Arene–Molybdenum Chemistry: Olefin and Hydride Derivatives†

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Reduction using sodium amalgam of the complex [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_3$H$_5$)]$^+$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) in the presence of the olefins L = ethylene, propene, or cyclopentene gives the neutral η^2-olefin compounds [Mo(η-C$_6$H$_6$)(dmpe)L]. The η-ethylene compound readily protonates forming the hydrido-cation [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)H]$^+$. Treatment of this with the tertiary phosphines PR$_3$, where R$_3$ = Me$_3$ or Me$_2$Ph, gives the η-ethylbenzene compounds [Mo(η-C$_6$H$_5$Et)(dmpe)(PR$_3$)H]PF$_6$. The new compounds *trans*-[Mo(η-C$_6$H$_6$)(dmpe)H$_2$], [{Mo(η-C$_6$H$_6$)(dmpe)}$_2$(μ-dmpe)], [{Mo(η-C$_6$H$_6$)(dmpe)H}$_2$(μ-dmpe)][PF$_6$]$_2$, [Mo(η-C$_6$H$_6$)-(η-C$_3$H$_5$)(PMe$_3$)Cl], [Mo(η-C$_6$H$_6$)(PMe$_3$)$_3$], and [Mo(η-C$_6$H$_6$)(PMe$_3$)$_3$H]PF$_6$ are also described.

Compounds of the type [W(η-C$_5$H$_5$)$_2$Me(L)]PF$_6$, where L = R$_2$S, η-C$_2$H$_4$, or PMe$_3$, react with certain tertiary phosphines PR$'_3$, *e.g.* PMe$_2$Ph, giving the derivatives [W(η-C$_5$H$_5$)$_2$-(CH$_2$PR$'_3$)H]PF$_6$ and the reaction has been shown to involve a 1,2-hydrogen-shift mechanism.[1,2] In a search for further examples where reversible 1,2-hydrogen-shift processes might occur it was decided to attempt to synthesise the compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)Me]PF$_6$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) which can be seen to be a d^4 analogue of [W(η-C$_5$H$_5$)$_2$Me(L)]PF$_6$ and to study its reaction with tertiary phosphines. Further, since the moiety Mo(η-C$_6$H$_6$)(dmpe) is a d^4 analogue of W(η-C$_5$H$_5$)$_2$ we decided to attempt to prepare and study the compound *cis*-[Mo(η-C$_6$H$_6$)(dmpe)H$_2$] with a particular view to reactions with dinitrogen or its photoinduced activation of C–H bonds. Unexpected results were obtained as described below. A brief summary of part of this work has appeared.[3]

Results and Discussion

A suspension of the compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_3$H$_5$)]PF$_6$, (1), in tetrahydrofuran under an atomosphere of ethylene was treated with sodium amalgam giving red crystalline [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)], (2). Comparison of the ^{1}H n.m.r. spectra of the ethylene compound (2) at 90 and 300 MHz shows that there are, as expected, two bands assignable to the chemically distinct 'up' and 'down' pairs of methyl groups of the dmpe ligand. However, the ^{13}C n.m.r. spectrum does not differentiate between the two pairs of carbon atoms of the same groups. Compound (2) is soluble in non-polar hydrocarbons and its solutions are rapidly decomposed upon exposure to air.

In a similar manner, treatment of (1) in tetrahydrofuran in the presence of 1 atm propene with sodium amalgam gave red crystals of the η^2-propene derivative [Mo(η-C$_6$H$_6$)(dmpe)(η-CH$_2$CHMe)], (3). The data in the Table are fully consistent with the formulation as an η^2-propene compound, but do not allow distinction between possible isomers which can arise according to the orientation of the η^2-propene ligand. The η^2-cyclopentene compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_5$H$_8$)], (4), was similarly prepared from the sodium amalgam reduction of (1) in the presence of cyclopentene, as yellow needles which contained a small quantity of (3). It was not found possible to separate (4) from (3) and the characterisation of (4) depends

largely on detailed n.m.r. studies. The ^{1}H n.m.r. spectrum of compound (4) was obtained by subtraction of the spectrum of (3) from that of the mixture of (3) and (4). The bands assignable to the C$_6$H$_6$ and dmpe hydrogens are readily identified (Table). The assignment of bands arising from the η^2-cyclopentene ligand was assisted by double-resonance experiments. For example, broad-band decoupling greatly simplified the band centred at τ 7.79 so that it was assignable to olefinic hydrogens. Double resonance showed the connectivity between protons giving rise to the bands at τ 7.22, 7.79, 7.90, and *ca.* 8.35, some of the associated coupling constants (Hz) being J(H$_a$–H$_b$) 3.5, J(H$_b$–H$_c$) and J(H$_b$–H$_c$) 8 and 12 or 12 and 8, and J(H$_b$–H$_c$) and J(H$_b$–H$_c$) 8 and 1 or 1 and 8. The origin of (3) is not known; presumably the propene is derived from the η-allyl ligand.

Treatment of compound (2) in diethyl ether at −40 °C with tetrafluoroboric acid in diethyl ether gave immediate precipitation of a yellow-green solid. This was dissolved in an acetone–water mixture and addition of ammonium hexafluorophosphate precipitated the ethylene hydrido-compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)H]PF$_6$, (5), as a yellow powder. The ^{1}H n.m.r. spectrum of (5) at room temperature is very complex and shows no high-field resonance assignable to Mo–H. However, the ^{1}H n.m.r. spectrum at −50 °C at 300 MHz showed a number of resolved bands including a doublet of doublets at τ 16.82 assignable to a hydride coupled to two inequivalent ^{31}P nuclei. The spectrum at −90 °C and 400 MHz was essentially identical to that at −50 °C. The low-temperature spectra showed the presence of four sharp doublets assignable to four inequivalent PMe groups. In the region τ 7—9, in which the PMe resonances occurred there were also a series of weak, very complex bands which can be assigned to the four inequivalent hydrogens of the PCH$_2$CH$_2$P group together with the four inequivalent hydrogens arising from the ethylene moiety. Double-resonance experiments showed no evidence for coupling between the high-field band and hydrogens in the region τ 7—9. The i.r. spectrum of compound (5) shows a weak band at 1 800 cm^{-1} which may be tentatively assigned to an Mo–H stretch. We conclude that on balance the data are most consistent with the formulation of (5) at low temperatures as an ethylene hydride derivative with the *trans* structure shown in Scheme 1. The variable-temperature ^{1}H n.m.r. spectra show that compound (5) is fluxional and that the hydride is equilibrating with the hydrogens of the η-C$_2$H$_4$ group, presumably *via* an intermediate ethyl derivative, as is found, for example, in the compounds [Co(CH$_2$CH$_2$–H)(η-C$_2$H$_4$)-(η-C$_5$Me$_5$)]BF$_4$[4] and [Rh(η-C$_5$H$_5$)(η-C$_2$H$_4$)H]$^+$.[5] It must be

Table. Analytical and spectroscopic data

Compound	Colour	Analyses (%)[a] C	Analyses (%)[a] H	^{1}H, ^{13}C, and ^{31}P n.m.r.[b]
(2)	Red	46.0 (47.0)	7.3[c] (7.4)	6.07 [t, 6 H, J(P–H) 2.7, η-C_6H_6], 8.39 [t, 4 H, J(P–H) 5.4, C_2H_4], 9.03 [t, 12 H, J(P–H) 6.3, 2 PMe_2], 8.70—9.20 (c, 4 H, 2 PCH_2)[d] ^{13}C N.m.r.: 73.47 (s, η-C_6H_6), 29.72 [t, J(C–P) 83.7, CH_2=CH_2], 18.93 [t, J(C–P) 36.45, 2 CH_2P], 12.98 [t, J(P–C) 41.4, 4 Me][e]
(3)	Red	48.5 (49.2)	7.2[f] (7.6)	6.10 [t, 6 H, J(P–H) 2.5, η-C_6H_6], 7.83 (c, 1 H, CH), 8.09 (d, 3 H, CH_3 of propene), 8.43—9.00 (c, 6 H, CH_2 of propene and PCH_2CH_2P), 8.89 [d, 3 H, J(P–H) 6.4, PMe], 9.04 [d, 3 H, J(P–H) 6.2, PMe], 9.08 [d, 3 H, J(P–H) 5.9, PMe], 9.14 [d, 3 H, J(P–H) 6.2, PMe][e] ^{31}P N.m.r.: 2.0 (d), −1.8 (d)[e]
(4)[g]				6.17 [t, 6 H, J(P–H) 26, η-C_6H_6], 7.22 (ddt, 2 H[h]), 7.79 (c, 2 H, CH=CH[i]), 7.90 [ddd, 2 H, J(H–H) 1, 8, 12, 2 CH[j]], ca. 8.35 (c, ca. 2 H[k]), 8.25—8.80 (c, ca. 4 H, PCH_2CH_2P), 9.01 [d, 6 H, J(P–H) 6.6, 2 PMe], 9.05 [d, 6 H, J(P–H) 6.0, 2 PMe][e,l] ^{31}P N.m.r.:[e] −0.61
(5)	Yellow	33.9 (33.7)	5.8 (5.4)	15 °C (300 MHz): 4.63 [t, 6 H, J(P–H) 1.5, η-C_6H_6], 8.38 [d, 6 H, J(P–H) 8.5, 2 PMe], 8.60 (br, 6 H, 2 PMe).[m] At − 50 °C: 4.61 (br s, 6 H, η-C_6H_6), 8.25 [d, 3 H, J(P–H) 9.5, PMe], 8.27 [d, 3 H, J(P–H) 8.9, PMe], 8.53 [dd, 3 H, J(P–H) 8.4, PMe], 8.87 [d, 3 H, J(P–H) 9.0, PMe], 7.5—8.8 (br, 2 PCH_2 and η-C_2H_4), 16.82 [dd, 1 H, J(P_{trans}–H) 53.0, J(P_{cis}–H) 13.2, Mo–H][n] ^{13}C N.m.r. at −60 °C: 93.0 (s, C_6H_6), 39.7 (br, H_2C=), 29.1, 28.5 (d, PCH_2CH_2), 22.0, 21.0, 16.4, 7.2 (d, 4 PMe). At 30 °C: 92.5 (s, C_6H_6), 33.5 (s, C_2H_4), 18.8 (dmpe)[n]
(6)	Red	35.7 (35.5)	7.3 (6.3)	4.66 (c, 2 H, 2 m-H of Ph), 4.84 (q, 2 H, 2 o-H of Ph), 4.96 (t, 1 H, p-H of Ph), 7.80 [dq, 2 H, J(H–H of Me) 7.2, J(H–H of Mo) 1.3,[o] CH_2 of Et], 8.18 (c, 4 H, 2 CH_2P), 8.36 (three lines with separation 4.5 Hz, 6 H, 2 PMe), 8.44 (three lines with separation 4.3 Hz, 6 H, 2 PMe), 8.46 [d, 9 H, J(P–H) 7.3, PMe_3], 8.85 [t, 3 H, J(H–H) 7.3, Me of Et], 17.40 {dt,[p] 1 H, J[H–P(PMe_3)] 54.9, J[H–P(dmpe)] 37.2, MoH}[q] ^{13}C-{^{1}H} N.m.r.:[r] 16.08 (q, {s}, Me), 22.12 (symmetrical multiplet, {t[s]}, 2 Me_eP or 2 Me_fP), 23.59 (symmetrical multiplet, {t[s]}, 2 Me_eP or 2 Me_fP], 27.30 [{d[s]}, PMe_3], 31.29 [{t[s]}, 2 PCH_2), 86.39 (d, {s}, 2 C_b), 87.48 (d, {s}, 2 C_c), 99.54 (d, {s}, C_a), 114.98 (s, {s}, C_d) ^{31}P N.m.r.: 78.54 [d, 2 P, J(P–P) 24.0, dmpe], 33.11 [t, 1 P, J(P–P) 24.0, PMe_3][n,t]
(8)	Yellow[u]			6.08 (qt, 12 H, 2 η-C_6H_6), 8.45 (c, 4 H, bridging PCH_2CH_2P), 8.65 [d, 12 H, J(P–H) 5.1, 4 PMe], 8.76 [d, 12 H, J(P–H) 6.1, 4 PMe], 8.89 [d, 12 H, J(P–H) 4, 4 PMe][d] ^{31}P N.m.r.: 9.3 (c, 2 P of bridge), 38.7 (c, 4 P of two chelate ligands)[d]
(9)	Red-pink	33.4 (33.0)	5.6 (5.7)	4.92 (br s, 12 H, 2 η-C_6H_6) 8.25 (c, 8 H, 2 PCH_2CH_2P), 8.28 (br, 4 H, PCH_2CH_2P bridging), 8.45 [c, 12 H, 4 PMe (chelate)], 8.52 [c, 12 H, 4 PMe (chelate)], 8.67 [d, 12 H, J(P–H) 6.7, 4 PMe bridging], 17.69 [dt, 2 H, J(P_{trans}–H) 51, J(P_{cis}–H) 31, 2 Mo–H][v] ^{31}P N.m.r.: 9.5 (c, 2 P bridge), 24.2 [c, 4 P (chelate)][v]
(10)	Red	44.3 (44.2)	7.4 (7.4)	5.45 [m, 6 H, (width at half-height 2.63), η-C_6H_6], 8.45 [d, 12 H, J(P–H) 7.5, 4 Me], 8.70 [d, 4 H, J(P–H) 13.5, 2 CH_2], 16.65 [t, 2 H, J(P–H) 55.5, MoH_2].[c] ^{13}C N.m.r.: 80.64 (s, η-C_6H_6), 33.28 [t, J(P–C) 77.4, 2 CH_2P], 27.40 [t, J(P–C) 48.6, 2 PMe_2][e]
(11)	Orange	55.7 (54.8)	4.5 (4.4)	2.15—2.65 (c, 20 H, 4 Ph), 4.74 [t, 6 H, J(P–H) 1.2, η-C_6H_6], 5.01—5.21 (c, 2 H, PCH_2P), 6.22 (c, 1 H, CH of C_3H_5), 7.46 [q, 2 H, J(P–H) 5.4, H_{syn}], 8.10 [d, 2 H, J(P–H) 9, H_{anti}][e]
(12)	Purple	45.2 (44.1)	6.6 (6.1)	5.92 [d, 6 H, J(P–H) 1.2, η-C_6H_6], 5.96 (c, 1 H, CH of C_3H_5), 7.16—7.36 (c, 2 H, H_{syn}), 8.41—8.90 (c, 2 H, H_{anti}), 9.07 [d, 9 H, J(P–H) 8.4, PMe_3][e]
(13)	Orange	44.9 (44.7)	8.5[w] (8.2)	6.34 [q, 6 H, J(P–H) 2.4, η-C_6H_6], 8.82 (m, 27 H, 3 PMe_3)[e]
(14)	Red	32.5 (32.9)	5.9 (6.2)	5.17 [dq, 6 H, J(P–H) 3.6, J(H–H) 2.4, η-C_6H_6], 8.42 (m, 27 H, 3 PMe_3), 13.17 [quartet of septuplets, 1 H, J(P–H) 67.5, J(H–H) 2.4. Mo–H][n]

[a] Calculated values are given in parentheses. [b] Given as chemical shift in τ (multiplicity, relative intensity, J in Hz, assignment); c = complex. For ^{1}H n.m.r. unless otherwise stated. [c] The mass spectrum showed a parent-ion peak at m/e = 354 and a fragment at m/e = 326 assignable to [Mo(η-C_6H_6)(dmpe)]$^+$. [d] In $CD_3C_6H_5$. [e] In C_6H_6. [f] Mass spectrum: m/e 368 (32), P^+; 326 (100%), [P − C_3H_6]$^+$. [g] Obtained as a mixture with compound (3). [h] H_b, see text; for labelling see Scheme 1. [i] This band was greatly simplified in the ^{31}P-decoupled spectrum: H_a and $H_{a'}$. [j] H_b, see text. [k] H_c and $H_{c'}$, see text. [l] Assignments confirmed by double-resonance experiments. [m] The spectrum had broad ill defined bands in region τ 7—9 indicative of exchange processes. [n] In $(CD_3)_2CO$. [o] The doublet coupling due to Mo–H disappears upon irradiation of the band at τ 17.40. [p] The coupling with the CH_2 of the Et is not resolved. [q] Also very weak bands at τ 4.57 and 17.46 assignable *cis* isomer, see text. [r] Spectrum in CD_3CN shows a band at τ 29.84 [t, {s}, CH_2 of Et]. For labelling see Scheme 1; { } indicates the ^{1}H-decoupled spectrum. [s] Coupling with ^{31}P nuclei. [t] Also weaker bands at τ 78.42 [d, 2 P, J(P–P) 24.0] and 32.89 [t, 1 P, J(P–P) 26.0] assignable to an isomer, see text. [u] Mass spectrum: m/e 476 (30), [P − Mo(C_6H_6)]$^+$; 396 (100); and 326 (71%), $\frac{1}{2}$ P^+. [v] In $(CD_3)_2SO$. [w] Mass spectrum shows a highest peak at m/e = 404 corresponding to the parent ion.

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the case that olefin rotation in (5) occurs more rapidly than the ethylene–hydride to ethyl exchange. The room-temperature ^{13}C n.m.r. spectrum of compound (5) shows a singlet for the two carbons of the ethylene group whereas at −60 °C there are two bands, one at 39.7 p.p.m. and the other under the acetone resonance. The intermediacy of the Mo–Et system accords with the observation of coalescence at 15 °C, of the two phosphine *exo*-methyl groups, and at the same temperature of the *endo*-methyl groups.

Treatment of the η-propene compound (3) with methyl iodide followed by extraction into water and addition of ammonium hexafluorophosphate gave the η-allyl compound (1).

Treatment of compound (5) with trimethylphosphine in acetone caused a smooth reaction with formation of a red crystalline compound. The analytical and especially ^{1}H n.m.r. data discussed below show it to be the η-ethylbenzene derivative [Mo(η-C_6H_5Et)(dmpe)(PMe_3)H]PF_6 (6). The assignments for most of the n.m.r. data are given in the Table. The doublet of
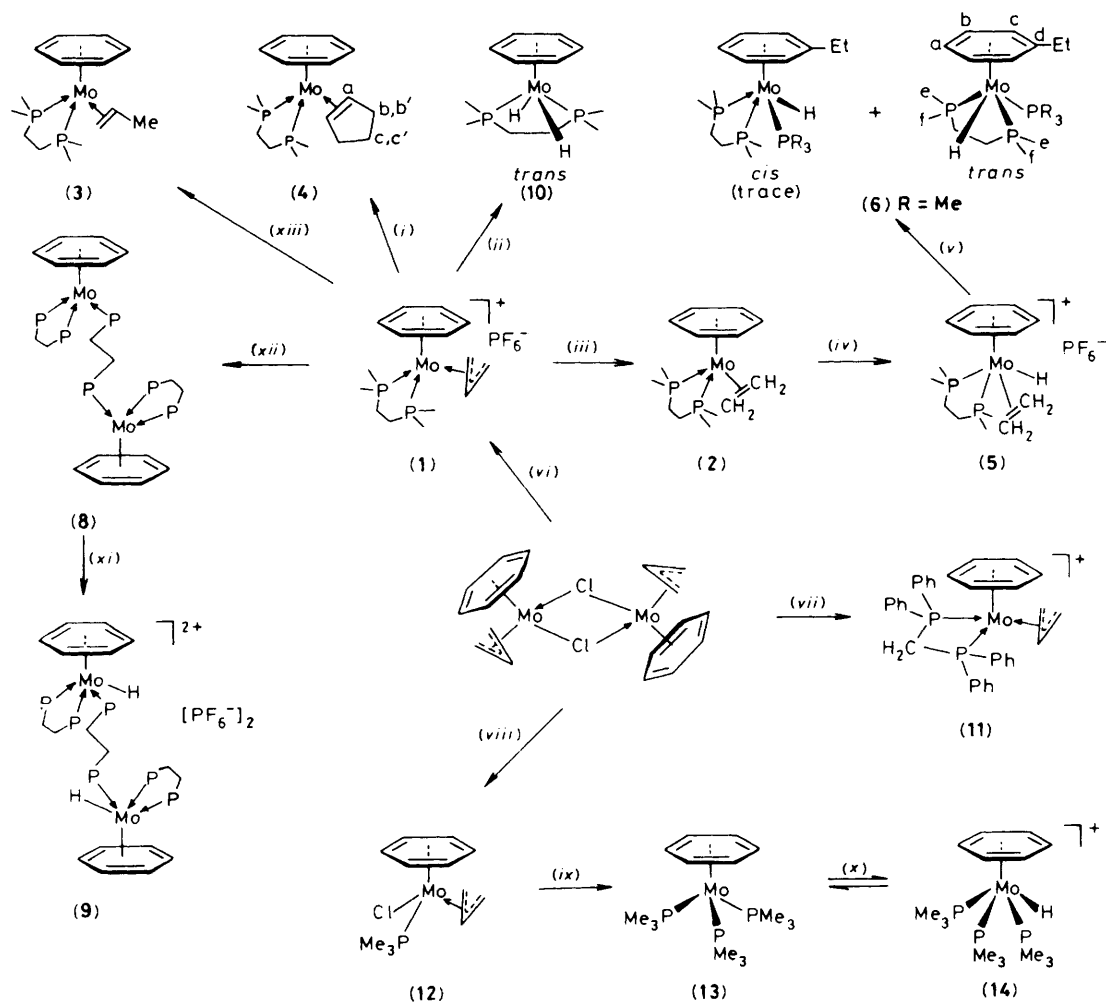
Scheme 1. (*i*) Na–Hg in tetrahydrofuran (thf), cyclopentene at r.t., yield 20%; (*ii*) Na–Hg in thf, H$_2$ at 1 atm, 80%; (*iii*) Na–Hg in thf, ethylene at 1 atm, 80%; (*iv*) HBF$_4$ in Et$_2$O at −40 °C, NH$_4$PF$_6$ (aq), 74%; (*v*) PR$_3$, R$_3$ = Me$_3$ or Me$_2$Ph, in acetone at r.t., >90%; (*vi*) dmpe in ethanol, reflux 4 h, 90%; (*vii*) Ph$_2$PCH$_2$PPh$_2$ in ethanol, reflux 4 h, 90%; (*viii*) PMe$_3$ in ethanol, reflux 2 h, 80%; (*ix*) NaBH$_4$ and PMe$_3$ in ethanol, r.t. for 60 h, 45%; (*x*) HCl (aq), then NH$_4$PF$_6$ (aq), 90%; (*xi*) HCl gas, then NH$_4$PF$_6$ (aq), 73%; (*xii*) Na–Hg in thf with dmpe, >90%; and (*xiii*) Na–Hg in thf with propene at 1 atm, 50%

triplets at τ 17.40 may be assigned to a hydride coupling to two equivalent and one other ^{31}P nuclei. This band had the same appearance at 90 and 300 MHz. The ^{1}H n.m.r. spectrum of the same sample at 400 MHz showed the presence of a very weak, second band (doublet of triplets) assignable to a hydride. The relative intensity of the two Mo–H bands was *ca.* 1:10. Apart from a very low-intensity triplet, and some weak bands in the region τ 4.6—4.5, no other bands assignable to the minor hydride species could be detected. It seems probable that the compound (6) is formed as a mixture of *cis* and *trans* isomers: the former is shown in Scheme 1. The spectrum of (6) shows the presence of two pairs of equivalent PMe groups assignable to the dmpe ligand. This observation is only consistent with the *trans* structure since the *cis* isomer should show four inequivalent methyl groups for the dmpe ligand.

The evidence for the presence of an ethyl group in compound (6) arises from the triplet at τ 8.85 and a doublet of quartets at τ 7.80 which were shown to be coupled by double-resonance experiments. The shift at τ 7.80 is inconsistent with the ethyl group being attached to an electropositive molybdenum centre. Further, there is no evidence for coupling of the CH$_2$ group with any ^{31}P nuclei as would have been expected if the ethyl group was bonded to the molybdenum. The ^{13}C spectrum of

compound (6) strongly supports the structure proposed. Also, the i.r. spectrum shows a medium-intensity band at 1 830 cm^{-1} assignable to a molybdenum–hydrogen stretching frequency.

The reaction between compound (5) and PMe$_2$Ph in (CD$_3$)$_2$CO was monitored by n.m.r. spectroscopy. After 4 h at room temperature the original spectrum had disappeared and the new bands corresponded to the compound [Mo(η-C$_6$H$_5$Et)(dmpe)(PMe$_2$Ph)H]PF$_6$, (7). The ^{1}H n.m.r. data corresponded closely in all important respects to those of compound (6): for (7) at room temperature (r.t.), τ 2.23—2.83 (c, 5 H, PhP), 4.56 (c, 2 H, 2 *m*-H of η-Ph), 4.82 (t, 1 H, *p*-H of η-Ph), 4.92 (d, 2 H, 2 *o*-H of η-Ph), 8.07 (q, 2 H, CH$_2$ of Et), 8.22 (d, 6 H, PMe$_2$), *ca.* 8.20—8.40 (c br, 2 PCH$_2$), 8.40 (t, 6 H, 2 PMe), 8.53 (t, 6 H, 2 PMe), 8.99 (t, 3 H, Me of Et), and 16.77 (dt, 1 H, MoH). The ^{1}H n.m.r. spectrum of (6) in acetone with an excess of PMe$_2$Ph at 80 °C for 20 h showed that no reaction had occurred.

In a preliminary report, incorrect structures were proposed for compounds (5) and (6).* This was due to the complexity of the ^{1}H n.m.r. spectra of (5) at intermediate temperatures and the absence of any resonance assignable to a hydride at room

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* Structures (1) and (2) in Figure 3, p. 131, of ref. 3.

temperature. The subsequent availability of n.m.r. data at 300 and 400 MHz allows the new interpretation given above.

Reduction of compound (1) by sodium amalgam in the presence of excess of dmpe gave, as the major product, yellow crystals of the compound (8) together with a small quantity of the η-propene compound (3). Despite repeated recrystallisations the carbon and hydrogen analyses were always a few % higher than the expected values. However, treatment of (8) with hydrogen chloride followed by the addition of aqueous ammonium hexafluorophosphate gave red-pink needles of the dihydrido-cation [{Mo(η-C_6H_6)(dmpe)H}$_2$(μ-dmpe)][PF_6]$_2$, (9), for which satisfactory analyses and fully diagnostic n.m.r. data were obtained. During the course of the work it was found that when compound (1) in tetrahydrofuran was reduced by sodium amalgam in the absence of further added substrate then the compounds (8) (10%) and (3) (33%) were formed.

It was decided to attempt the synthesis of the compound [Mo(η-C_6H_6)(dmpe)H$_2$], (10), which is a d^2 analogue of [W(η-C_5H_5)$_2$H$_2$] and then to explore its photochemical reactions to discover whether dihydrogen evolution would occur and, if so, whether the resulting 16-electron intermediate would add to carbon–hydrogen bonds in an analogous manner to tungstenocene.[6] Reduction of the compound [Mo(η-C_6H_6)(dmpe)(η-C_3H_5)]PF_6, (1), in tetrahydrofuran with sodium amalgam under an atmosphere of dihydrogen gave red air-sensitive crystals of the dihydride (10). This compound was indefinitely stable in deuteriobenzene solution at 65 °C. Its n.m.r. spectra show that the four methyl groups are equivalent as are the two hydrides. Therefore, either the molecule has a *cis* structure and is fluxional or it has a *trans* structure. It is difficult to envisage any simple manner in which a fluxional process could make the methyl groups equivalent. Also, the crystal structure of the related compound *trans*-[Mo(η-C_6H_6)(PMe$_3$)$_2$Me$_2$] shows a *trans* orientation of the two methyl groups.[7] On this basis we propose that the compound (10) has the *trans* structure shown in Scheme 1. Its photoelectron spectrum, which will be discussed in detail elsewhere,[8] has a lowest ionisation band at 5.84 eV and thus the compound may be classed as a high-energy (electron-rich) molecule. A solution of (10) in C_6D_6 was photolysed for 12 h and the reaction was monitored by ^{1}H n.m.r. spectroscopy. Significant decomposition occurred and there was no evidence for hydrogen–deuterium exchange.

Treatment of compound (10) with dilute aqueous hydrochloric acid caused it to dissolve giving a yellow solution from which a yellow hexafluorophosphate salt could be obtained. Attempts to obtain the ^{1}H n.m.r. spectrum of the compound in (CD$_3$)$_2$SO, (CD$_3$)$_2$CO, or CD$_3$CN were unsuccessful since the initially yellow solutions turned red within a few minutes and the spectra of these solutions gave only broad bands. When the freshly prepared yellow solution of (10) in hydrochloric acid was immediately treated with aqueous sodium hydroxide then compound (10) could be recovered from the aqueous layer. Therefore it seems probable that, initially, (10) is protonated to the trihydride cation [Mo(η-C_6H_6)(dmpe)H$_3$]$^+$. Compound (10), unlike the analogue [Mo(η-C_6H_6)(PMe$_3$)$_2$H$_2$],[9] showed no reaction with dinitrogen at atmospheric pressure. Also, it did not react with 1 atm ethylene.

In the course of this work the compound [Mo(η-C_6H_6)(dppm)(η-C_3H_5)]PF_6, (11), was prepared by treatment of [{Mo(η-C_6H_6)(η-C_3H_5)Cl}$_2$] with Ph$_2$PCH$_2$PPh$_2$ (dppm). It is soluble in dichloromethane, acetone, and dimethyl sulphoxide. Also, treatment of [{Mo(η-C_6H_6)(η-C_3H_5)Cl}$_2$] with trimethylphosphine gives good yields of purple, crystalline [Mo(η-C_6H_6)(η-C_3H_5)(PMe$_3$)Cl], (12). Reduction of (12) with sodium tetrahydroborate in the presence of an excess of trimethylphosphine gave red crystals of the highly air-sensitive but thermally stable [Mo(η-C_6H_6)(PMe$_3$)$_3$], (13). As expected,

this was readily protonated by aqueous hydrochloric acid and addition of ammonium hexafluorophosphate gave the orange, air-stable compound [Mo(η-C_6H_6)(PMe$_3$)$_3$H]PF_6, (14).

Discussion

The new compounds (2)—(14) are characterised by the data in the Table and, apart from the comments above, they require no further discussion. The proposed structures are shown in Scheme 1.

The failure of compound (10) to react with dinitrogen to give [Mo(η-C_6H_6)(dmpe)(N$_2$)] contrasts with the reaction of [Mo(η-C_6H_6)(PMe$_3$)$_2$H$_2$] with dinitrogen which readily forms [Mo(η-C_6H_6)(PMe$_3$)$_2$(N$_2$)].[9] Also, the compound [{Mo(η-C_6H_6)(dmpe)}$_2$(μ-N$_2$)] has been shown to be stable to isolation.[9] We attribute the inertness of (10) towards dinitrogen to the observed *trans* configuration. It would be necessary for this compound to isomerise to the *cis* structure before undergoing a homolytic binuclear elimination of dihydrogen. Such a rearrangement can be more easily envisaged for [Mo(η-C_6H_6)(PMe$_3$)$_2$H$_2$] where there are two unidentate tertiary phosphine ligands. The inability of compound (10) to undergo a photoinduced elimination of dihydrogen can similarly be attributed to the *trans* disposition of the dmpe ligand.

The mechanism of the formation of compound (6) from (5) is not known. There are several examples of reactions between ethylene–hydride compounds with tertiary phosphine ligands giving ethyl derivatives, e.g. M(η-C_2H_4)H + PR$_3$——→MEt-(PR$_3$), where M = [Mo(η-C_5H_5)$_2$]$^+$ and [Nb(η-C_5H_5)$_2$].[10,11]
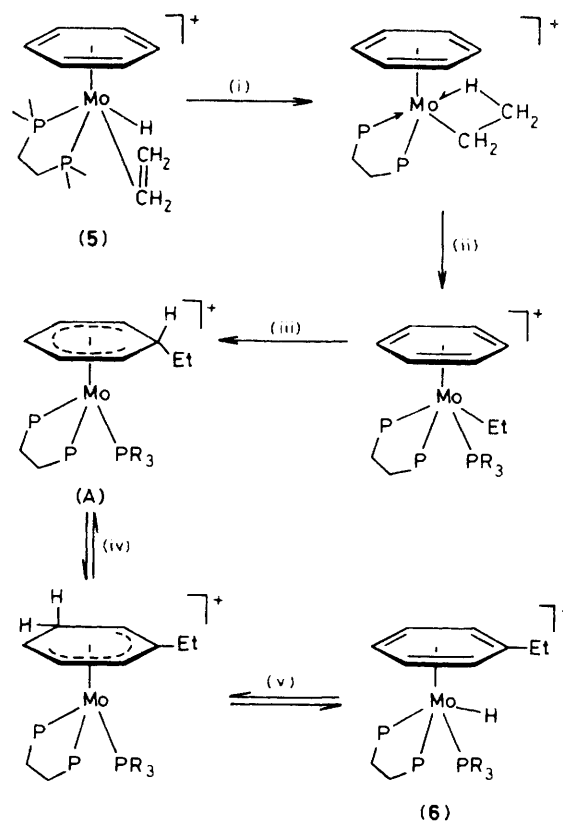
Scheme 2. Possible mechanisms for conversion of compound (5) into (6). (i) Hydrogen adds to the η-ethylene giving Mo–Et, possibly with an agostic hydrogen; (ii) addition of PMe$_3$; (iii) migration step of ethyl; (iv) suprafacial shift of *exo*-hydrogen; and (v) migration to ring of *endo*-hydrogen

(ref. 10)

(ref. 12)

(ref. 13)
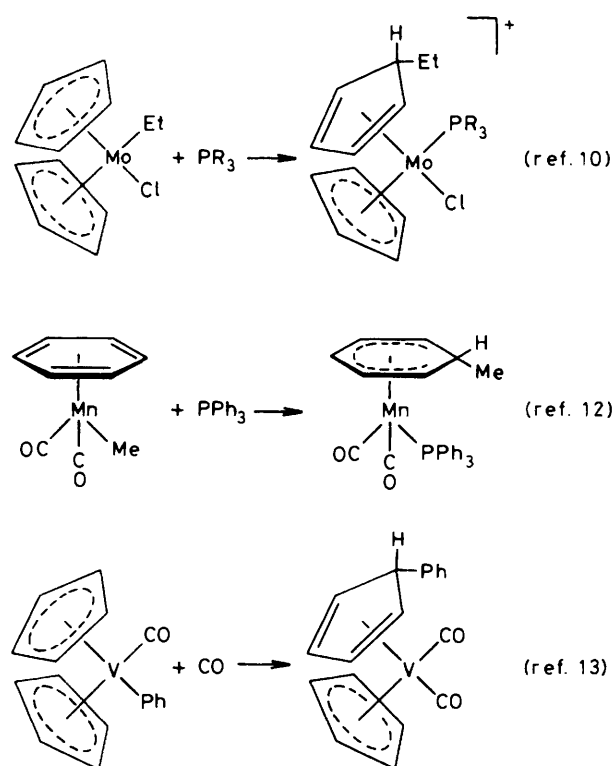
Scheme 3.

By analogy, it seems reasonable to propose that there is an initial reaction between compound (5) and PMe$_3$ giving the ethyl cation [Mo(η-C$_6$H$_6$)(dmpe)Et(PMe$_3$)]$^+$. In order to obtain the product (6) it is then necessary to interchange a hydrogen of the η-C$_6$H$_6$ ring with the ethyl group. A possible mechanism for this reaction would be migration of the ethyl

group to the *endo* side of the benzene ring giving the *endo*-ethylcyclohexadienyl intermediate [Mo(η-C$_6$H$_6$-Et-*endo*)-(dmpe)(PMe$_3$)]$^+$, A (see Scheme 2). This could be followed by migration of the *exo*-hydrogen from the C–Et carbon to adjacent carbons which would create methylene groups with *endo*-hydrogens. Finally, oxidative addition of an *endo*-C–H group to the metal centre would form the η-ethylbenzene and M–H groups. In support of this proposed mechanism there are previous observations of metal-to-ring migrations of methyl, ethyl, and phenyl groups (Scheme 3). The reverse of this reaction, namely the oxidative addition of the C–C bond of *endo*-alkyls to metal centres, has been demonstrated in several instances.[14] Further, there have been a number of previous postulates of the ring-migration reactions of *exo*-hydrogens of methylene groups in open η-polyene–metal compounds.[5] Finally, the oxidative addition of *endo*-C–H groups to metal centres is well established.

If it is assumed that all the steps in the conversion of compound (5) into (6) are reversible then the principal driving force for the isolation of (6) could be considered to arise from bond-strength differences: the M–H bond is 30—40 kcal mol^{-1} stronger than the M–C bond, whilst for the C–H and C–C bonds the difference is only 15—20 kcal mol^{-1}.[15]

Presently, there are no data available to distinguish between intermediates which may be involved in the actual migration step in Scheme 2. We envisage several possibilities; these are shown in Scheme 4.

Experimental

All reactions and manipulations were carried out under argon or *in vacuo*. All hydrocarbon solvents were dried by refluxing them over sodium–potassium alloy or sodium metal under dinitrogen, and were distilled immediately before use. Microanalyses were carried out by the microanalytical laboratory of this department. Infrared spectra were determined using mulls on a Perkin-Elmer 457 instrument and were calibrated using polystyrene film. Mass spectra were determined
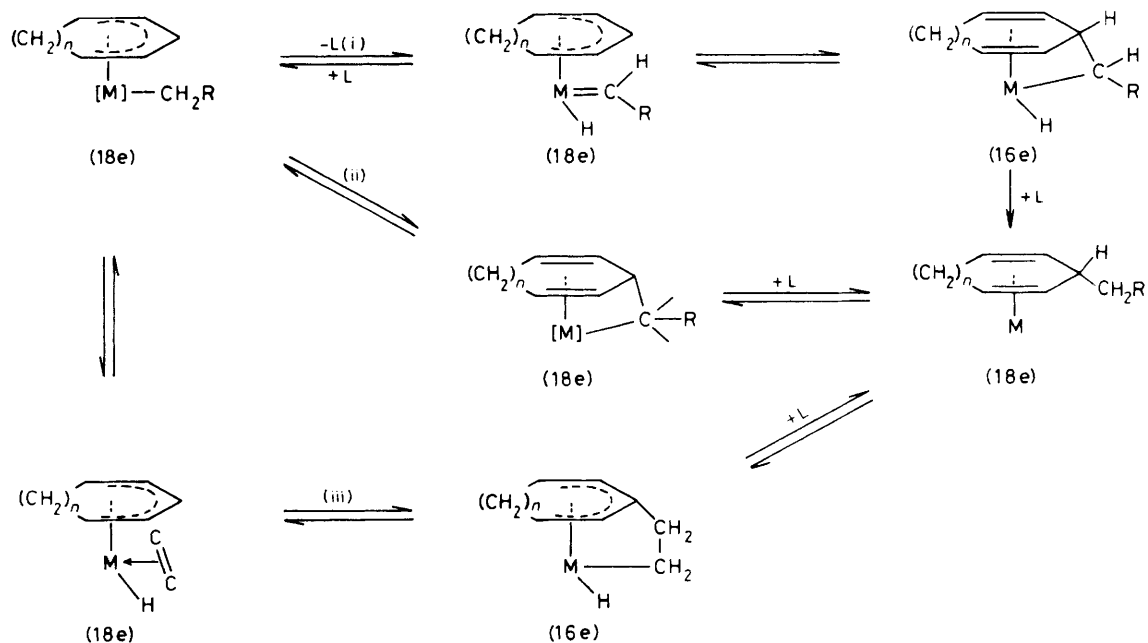
Scheme 4. Possible pathways for metal-to-ring migration reactions. (i) *via* a 1,2-hydrogen-shift process; (ii) involving a bridging three-centre two-electron bond; (iii) involving a bridging (CH$_2$)$_2$ system analogous to those found in [W(η-C$_5$Me$_4$CH$_2$)(η-C$_5$Me$_5$)] and [Mo(η-C$_5$H$_4$CH$_2$CH$_2$)$_2$].[14] Intermediates involving M–H–C bonds[12] may be inserted into each pathway[16]

using an M.S.902 instrument upgraded with a console supplied by Mass Spectroscopy Services Ltd. Chromatography was carried out using alumina (100—200 mesh) supplied by East Anglia Chemicals and was deactivated by the addition of 6% by weight of water before use. Columns were made up in light petroleum (b.p. 40—60 °C). Proton n.m.r. spectra were recorded on a JEOL C60HL or a Bruker WH-300 spectrometer, ^{13}C and ^{31}P n.m.r. spectra using a Bruker WH90 spectrometer. The compounds [{Mo(η-C$_6$H$_6$)(η-C$_3$H$_5$)Cl}$_2$] and [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_3$H$_5$)]PF$_6$ were prepared as described.[17]

(η-Benzene)[1,2-bis(dimethylphosphino)ethane](η-ethylene)-molybdenum, (2).—A suspension of the compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_3$H$_5$)]PF$_6$ (0.66 g, 1.29 mmol) in tetrahydrofuran (80 cm^3) was treated with sodium amalgam (15 g of 1%Na in Hg, 6.52 mmol) under an atmosphere of ethylene for 18 h. The resulting red solution was filtered and the solvent then removed from the filtrate under reduced pressure. The crude product was dried for 2 h at 50 °C under vacuum and then extracted with light petroleum (b.p. 40—60 °C) giving a red solution which was filtered and concentrated. The concentrate was cooled to −20 °C for 2 d giving red crystals. These were separated, washed with light petroleum (b.p. 30—40 °C), and dried in vacuo, yield 0.36 g (80%).

(η-Benzene)[1,2-bis(dimethylphosphino)ethane](η-propene)-molybdenum, (3).—A suspension of compound (1) (0.75 g, 1.5 mmol) in tetrahydrofuran (100 cm^3) was treated with sodium amalgam (8 g). The mixture was cooled to −50 °C and treated with propene for 3 min. The reaction mixture was allowed to warm to r.t. and stirred for 2 d. The resulting red solution was filtered and the solvent was removed from the filtrate under reduced pressure. The red solid residue was extracted with light petroleum (b.p. 40—60 °C) (3 × 60 cm^3) and the extract was filtered, concentrated, and cooled to −20 °C. Red cryst. separated which were collected, washed with cold light petroleum (b.p. 40—60 °C), and dried in vacuo, yield 0.28 g (51%).

(η-Benzene)[1,2-bis(dimethylphosphino)ethane](η-cyclo-pentene)molybdenum, (4).—A suspension of [Mo(η-C$_6$H$_6$)-(dmpe)(η-C$_3$H$_5$)]PF$_6$ (1.6 g, 3.1 mmol) in tetrahydrofuran was treated with cyclopentene (2.8 g, 41 mmol) and sodium amalgam (60 g, 1%). The mixture was stirred for 1 d at r.t. The suspension dissolved giving a red solution. The mixture was filtered through Celite and the solvent removed from the filtrate under reduced pressure. The residue was extracted with light petroleum (b.p. 40—60 °C) until pale extracts were obtained. An orange solid remained undissolved and was recrystallised from toluene–light petroleum (b.p. 100—120 °C) as yellow needles. The ^{1}H n.m.r. data showed this product to be compound (8), ca. 15%.

The red light petroleum extract was concentrated and cooled giving red crystals of [Mo(η-C$_6$H$_6$)(dmpe)(η^2-C$_5$H$_8$)] and [Mo(η-C$_6$H$_6$)(dmpe)(η^2-C$_3$H$_6$)]. Attemps failed to separate the mixture by recrystallisation, sublimation, and chromatography. The spectroscopic data were obtained from the mixture of the two complexes, see the text. The combined yield was 0.36 g, ca. 30%. The ratio of (4) to (3) was 5:1.

(η-Benzene)[1,2-bis(dimethylphosphino)ethane](η-ethylene)-hydridomolybdenum Hexafluorophosphate, (5).—Method (a). The compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)] (0.80 g, 2.3 mmol) in diethyl ether (80 cm^3) was cooled to −40 °C and treated in a dropwise manner with tetrafluoroboric acid in diethyl ether (2 cm^3 of a solution of 1 cm^3 of 40% aqueous tetrafluoroboric acid in 25 cm^3 of Et$_2$O). The resulting pale yellow-green precipitate was separated, washed with light

petroleum (40—60 °C), and then extracted with acetone (200 cm^3). The extract was concentrated giving a yellow solid. This was extracted into acetone–water (1:1, 200 cm^3) and aqueous ammonium hexafluorophosphate was added. Concentration of the resulting solution under reduced pressure gave a yellow powder which was washed twice with water and dried in vacuo, yield 0.85 g (74%).

Method (b). The compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)] (0.35 g, 0.99 mmol) in light petroleum (b.p. 40—60 °C, 100 cm^3) was treated with excess of methyl iodide (1 g, 7.0 mmol). The reaction mixture was stirred at r.t. for 2 d. A pale yellow precipitate was slowly formed. The resulting suspension was filtered and the solid residue washed twice with light petroleum (b.p. 40—60 °C). This was extracted with acetone–water (1:1) and then treated with NH$_4$PF$_6$. Removal of the acetone under reduced pressure gradually precipitated a yellow solid. This was recrystallised from acetone–water, yield 0.32 g (64%).

[1,2-Bis(dimethylphosphino)ethane](η-ethylbenzene)hydrido-(trimethylphosphine)molybdenum Hexafluorophosphate, (6).—The compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)H]PF$_6$ (0.25 g) in acetone (20 cm^3) was treated with an excess of trimethylphosphine (2 cm^3) at r.t. for 2 d. The solvent was removed from the resulting red solution under reduced pressure and the red residue was washed with light petroleum (b.p. 40—60 °C) (3 × 15 cm^3). The residue was then extracted with acetone and crystallised from acetone–water giving red crystals, yield 0.27 g (90%). When the same reaction was carried out using PMe$_2$Ph instead of PMe$_3$ then an essentially identical reaction occurred giving the compound [Mo(η-C$_6$H$_6$)(dmpe)-(PMe$_2$Ph)H]PF$_6$.

μ-[1,2-Bis(dimethylphosphino)ethane]-bis{(η-benzene)[1,2-bis(dimethylphosphino)ethane]molybdenum}, complex (8).—A suspension of [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_3$H$_5$)]PF$_6$ (0.80 g, 1.6 mmol) in tetrahydrofuran (120 cm^3) and Me$_2$PCH$_2$CH$_2$PMe$_2$ (0.10 g, 0.67 mmol) were treated with sodium amalgam (25 g, 1%). After stirring for 2 h at r.t. the solution became red and after a further 24 h a yellow crystalline solid was observed. More tetrahydrofuran was added to dissolve the yellow product. The reaction mixture was then filtered through Celite. Removal of the solvent under reduced pressure precipitated yellow needles. The suspension was cooled to −20 °C for 12 h. The mother-liquor (A) was decanted and the residual yellow solid was washed with cold light petroleum (b.p. 40—60 °C). The yield based on Me$_2$PCH$_2$CH$_2$PMe$_2$ was 0.50 g (94%). Solvent was removed from the mother-liquor (A). The solid residue was extracted with light petroleum (b.p. 40—60 °C) giving a red solution which after concentrating and cooling gave crystals of [Mo(η-C$_6$H$_6$)(dmpe)(η^2-C$_3$H$_6$)], yield 0.04 g (7%).

μ-[1,2-Bis(dimethylphosphino)ethane]-bis{(η-benzene)[1,2-bis(dimethylphosphino)ethane]hydridomolybdenum} Bis(hexafluorophosphate), (9).—Compound (8) (0.20 g, 0.25 mmol) in toluene (150 cm^3) was treated with hydrogen chloride gas for 3 min and a solid deposited immediately. The solvent was decanted and the residue extracted with acetone–water (1:1) (40 cm^3) giving a red solution. Aqueous ammonium hexafluorophosphate was added giving a pink precipitate. Acetone was removed under reduced pressure, the water was decanted, and the residual solid washed twice with water. The solid was then redissolved in acetone–water and slow removal of the acetone under reduced pressure gave red-pink needles which were collected, washed with water, and dried in vacuo, yield 0.20 g (73%).

(η-Benzene)[1,2-bis(dimethylphosphino)ethane]dihydrido-molybdenum, (10).—A suspension of [Mo(η-C$_6$H$_6$)(dmpe)(η-

C_3H_5)]PF_6 (0.87 g, 1.71 mmol) in tetrahydrofuran (80 cm^3) was treated with sodium amalgam (15 g of 1% amalgam, 6.52 mmol) and the mixture was rapidly stirred under 1 atm of dihydrogen for 17 h. The resulting red solution was filtered and the solvent was removed from the filtrate under reduced pressure. The residue was extracted with light petroleum (b.p. 40—60 °C) and the red extract was filtered and concentrated until it appeared to be saturated. After cooling to −78 °C for 7 h red crystals separated. These were collected, washed with light petroleum (b.p. 30—40 °C), and dried in vacuo, yield 0.45 g (80%). The mass spectrum showed a parent-ion peak at $m/e = 328$ and peaks at 326 and 248 corresponding to the ions [Mo(η-C_6H_6)(dmpe)]$^+$ and [Mo(dmpe)]$^+$.

(η-Allyl)(η-benzene)[1,2-bis(diphenylphosphino)methane]-molybdenum Hexafluorophosphate, (11).—A suspension of [{Mo(η-C_6H_6)(η-C_3H_5)Cl}$_2$] (1.0 g, 2 mmol) in ethanol (95%, 75 cm^3) was treated with $Ph_2PCH_2PPh_2$ (1.7 g, 4.43 mmol) and the mixture was heated under reflux for 4 h. The solvent was removed under reduced pressure and the red residue washed with light petroleum (b.p. 40—60 °C). The residue was extracted with ethanol (95%, 100 cm^3) and the extract was filtered. Aqueous ammonium hexafluorophosphate was added to the filtrate giving an orange precipitate. This was collected, washed with water (2 × 10 cm^3), and crystallised from acetone–ethanol, yield 2.68 g (90%).

(η-Allyl)(η-benzene)chloro(trimethylphosphine)molybdenum, (12).—The dimer [{Mo(η-C_6H_6)(η-C_3H_5)Cl}$_2$] (2.0 g, 3.99 mmol) in ethanol (100 cm^3) was treated with trimethylphosphine (1.5 g, 19.74 mmol) and the mixture was refluxed for 2 h giving a purple solution. This was concentrated under reduced pressure and cooled to −20 °C giving purple crystals which were washed with light petroleum (b.p. 40—60 °C) and dried in vacuo, yield 2.08 g (80%).

(η-Benzene)tris(trimethylphosphine)molybdenum, (13).—The compound [Mo(η-C_6H_6)(η-C_3H_5)(PMe$_3$)Cl] (0.5 g, 1.53 mmol) was added to trimethylphosphine (1.0 g, 13.16 mmol) in ethanol (95%, 75 cm^3) and then NaBH$_4$ (2.0 g, 52.63 mmol) was added. The mixture was stirred at r.t. for 60 h giving an orange solution. The solution was filtered and concentrated under reduced pressure forming orange crystals which were separated, washed with water, and recrystallised from light petroleum (b.p. 40—60 °C), yield 0.28 g (45%).

(η-Benzene)hydridotris(trimethylphosphine)molybdenum Hexafluorophosphate, (14).—The compound [Mo(η-C_6H_6)(PMe$_3$)$_3$] (0.2 g, 0.8 mmol) in light petroleum (b.p. 30—40 °C, 50 cm^3) was treated with aqueous ammonium hexafluorophosphate containing a drop of dilute hydrochloric acid. A yellow-cream precipitate separated which was collected, washed with water, and recrystallised from acetone–water giving red crystals, 0.24 g (90%).

Reduction of [Mo(η-C_6H_6)(dmpe)(η-C_3H_5)]PF_6 with Sodium Amalgam.—A suspension of [Mo(η-C_6H_6)(dmpe)(η-C_3H_5)]PF_6 (1.3 g, 25 mmol) in tetrahydrofuran (200 cm^3) was treated with sodium amalgam (80 g, 1%) and stirred at r.t. for 2 d giving a red suspension. The reaction mixture was filtered through Celite and the solvent removed under reduced pressure. The residue was extracted with light petroleum (b.p. 40—60 °C, 50 cm^3) giving a red solution (A) and leaving an orange solid.

The latter was recrystallised from toluene to give a yellow solid which was identified as [{Mo(η-C_6H_6)(dmpe)}$_2$(μ-dmpe)] by comparison of the ^{1}H n.m.r. spectrum with that of an authentic sample, yield 0.10 g (10%). The red light petroleum extract (A) was concentrated and cooled to −20 °C giving a red precipitate, identified as [Mo(η-C_6H_6)(dmpe)(η^2-C_3H_6)] by comparison of the ^{1}H n.m.r. spectrum with that of an authentic sample, yield 0.30 g (33%).

Reaction of [Mo(η-C_6H_6)(dmpe)(η^2-C_3H_6)] with Methyl Iodide.—Compound (3) (0.58 g, 1.6 mmol) in light petroleum (b.p. 40—60 °C) was treated with excess of methyl iodide (1.0 g, 7.0 mmol). After several minutes a solid precipitated. After 2 h the suspension had become green and after another hour it was red again. The mixture was filtered and the residue was extracted with acetone–water (1:1). The extract was treated with aqueous NH$_4$PF$_6$. Removal of the acetone under reduced pressure gradually precipitated an orange solid. This was recrystallised from acetone–water. Comparison of the ^{1}H n.m.r. and i.r. spectra with those of [Mo(η-C_6H_6)(dmpe)(η-C_3H_5)]PF_6 showed them to be identical. Yield 0.20 g (25%).

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