (*iii*) dilute hydrochloric acid, then $[NH_4][PF_6]$, 80%; (*iv*) sodium hydroxide, 90%; (*v*) in acetonitrile, PhC≡CPh at 70 °C for 5 min, 80%; (*vi*) $CHCl_3$ at r.t. for 2 weeks, 90%; (*vii*) $Na[BH_4]$ in thf, then CH_2Cl_2 and HCl gas, *ca.* 2%; (*viii*) $Na[BH_4]$ in thf, then toluene extract with HCl gas, 30%; (*ix*) cyclohexane and $Na[Al(OCH_2CH_2OMe)_2H_2]$ for 24 h, *ca.* 30%; (*x*) $CHCl_3$ at r.t. several weeks, *ca.* 80% yield

sistent with a formulation analogous to that of (6). However, despite recrystallisation and chromatography it was not found possible to obtain analytically pure samples of the compounds. It was assumed that the main impurity was solvent.

A study has been made of the change in the ^1H n.m.r. spectrum of a solution of (4) in deuteriobenzene. The solutions become deep red within a few hours. Over a period of several days the resonances due to the MoH_3, η-C_5H_5, and PMe_2 groups diminish in intensity and yet no other new hydrogen resonances appear, except that there is a marked increase in the signal to noise for the ^1H impurity resonance of the deuteriobenzene sample. Also, an investigation of a sample of (4) in benzene after two weeks at 60 °C showed that *ca.* 50% of the starting compound (4) was recoverable by sublimation. This preliminary observation suggested that compound (4) has undergone statistical equilibration of its hydrogen atoms, except those of the CH_2CH_2 group, with the deuterium atoms of the deuteriobenzene. A further more detailed investigation into this phenomenon will be described separately.

Finally, compound (2) reacts with water giving, after addition of hexafluorophosphate, red crystals of the oxo-cation $[Mo(\eta\text{-}C_5H_5)(dmpe)O][PF_6]$, (8). The crystal structure of (8) has been determined and is discussed in detail elsewhere.[6] Compound (8) could also be isolated from reaction between (5) and acetone which presumably contained a small quantity of water. It was generally observed that solutions of (5); for example, in nitromethane, acetone, and acetonitrile deuteriated although the nature of the products has not yet been ascertained.

DISCUSSION

The compounds of stoicheiometry $[Mo(\eta\text{-}C_5H_5)(dmpe)X_3]$ can have two idealised geometries based on an essentially octahedral disposition of the ligands, treating for the sake of simplicity the η-C_5H_5 group as occupying only one of the ' octahedral ' positions, as shown in the Scheme. Based on this ligand disposition then the compound (3) has four possible geometrical isomers. The occurrence of the η-C_5H_5 hydrogens of (2) as a double doublet suggests the two ^{31}P nuclei to be inequivalent and this supports the structural type *mer* isomer for (2) shown in the Scheme. In contrast for (3) it appears from the ^1H n.m.r. that either the molecule is fluxional or that the ^{31}P nuclei are equivalent as would be the case for the structure shown for (3) in the Scheme. Since the ^1H n.m.r. shows Mo–H bonds of (4) to be equivalent then the molecule must be fluxional. Similarly, the equivalence of the four molybdenum–hydrogen bonds of (5) suggest it to be fluxional although a suitably symmetrical state structure such as is shown in the Scheme may be envisaged. As discussed above, the data suggest the structure for (6) shown in the Scheme.

In conclusion, the compound $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$, (4), is a high-energy molecule which has the ability to activate aromatic carbon–hydrogen bonds and this aspect will be further studied.

EXPERIMENTAL

All preparations and manipulations were carried out *in vacuo* or under an inert atmosphere. Solvents were dried and distilled before use. Infrared spectra were determined as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Hydrogen-1 n.m.r. spectra were determined on a JEOL C-60HL or Bruker 90 or 270 MHz instruments. Mass spectra were determined using an M.S.9 spectrometer. The compound $[Mo(\eta\text{-}C_5H_5)_2I_2]$ was prepared as previously described.[7]

[1,2-Bis(dimethylphosphino)ethane]bis(η-cyclopentadienyl)-molybdenum Bis(hexafluorophosphate), (1).—The compound $[Mo(\eta\text{-}C_5H_5)_2I_2]$ (16 g, 33 mmol) in tetrahydrofuran (thf) (150 cm^3) was treated with dmpe (1.6 g, 44 mmol) and the mixture was stirred at room temperature (r.t.) for 5 days. A grey-yellow precipitate formed which was collected and extracted with acetone. The acetone extract was filtered giving an orange filtrate. Aqueous ammonium hexafluorophosphate was added (6.0 g in 20 cm^3 water) and the solution was slowly concentrated under reduced pressure. A bright yellow precipitate separated which was collected, washed with water, and dried *in vacuo*, 20 g, *ca.* 90%.

[1,2-Bis(dimethylphosphino)ethane]trichloro(η-cyclopentadienyl)molybdenum, (2).—The compound $[Mo(\eta\text{-}C_5H_5)_2(dmpe)][PF_6]_2$ (2.0 g, 3.0 mmol) in thf (40 cm^3) was treated with sodium tetrahydroborate (0.6 g, 15 mmol). The mixture was stirred at r.t. for 24 h giving an orange solution and grey-white precipitate.

Filtration gave an orange filtrate from which solvent was removed under reduced pressure. The orange solid residue was extracted with toluene (3 × 30 cm^3), the combined extracts were filtered, and the filtrate was cooled to −78 °C. Hydrogen chloride gas was passed through the solution for 10 min giving a purple-red oily precipitate and a pale red-purple solution. The solid was separated and then extracted with hot toluene (3 × 20 cm^3 at 80 °C). The combined extracts were filtered and the filtrate was concentrated under reduced pressure and then cooled to −5 °C for 14 h. Further cooling to −78 °C separated fine purple needles. These were collected, washed with light petroleum (b.p. 30—40 °C), and dried *in vacuo*, 0.36 g, ~30%.

[1,2-Bis(dimethylphosphino)ethane]dichloro(η-cyclopentadienyl)hydridomolybdenum, (3).—This compound was formed in the reaction which gives the compound $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_3]$ as described above except that instead of using toluene as the solvent for the reaction with hydrogen chloride dichloromethane was used at −78 °C. The resulting purple precipitate was extracted as before with toluene leaving a dark residue which was then further extracted with dichloromethane giving a red solution. This was concentrated and cooled to −5 °C for 16 h. Red needle crystals separated which were collected and washed with toluene, then light petroleum (b.p. 30—40 °C), and dried *in vacuo*, 0.17 mg, 5—10%.

[1,2-Bis(dimethylphosphino)ethane](η-cyclopentadienyl)-trihydridomolybdenum, (4).—The compound $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_3]$ (1.0 g, 2.4 mmol) in cyclohexane (80 cm^3) was treated with $Na[Al(OCH_2CH_2OMe)_2H_2]$ (5 cm^3 of a 70% solution in benzene) and the mixture was stirred at r.t. for 24 h. The suspension dissolved slowly giving a yellow solution.

This was cooled and treated with water (30 cm^3) in a dropwise manner. The organic layer was separated and solvent was removed under reduced pressure giving a brown solid. This was sublimed at 120—140 °C and 5 × 10^{-3} Torr giving the pure yellow product, 0.25 g, 30%.

[1,2-Bis(dimethylphosphino)ethane](η-cyclopentadienyl)-tetrahydridomolybdenum Hexafluorophosphate, (5).—The

compound $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$ (0.4 g, 1.3 mmol) was treated with hydrochloric acid (1 mol dm^{-3}, 30 cm^3), the resulting solution was filtered, and the filtrate was treated with aqueous ammonium hexafluorophosphate (0.5 g in 10 cm^3), giving a white precipitate. This was collected and washed with water and then dried *in vacuo* at 50 °C, 0.42 g, 80%.

Treatment of [1,2-*Bis*(*dimethylphosphino*)*ethane*](η-*cyclopentadienyl*)*tetrahydridomolybdenum Hexafluorophosphate with Base.*—The compound $[Mo(\eta\text{-}C_5H_5)(dmpe)H_4][PF_6]$ (0.1 g, 0.22 mmol) in acetone (20 cm^3) was treated with aqueous sodium hydroxide (0.5 g in 10 cm^3). The solution was concentrated under reduced pressure until most of the acetone had evaporated. The resulting pale yellow-white suspension was collected, washed with water, and dried *in vacuo*. It was identified as the trihydrido-compound (4) by comparison of the i.r. spectrum with that of an authentic sample.

[1,2-*Bis*(*dimethylphosphino*)*ethane*](η-*cyclopentadienyl*)-(*diphenylacetylene*)*molybdenum Hexafluorophosphate*, (6).—The compound $[Mo(\eta\text{-}C_5H_5)(dmpe)H_4][PF_6]$ (0.4 g, 0.86 mmol) in acetonitrile (15 cm^3) was treated with diphenylacetylene (0.3 g) and the mixture was warmed to 70 °C for 5 min. The initially colourless solution became deep green. After 10 min, the solvent was concentrated under reduced pressure and diethyl ether was added slowly. Green crystals separated which were collected, washed with diethyl ether, and dried *in vacuo*, 0.46 g, 80%.

[1,2-*Bis*(*dimethylphosphino*)*ethane*](*but*-2-*yne*)(η-*cyclopentadienyl*)*molybdenum Hexafluorophosphate*, (7).—The compound $[Mo(\eta\text{-}C_5H_5)(dmpe)H_4][PF_6]$ (0.33 g, 0.72 mmol) in acetonitrile (15 cm^3) was treated with but-2-yne (0.1 cm^3) and the mixture was heated at 70 °C for 10 min. The resulting dark blue solution was evaporated to dryness under reduced pressure. The resulting blue-green solid was dissolved in the minimum quantity of acetonitrile and diethyl ether was added giving a blue-green precipitate. This was collected, washed with diethyl ether, and dried *in vacuo*, *ca.* 60%.

[1,2-*Bis*(*dimethylphosphino*)*ethane*](η-*cyclopentadienyl*)*oxomolybdenum Hexafluorophosphate*, (8).—(*i*) *From* $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_3]$, (2). Compound (2) (1.0 g, 2.4 mmol) was stirred vigorously with water (10 cm^3) giving a deep red solution (1 h). Addition of aqueous ammonium hexafluorophosphate precipitated a red solid. This was collected and crystallised from acetone–water, yield *ca.* 80%.

(*ii*) *From* $[Mo(\eta\text{-}C_5H_5)(dmpe)H_4][PF_6]$ (5).—Compound (5) was dissolved in wet acetone. After 24 h the initially pale green solution had become red. Addition of water and concentration under reduced pressure yielded red *crystals* of the title compound, *ca.* 70%.

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