Mechanism of the Reaction of [Mo(η-C$_6$H$_6$)(Me$_2$PCH$_2$CH$_2$PMe$_2$)(η-C$_2$H$_4$)H]$^+$ with PMe$_3$ giving [Mo(η-C$_6$H$_5$Et)(dmpe)(PMe$_3$)H]$^+$: Metal-to-Ring Migration of an Ethyl Group*

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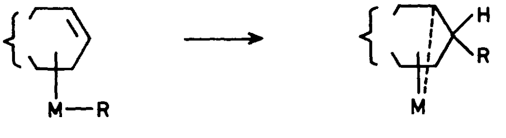
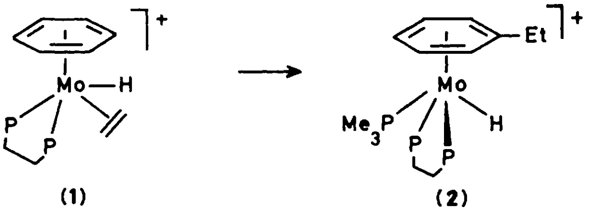
The *cis*-ethylenehydride compounds [Mo(η-C$_6$H$_6$)(L$_2$)(η-C$_2$H$_4$)H]PF$_6$ [L$_2$ = Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe) or *o*-C$_6$H$_4$(EMe$_2$)$_2$ (E = P, pdmp, or As, pdma)] react with trimethylphosphine to give the η-ethylbenzene compounds [Mo(η-C$_6$H$_5$Et)(L$_2$)(PMe$_3$)H]PF$_6$. Detailed studies of the mechanism of this reaction show that there is an initial reaction, at low temperatures, giving isomeric mixtures of thermally unstable η-cyclohexadienyl derivatives [Mo(η-C$_6$H$_7$)(dmpe)(PMe$_3$)(η-C$_2$H$_4$)]$^+$. The combined evidence from n.m.r. spectra, including kinetic studies, and from the preparation and reactions of intermediates shows that the η-ethylbenzene compound is formed by the sequence [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)H]$^+$ $\longrightarrow$ [Mo(η-C$_6$H$_6$)(dmpe)(PMe$_3$)Et]$^+$ $\longrightarrow$ [Mo(η-C$_6$H$_6$Et-*endo*)(dmpe)(PMe$_3$)(solvent)]$^+$ $\longrightarrow$ [Mo(η-C$_6$H$_5$Et)(dmpe)(PMe$_3$)] + H$^+$ $\longrightarrow$ [Mo(η-C$_6$H$_5$Et)(dmpe)(PMe$_3$)H]$^+$. The following new compounds have been prepared and characterised: [Mo(η-C$_6$H$_6$){P(OMe)$_3$}$_2$(η-C$_3$H$_5$)]PF$_6$, [Mo(η-C$_6$H$_6$)(pdmp)(η-C$_3$H$_5$)]PF$_6$, [Mo(η-C$_6$H$_6$)(pdma)(η-C$_3$H$_5$)]PF$_6$, [Mo(η-C$_6$H$_6$)(pdmp)(η-C$_2$H$_4$)], [Mo(η-C$_6$H$_6$)(pdma)(η-C$_2$H$_4$)], [Mo(η-C$_6$H$_6$)(pdmp)(η-C$_2$H$_4$)H]PF$_6$, [Mo(η-C$_6$H$_6$)(pdma)(η-C$_3$H$_5$)]PF$_6$, [Mo(η-C$_6$H$_6$)(pdmp)(η-C$_2$H$_4$)], [Mo(η-C$_6$H$_6$)(pdma)(η-C$_2$H$_4$)], [Mo(η-C$_6$H$_6$)(pdmp)(η-C$_2$H$_4$)H]PF$_6$, [Mo(η-C$_6$H$_6$)(pdma)(η-C$_2$H$_4$)H]PF$_6$, [Mo(η-C$_6$H$_5$Et)(pdmp)(PMe$_3$)H]PF$_6$, [Mo(η-C$_6$H$_5$Et)(pdma)(PMe$_3$)H]PF$_6$, [Mo(η-C$_6$H$_6$)(dmpe)(PMe$_3$)D]PF$_6$, [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)], [Mo(η-C$_6$H$_6$Et-*endo*)(dmpe)$_2$]PF$_6$, [Mo(η-C$_6$H$_6$)(dmpe){P(OMe)$_3$}H]PF$_6$, [Mo(η-C$_6$H$_6$)(dmpe)(CO)H]PF$_6$, [Mo(η-C$_6$H$_6$)(dmpe)(2,6-Me$_2$C$_6$H$_3$NC)]PF$_6$, [Mo(η-C$_6$H$_5$Me)(dmpe)(η-C$_2$H$_4$)H]PF$_6$, [Mo(C$_6$H$_4$Me-2-Et-1)(dmpe)(PMe$_3$)H]PF$_6$, [Mo(C$_6$H$_4$Me-3-Et-1)(dmpe)(PMe$_3$)H]PF$_6$, [Mo(C$_6$H$_5$Me-1-Et-6-*endo*)(dmpe)$_2$]PF$_6$, [Mo(C$_6$H$_5$Me-2-Et-6-*endo*)(dmpe)$_2$]PF$_6$, and [Mo(η-C$_6$H$_6$Et-*endo*)(pdmp)$_2$]PF$_6$.

The migration of an alkyl group attached to a metal to the carbon atom of a polyene ligand, which is η-bonded to the metal, has been observed in several reactions and has been postulated to occur in a number of others.[1–4] This migration reaction, which may be represented generally as in equation (1),[5] results in the creation of a vacant site on the metal centre.



(1)

Recently,[6] we described the reaction (2) between the *cis*-ethylenehydride compound [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_2$H$_4$)H]-



(2)

(1) **(2)**

PF$_6$ (**1**; dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) and trialkylphosphines, PR$_3$ (R$_3$ = Me$_3$ or PhMe$_2$), giving the η-ethylbenzene compounds [Mo(η-C$_6$H$_5$Et)(dmpe)(PR$_3$)H]PF$_6$ [R$_3$ = Me$_3$, (**2**), or PhMe$_2$, (**3**)]. Here we report a detailed study on the mechanism of this reaction.

Results and Discussion

Synthesis of New Compounds.—The study of the mechanism of reaction (2) necessitated the synthesis of several new compounds which will be described before the mechanistic studies. The analytical, mass, n.m.r., and i.r. spectroscopic data which characterise the new compounds are given in Table 1. These data are not discussed further except where the interpretation is not straightforward. The structures proposed for the new compounds are shown in the Schemes 1—4.

The η-toluene analogue of (**1**), namely [Mo(η-C$_6$H$_5$Me)(dmpe)(η-C$_2$H$_4$)H]PF$_6$, (**4**), was prepared in 60% yield by reduction of [Mo(η-C$_6$H$_5$Me)(dmpe)(η-C$_3$H$_5$)]PF$_6$ using sodium amalgam in the presence of ethylene, followed by the addition of aqueous NH$_4$PF$_6$.

Treatment of compound (**1**) with trimethyl phosphite, carbon monoxide, or isocyano-2,6-dimethylbenzene gives the compounds *trans*-[Mo(η-C$_6$H$_6$)(dmpe){P(OMe)$_3$}H]PF$_6$, (**5**), *trans*-[Mo(η-C$_6$H$_6$)(dmpe)(CO)H]PF$_6$, (**6**), and *trans*-[Mo(η-C$_6$H$_6$)(dmpe)(2,6-Me$_2$C$_6$H$_3$NC)H]PF$_6$, (**7**), respectively (see Scheme 2). The formation of (**5**) is discussed in more detail below.

Reduction of [Mo(η-C$_6$H$_6$)(dmpe)(η-C$_3$H$_5$)]PF$_6$ in the presence of trimethylphosphine gives the neutral, air-sensitive [Mo(η-C$_6$H$_6$)(dmpe)(PMe$_3$)], (**8**). Treatment of the latter with MeOSO$_2$CF$_3$ followed by aqueous NH$_4$PF$_6$ gives the η-toluene derivative [Mo(η-C$_6$H$_5$Me)(dmpe)(PMe$_3$)H]PF$_6$, (**9**): this reaction is discussed in more detail below.

Treatment of the dimer [{Mo(η-C$_6$H$_6$)(η-C$_3$H$_5$)(μ-Cl)}$_2$] with *o*-C$_6$H$_4$(EMe$_2$)$_2$ [E = P (pdmp) or As (pdma)] or with trimethyl phosphite, followed by addition of aqueous ammonium hexafluorophosphate, gives [Mo(η-C$_6$H$_6$)(pdmp)(η-C$_3$H$_5$)]PF$_6$, (**10**), [Mo(η-C$_6$H$_6$)(pdma)(η-C$_3$H$_5$)]PF$_6$, (**11**), and

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* *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} J, atm = 101 325 Pa.

Table 1. Analytical and spectroscopic data[a]

Compound, colour, and analysis (%)	N.m.r. data (^{1}H, ^{13}C, and ^{31}P)
(1) [Mo(η-C_6H_6)(dmpe)(η-C_2H_4)H]PF_6 Pale green C, 34.0 (33.8); H, 5.6 (5.5)	^{1}H at 25 °C: 1.43 [br s, 6 H, P(CH_3)$_2$], 1.64 [d, 6 H, *J*(P–H) 8.5, P(CH_3)$_2$], 1.96 (br m, 4 H, PCH_2CH_2P), 5.39 [t, 6 H, *J*(P–H) 1.5, C_6H_6][b] At −60 °C: −6.83 [dd, 1 H, *J*(P–H) 13.5, 53.5, Mo–H], 0.96 [d, 3 H, *J*(P–H) 9, PCH_3], 1.16 (m, 1 H, η-$CH_2{=}CH_2$), 1.47 [d, 3 H, *J*(P–H) 8.5, PCH_3], 1.72 [d, 3 H, *J*(P–H) 9, PCH_3], 1.73 [d, 3 H, *J*(P–H) 9.5, PCH_3], 1.86 (br m, 5 H, $CH_2{=}CH_2$ + PCH_2CH_2P), 2.12 (m, 1 H, $CH_2{=}CH_2$), 2.41 (q, 1 H, $CH_2{=}CH_2$), 5.39 (t, 6 H, C_6H_6)[b] At 60 MHz, r.t.: 0.20 [br s, 5 H, η-$CH_2{=}CH_2$ + Mo–H], 1.42 [vt, 6 H, *J′* 10, P(CH_3)$_2$], 1.63 [vt, 6 H, *J′* 9, P(CH_3)$_2$], 1.88 (br s, 4 H, PCH_2CH_2P), 5.35 [t, 6 H, *J*(P–H) 1.5, C_6H_6][b] Fully ^{1}H-coupled ^{13}C n.m.r. at 30 °C: 18.3 [qd, *J*(C–H) 125, *J*(P–C) 20, P(CH_3)$_2$], 32.7 [sxt, *J*(C–H) 61, η-$CH_2{=}CH_2$], 91.9 [d, *J*(C–H) 176, C_6H_6][b,c]
(2) [Mo(η-C_6H_5Et)(dmpe)(PMe_3)H]PF_6 Red C, 35.2 (35.5); H, 6.3 (6.3)	^{1}H: −7.38 [dt, 1 H, *J*(P–H) 55.0, 37.2, Mo–H], 1.15 [t, 3 H, *J*(H–H) 7.3, CH_3 of ethyl], 1.54 [d, 9 H, *J*(P–H) 8, P(CH_3)$_3$], 1.60 [vt, 6 H, *J′* 9, P(CH_3)$_2$], 1.65 [vt, 6 H, *J′* 10, P(CH_3)$_2$], 1.90 (br, m, 4 H, PCH_2CH_2P), 2.23 [q, 2 H, *J*(H–H) 7.3, CH_2 of ethyl], 5.08 (t, 1 H, *p*-H of Ph), 5.19 (d, 2 H, *o*-H of Ph), 5.36 (t, 2 H, *m*-H of Ph)[b]
(4) [Mo(η-C_6H_5Me)(dmpe)(η-C_2H_4)H]PF_6 Pale green C, 35.1 (35.2); H, 5.7 (5.7)[d]	^{1}H: 1.39 [br s, 6 H, P(CH_3)$_2$], 1.62 [br d, 6 H, P(CH_3)$_2$], 1.96 (m, 4 H, PCH_2CH_2P), 2.18 (d, 3 H, aryl CH_3), 5.12 (br s, 2 H, *o*- or *m*-H of Ph), 5.29 (tt, 1 H, *p*-H of Ph), 5.37 (br s, 2 H, *m*- or *o*-H of Ph)[b]
(5) [Mo(η-C_6H_6)(dmpe){P(OMe)$_3$}H]PF_6 Orange C, 29.9 (30.3); H, 5.2 (5.4)	^{1}H: −7.81 [dt, 1 H, *J*(P–H) 62, 35, Mo–H], 1.60 [vt, 6 H, *J′* 10, P(CH_3)$_2$], 1.63 [vt, 6 H, *J′*(P–H) 10, P(CH_3)$_2$], 1.80 (m, 4 H, PCH_2CH_2P), 3.55 [d, 9 H, *J*(P–H) 12, P(OCH_3)$_3$], 5.45 (s, 6 H, C_6H_6)[b] Off-resonance decoupled ^{13}C n.m.r.: 21.4 [qt, *J*(P–C) 13, P(CH_3)$_2$], 22.3 [qt, *J*(P–C) 16, P(CH_3)$_2$], 30.9 [tt, *J*(P–C) 22.4, PCH_2CH_2P], 51.9 [qd, *J*(P–C) 6, P(OCH_3)$_3$], 91.7 (d, C_6H_6)[b] ^{31}P-{^{1}H}: 48.92 [d, 2 P, *J*(P–P) 40, dmpe], 185.0 [t, 1 P, P(OCH_3)$_3$][b]
(6) [Mo(η-C_6H_6)(dmpe)(CO)H]PF_6[e]	^{1}H: −6.74 [t, 1 H, *J*(P–H) 38, Mo–H], 1.68 [d, 6 H, *J*(P–H) 10, P(CH_3)$_2$], 1.80 [d, 6 H, *J*(P–H) 10, P(CH_3)$_2$], 5.98 (s, 6 H, C_6H_6)[b]
(7) [Mo(η-C_6H_6)(dmpe)(2,6-$Me_2C_6H_3NC$)H]PF_6 Orange-red C, 42.0 (42.0); H, 5.7 (5.4); N, 2.5 (2.3)	^{1}H: −6.28 [t, 1 H, *J*(P–H) 37.6, Mo–H], 1.70 [vt, 6 H, *J′*(P–H) 10, P(CH_3)$_2$], 1.75 [vt, 6 H, *J′*(P–H) 9, P(CH_3)$_2$], 1.99 (m, 4 H, PCH_2CH_2P), 2.37 (s, 6 H, aryl CH_3), 5.60 (s, 6 H, C_6H_6), 7.11 (m, 3 H, aryl H)[b]
(8) [Mo(η-C_6H_6)(dmpe)(PMe_3)][f] Red-orange	^{1}H: 1.11 [d, 9 H, *J*(P–H) 6, P(CH_3)$_3$], 1.20 [d, 6 H, *J*(P–H) 7, P(CH_3)$_2$], 1.29 [d, 6 H, *J*(P–H) 7, P(CH_3)$_2$], 1.55 (m, 4 H, PCH_2CH_2P), 3.86 [q, 6 H, *J*(P–H) 2.5, C_6H_6][g]
(9) [Mo(η-C_6H_5Me)(dmpe)(PMe_3)H]PF_6	−7.38 [dt, 1 H, *J*(P–H) 55.2, 36.9, Mo–H], 1.53 [d, 9 H, *J*(P–H) 7.5, P(CH_3)$_3$], 1.58 [vt, 6 H, *J′*(P–H) 9, P(CH_3)$_2$], 1.64 [vt, 6 H, *J′*(P–H) 10, P(CH_3)$_2$], 1.87 (m, 4 H, PCH_2CH_2P), 2.04 (s, partially obscured by solvent, aryl CH_3), 5.06 (t, 1 H, *p*-H of Ph), 5.18 (d, 2 H, *o*-H of Ph), 5.28 (t, 2 H, *m*-H of Ph)[b]
(10) [Mo(η-C_6H_6)(pdmp)(η-C_3H_5)]PF_6 Orange C, 36.3 (36.15); H, 3.2 (3.0)	^{1}H: 1.70 (d, 2 H, H_{anti} or H_{syn}), 1.85, 1.3 (2 × vt, 12 H, 2 PMe_2), 2.15 (q, 2 H, H_{syn} or H_{anti}), 3.5 (c, 1 H, H_c), 5.5 (s, 6 H, η-C_6H_6), 7.9, 7.6 (2 × c, 4 H, $C_6H_4P_2$)[b] ^{13}C: 17.8 (s, 2 PMe_2), 35.1 (s, 2 CH_2 of η-C_3H_5), 75.3 (s, CH of η-C_3H_5), 97.0 (s, η-C_6H_6), 131.8, 129.3 (2 × s, $C_6H_4P_2$)[b] ^{31}P: 41.5 (s)[b,h]
(11) [Mo(η-C_6H_6)(pdma)(η-C_3H_5)]PF_6 Dark orange C, 35.4 (35.3); H, 4.0 (4.3)	^{1}H: 0.67 (d, 2 H, H_{anti} or H_{syn}), 0.87, 0.5 (2 × vt, 12 H, 2 $AsMe_2$) 2.85 (s, 2 H, H_{syn} or H_{anti}), 3.55 (c, 1 H, H_c), 5.5 (s, 6 H, η-C_6H_6), 7.95, 7.6 (2 × c, 4 H, $C_6H_4As_2$) ^{13}C: 11.5 (2 × s, 2 $AsMe_2$), 35.2 (s, allyl), 71.1 (s, H_c), 95.3 (s, η-C_6H_6), 130.86 (d, 89.6, $C_6H_4As_2$)[i]
(12) [Mo(η-C_6H_6){P(OMe)$_3$}$_2$(η-C_3H_5)]PF_6 Orange C, 29.7 (29.6); H, 4.8 (4.7)	^{1}H: 2.08 (c, 2 H, H_{anti} or H_{syn}), 2.37 [q, 2 H, *J*(H–H) 5, H_{syn} or H_{anti}], 3.72 [vt, 18 H, 2 × P(OMe)$_3$], 3.87 (c, 1 H, H_c), 5.67 (s, 6 H, η-C_6H_6) ^{13}C: 38.80 (s, CH_2 of η-C_3H_5), 53.54 [s, P(OMe)$_3$], 80.37 (s, CH of η-C_3H_5), 98.18 (s, η-C_6H_6) ^{31}P: 165.57 (s)[b,j]
(13) [Mo(η-C_6H_6)(pdmp)(η-C_2H_4)][e] Crimson	^{1}H: 1.3, 1.17 (2 × vt, 12 H, 2 PMe_2), 1.77 [t, 4 H, *J*(P–H) 5, η-C_2H_4], 4.1 (t, 6 H, η-C_6H_6), 7.05, 7.35 (2 × c, 4 H, $C_6H_4P_2$)[g]
(14) [Mo(η-C_6H_6)(pdma)(η-C_2H_4)][e] Brick red	^{1}H: 1.08, 1.16 (2 × s, 12 H, 2 $AsMe_2$), 1.82 (s, 4 H, η-C_2H_4), 4.03 (s, 6 H, η-C_6H_6), 7.15, 7.47 (2 × c, 4 H, $C_6H_4As_2$)[g,k]
(15) [Mo(η-C_6H_6)(pdmp)(η-C_2H_4)H]PF_6 Green C, 39.3 (39.6); H, 4.8 (4.95)[m]	^{1}H: 1.30, 2.10 (2 × c, 12 H, 2 PMe_2), 5.57 (s, 6 H, η-C_6H_6), 7.73, 8.07 (2 × c, 4 H, $C_6H_4P_2$)[b,l]
(16) [Mo(η-C_6H_6)(pdma)(η-C_2H_4)H]PF_6 Olive green C, 33.3 (34.1); H, 4.3 (4.4)[o]	^{1}H: 1.71 (s, 12 H, 2 $AsMe_2$), 5.46 (s, 6 H, η-C_6H_6, isomer B), 5.57 (s, 6 H, η-C_6H_6, isomer A), 8.07, 8.23 (2 × c, 4 H, $C_6H_4As_2$)[b,n]
(17) [Mo(η-C_6H_5Et)(pdmp)(PMe_3)H]PF_6 Red	^{1}H: −7.0 [dt, 1 H, *J*(P–H) 60, 30, Mo–H], 1.18 [t, 3 H, *J*(H–H) 9, CH_3 of Et], 1.3 [d, 9 H, *J*(P–H) 9, PMe_3], 1.77, 1.98 (t, 12 H, 2 PMe_2), 2.29 [q, 2 H, *J*(H–H) 9, CH_2 of Et], 5.45 (c, 5 H, $η^6$-C_6H_5), 7.6, 7.95 (2 × c, 4 H, $C_6H_4P_2$)[b] ^{31}P: 4.2 (t, 90, PMe_3), 44.9 (d, 80, pdmp)[b]
(18) [Mo(η-C_6H_5Et)(pdma)(PMe_3)H]PF_6 Brown[e]	^{1}H: −6.69 (d, 1 H, 54, Mo–H), −6.58 (d, 1 H, 57, Mo–H), 1.18 [t, 3 H, *J*(H–H) 7.5, CH_3 of Et], 1.37 [t, 9 H, *J*(P–H) 10, PMe_3], 1.71 (2 × s, 12 H, 2 $AsMe_2$ of unknown compound), 1.90 (2 × s, 12 H, 2 $AsMe_2$), 2.32 [q, 2 H, *J*(H–H) 7.5, CH_2 of Et], 5.27 (s, 6 H, η-C_6H_6 of unknown compound), 5.33 (c, 5 H, C_6H_5Et), 7.65, 8.00 (2 × c, 4 H, $C_6H_4As_2$)[b]
(19) [Mo(η-C_6H_6Et-*endo*)(pdmp)$_2$]PF_6 Dark orange C, 46.5 (45.9); H, 5.85 (5.8)	^{1}H: 0.39 (t, 3 H, CH_3 of Et), 0.97 (c, 2 H, CH_2 of Et), 1.74, 2.08 (2 × s, 24 H, 2 PMe_2), 2.27 (d, 1 H, H_{exo}), 2.90 (c, 2 H, H^2 and H^6), 4.14 (t, 2 H, H^3 and H^5), 5.02 (c, 1 H, H^4), 7.60, 7.78 (2 × c, 8 H, $C_6H_4P_2$)[b,p]
(23) and **(24)**, [Mo(η-C_6H_7)(dmpe)(PMe_3)(η-C_2H_4)]PF_6, mixture of isomers	^{1}H −30 °C: **(23)** (major isomer), 0.62 (br s, 1 H, H^6, H^7, or $={CH_2}$), 1.24 [d, 9 H, *J*(P–H) 7, P(CH_3)$_3$], 1.34 [d, 3 H, *J*(P–H) 7.5, PCH_3], 1.45 [d, 3 H, *J*(P–H) 8, PCH_3], 1.55 [d, 3 H, *J*(P–H)

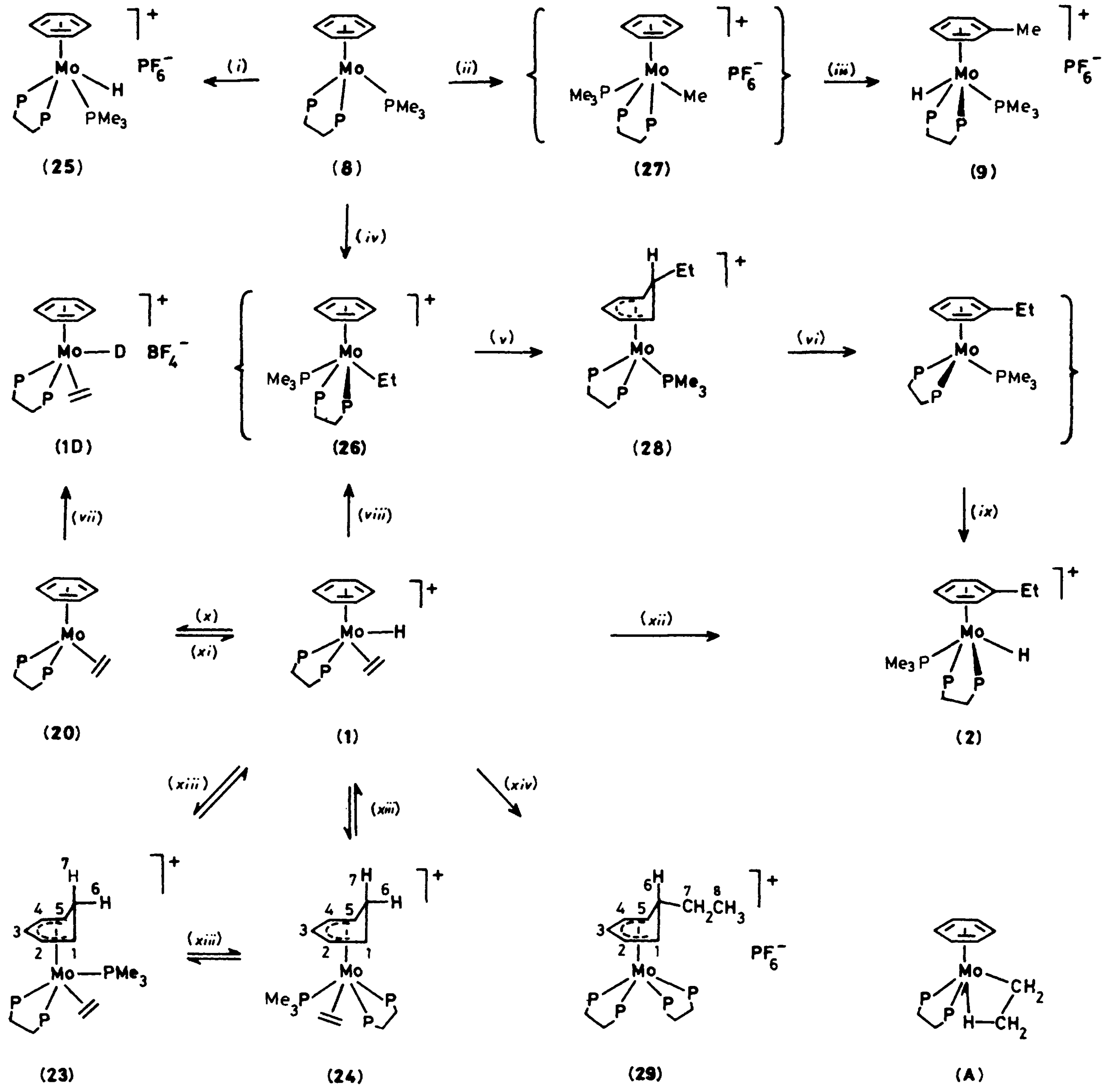
Table 1 (*continued*)

Compound, colour, and analysis (%)	N.m.r. data (^{1}H, ^{13}C, and ^{31}P)
(**23**) and (**24**), $[Mo(\eta\text{-}C_6H_7)(dmpe)(PMe_3)(\eta\text{-}C_2H_4)]PF_6$, mixture of isomers	7, PCH_3], 1.65 [d, 3 H, J(P–H) 7.5, PCH_3], 2.35 (m, 1 H, H^1), 3.34 (q, 1 H, H^5), 4.92 (br t, 1 H, H^2), 5.05 (t, 1 H, H^4), 6.05 (m, 1 H, H^3); (**24**) (minor isomer), 0.88 [d, 3 H, J(P–H) 8, PCH_3], 1.37 [d, 3 H, J(P–H) 7.5, PCH_3], 1.51 [d, 3 H, J(P–H) 7, PCH_3], 1.56 [d, 9 H, J(P–H) 8, $P(CH_3)_3$], 1.76 [d, 3 H, J(P–H) 8, PCH_3], 2.23 (m, 1 H, H^1, H^6, H^7, or =CH_2), 2.43 (d, 1 H, H^1, H^6, H^7, or =CH_2), 2.54 (br s, 1 H, H^1, H^6, H^7, or =CH_2), 3.15 (q, 1 H, H^5), 4.57 (br s, 1 H, H^2), 5.38 (t, 1 H, H^4), 5.72 (m, 1 H, H^3)[b,q] ^{31}P at −35 °C: (**23**), −3.79 [dd, 1 P, J(P–P) 42.3, 69.3], 30.50 [dd, 1 P, J(P–P) 11.3, 42.3], 44.30 [dd, 1 P, J(P–P) 69.4, 11.3]; (**24**), −12.92 [dd, 1 P, J(P–P) 70.7, 33.6], 32.14 [dd, 1 P, J(P–P) 33.5, 25.3], 43.43 [dd, 1 P, J(P–P) 25.6, 71.0] Fully ^{1}H-coupled ^{13}C at −30 °C: (**23**), 26.9 [t, J(C–H) 131, C^6], 32.0 [t, J(C–H) 155 CH_2], 40.9 [t, J(C–H) 152, CH_2], 42.7 [d, J(C–H) 165, C^1 or C^5], 47.8 [d, J(C–H) 174, C^5 or C^1], 87.7 [d, J(C–H) 170, C^2, C^3, or C^4], 92.2 [d, J(C–H) 168, C^2, C^3, or C^4], 103.3 [d, J(C–H) 165, C^2, C^3, or C^4];[b] (**24**), 43.6 [d, J(C–H) 165, C^1 or C^5], 57.2 [d, J(C–H) 171, C^5 or C^1], 79.5 [d, J(C–H) 161, C^2, C^3, or C^4], 91.5 (d, C^2, C^3, or C^4),[r] 96.5 (d, C^2, C^3 or C^4);[r] (**23**) or (**24**),[r,s] 5.0 [qd, J(P–C) 19], 6.4 [qd, J(P–C) 20], 13.6 [qd, J(P–C) 24], 14.3 [qd, J(P–C) 24], 14.9 [qd, J(P–C) 25], 15.0 [qd, J(P–C) 12], 17.4 [qd, J(P–C) 23], 17.4 [qd, J(P–C) 24], 17.6 [qd, J(P–C) 22], 18.42 [qd, J(P–C) 22]
(**25**) $[Mo(\eta\text{-}C_6H_6)(dmpe)(PMe_3)H]PF_6$[e]	^{1}H: −7.46 [dt, 1 H, J(P–H) 55, 36, Mo-H], 1.51 [d, 9 H, J(P–H) 8, $P(CH_3)_3$], 1.60 [vt, 6 H, J'(P–H) 9, $P(CH_3)_2$], 1.65 [vt, 6 H, J(P–H) 9, $P(CH_3)_2$], 1.80—1.95 (m, 4 H, PCH_2CH_2P), 5.18 (s, 6 H, C_6H_6)[b]
(**27**) $[Mo(\eta\text{-}C_6H_6)(dmpe)(PMe_3)Me]^{+}$[e]	−0.29 [td, 3 H, J(P–H) 11.6 and 3, $MoCH_3$], 1.53 [d, 9 H, J(P–H) 7, $P(CH_3)_3$], 1.6—1.7 [complex m, 12 H, $P(CH_3)_2$], 5.04 [d, 6 H, J(P–H) 3, C_6H_6][b]
(**29**) $[Mo(\eta\text{-}C_6H_6Et\text{-}endo)(dmpe)_2]PF_6$ Orange C, 36.6 (37.0); H, 6.6 (6.6)	^{1}H: 0.76 [t, 3 H, J(H^7–H^8) 7.7, CH_3], 1.39 [qnt, 2 H, J(H^7–H^8) = J(H^7–H^6) 7.7, CH_2], 1.47 [br s, 12 H, $P(CH_3)_2$], 1.65 [br s, 12 H, $P(CH_3)_2$], 2.12 (m, 8 H, PCH_2CH_2P), 2.24 (d, 2 H, H^1), 2.31 [spt, 1 H, J(H^6–H^7) 7.7, J(P–H^6) 3.8, H^6], 4.50 (t, 2 H, H^2), 5.50 (sxt, 1 H, H^3)[b] Off-resonance decoupled ^{13}C: 11.9 (q, C^8), 19.6 [q, $P(CH_3)$], 26.7 [qvt, J'(C–P) 22, $P(CH_3)$], 27.7 (t, C^7), 33.0 (tm, PCH_2CH_2P), 42.2 [dt, J(C–P) 3, C^6], 44.9 (d, C^1), 95.2 (d, C^2), 97.7 (d, C^3)[b] ^{31}P-{^{1}H}: 43.5 (br s)[b,t] ^{1}H-{^{31}P}: 2.31 (t, J 7.7)[b]
(**30**) $[Mo(C_6H_4Me\text{-}2\text{-}Et\text{-}1)(dmpe)(PMe_3)H]PF_6$ and (**31**) $[Mo(C_6H_4Me\text{-}3\text{-}Et\text{-}1)(dmpe)(PMe_3)H]$-$PF_6$ Red[e]	^{1}H at 500 MHz: (**30**), −6.96 [dt, 1 H, J(P–H) 53.5, 37.9, Mo–H], 1.14 [t, 3 H, J(H–H) 7.5, 8-CH_3], 1.50 [d, 9 H, J(P–H) 8, $P(CH_3)_3$], 2.15 [d, 3 H, J(P–H) 1, 9-CH_3], 2.18 [dq, 1 H, ^2J(H–H) 13.9, ^3J(H–H) 7.5, H$_a$ or H$_b$], 2.55 [dqd, 1 H, ^2J(H–H) 13.9, ^3J(H–H) 7.5, J(P–H) 0.5, H$_b$ or H$_a$];[b] (**31**), −7.35 [dt, 1 H, J(P–H) 58.6, 36.9, Mo–H], 1.18 [t, 3 H, J(H–H) 7.5, 8-CH_3], 1.53 [d, 9 H, J(P–H) 8, $P(CH_3)_3$], 2.16 [d, 3 H, J(P–H) 1.5, 9-CH_3], 2.34 (AB pair of ddq, 2 H, H$_a$ and H$_b$);[b] (**30**) and (**31**), 1.57—1.68 [m, 12 H, $P(CH_3)_2$], 1.80—1.96 (m, 4 H, PCH_2CH_2P), 5.10—5.35 [(multiplets), 4 H, aryl H][b] J-modulated ^{13}C: (**30**), 15.9 (s, −, C^8), 19.7 (s, −, C^9), 27.5 [d, −, J(P–C), 26, $P(CH_3)_3$], 28.1 (s, +, C^7), 31.8 (t, +, PCH_2CH_2P), 86.8, 88.6, 94.1 (all s, −, C^2, C^3, C^4, or C^5),[u] (**31**), 17.3 (s, −, C^8), 21.6 (s, −, C^9), 27.6 [d, −, J(P–C) 26, $P(CH_3)_3$], 29.7 (s, +, C^7), 31.7 (t, +, PCH_2CH_2P), 82.3, 88.0, 95.3, 97.6 (all s, −, C^2, C^3, C^4, or C^5), 107.2 (s, +, C^1 or C^2), 113.8 (s, +, C^2 or C^1);[b] (**30**) and (**31**), 22.6 [m, −, $P(CH_3)_2$], 24.3 [m, −, $P(CH_3)_2$][b] ^{31}P: (**30**), 3.80 [t, 1 P, J(P–P) 24.5, $P(CH_3)_3$], 48.47 [dd, 1 P, J(P–P) 24.5, 23.5, $P(CH_3)_2$];[b,v] (**31**), 4.51 [t, 1 P, J(P–P) 24.6, $P(CH_3)_3$], 49.58 [d, 2 P, J(P–P) 24.6, dmpe]
(**32**) $[Mo(dmpe)_2(\eta\text{-}C_6H_5Me\text{-}2\text{-}Et\text{-}6\text{-}endo)]PF_6$ (**33**) $[Mo(dmpe)_2(\eta\text{-}C_6H_5Me\text{-}1\text{-}Et\text{-}6\text{-}endo)]PF_6$ Orange C, 37.9 (38.1); H, 7.5 (6.9)	^{1}H at 500 MHz: (**32**), 0.80 [t, 3 H, J(H–H) 7,8-CH_3], 1.27 [ddq, 1 H, ^2J(H–H) 14, ^3J(H–H) 11 and 7, H$_a$ or H$_b$], *ca.* 1.58 (1 H, H$_b$ or H$_a$),[w] *ca.* 2.50 (1 H, H$_{exo}$), 2.22 (d, 1 H, H^5), 4.43 (d, 1 H, H^2), 4.48 (t, 1 H, H^3 or H^4), 5.29 (m, 1 H, H^4 or H^3);[b] (**33**), 0.77 [t, 3 H, J(H–H) 7, 8-CH_3], 1.38 (qnt, 2 H, H$_a$ and H$_b$), 2.44 (br s, 1 H, H$_{exo}$), 2.53 (br s, 1 H, H^5), 4.17 (t, 1 H, H^3 or H^4), 5.54 (br s, 1 H, H^4 or H^3); (**32**) and (**33**), 1.45—1.85 [complex bands, 27 H, $P(CH_3)_2$ + 9-CH_3], 1.85—2.25 [complex multiplets, PCH_2CH_2P + H^1 of (**33**)][b]

[a] Calculated analysis in parentheses. N.m.r. data given as: chemical shift (δ/p.p.m.), multiplicity, relative intensity, J in Hz, assignment; ^{1}H at 300 MHz, ^{13}C at 62.9 MHz, ^{31}P at 101 MHz, and ^{95}Mo n.m.r. at 90 MHz; unless otherwise indicated; vt = virtual triplet. The labelling of atoms is as given in the Schemes. [b] In $[^2H]_6$acetone. [c] The central dmpe carbons are buried under the solvent resonance. I.r. (mull): ν(Mo–H) 1 708w and 1 798w cm^{-1}. [d] I.r. (mull): ν(Mo–H) 1 798w cm^{-1}. [e] Characterised by n.m.r. data only, see the text. [f] Field-desorption mass spectrum: m/z 402 (100%), M^+. Photoelectron spectrum: first ionisation potentials 5.33 and 5.71 eV. [g] In C_6D_6. [h] ^{95}Mo N.m.r.: −1 249.5 (t) p.p.m., ^1J(^{95}Mo–^{31}P) = 156 Hz. [i] ^{95}Mo N.m.r.: −1 079.5 (s) p.p.m. [j] ^{95}Mo N.m.r.: −1 098.00 (t) p.p.m., ^1J(^{95}Mo–^{31}P) = 261 Hz. [k] ^{95}Mo N.m.r.: −1 721.11 (s) p.p.m. [l] ^{95}Mo N.m.r.: −1 735 (t) p.p.m., ^1J(^{95}Mo–^{31}P) = 137 Hz. [m] I.r. (mull): ν(Mo–H) 1 813w, br cm^{-1}. [n] ^{95}Mo N.m.r.: −1 077.00 p.p.m. [o] I.r. (mull): ν(Mo–H) 1 811w and 1 788w, br cm^{-1}. [p] Decoupling experiments: irradiation at 62.2 MHz. H$_a$, caused the complex peak at 60.97 MHz to collapse to a quartet, consistent with coupling of the CH_2 to the CH_3 group of the Et in the η^5-C_6H_6Et moiety; irradiation at 64.14 MHz, H$_c$, caused the complex peak at 62.90 p.p.m., H$_d$, to collapse to a singlet, consistent with a very small coupling constant of this proton to a proton *exo* to the η-C_6H_6 ring; irradiation at 65.02 MHz, H$_b$, caused the triplet at 64.14 MHz, H$_c$, to collapse to a doublet, consistent with coupling of this proton to one other adjacent proton on the ring, H$_d$, with no long-range coupling to the *exo*-proton; irradiation at 64.14 MHz, H$_c$, caused the complex peak at 65.02 MHz, H$_b$, to collapse to a triplet, consistent with a long-range coupling through the delocalised system of this proton to two equivalent protons, H$_d$. [q] The central dmpe protons (PCH_2CH_2P) and the remaining CH_2=CH_2 protons could not be distinguished; they presumably are buried in the very complex region, 1.0—2.5 p.p.m. [r] Coupling constants could not be observed directly; C–H multiplicities deduced from J-modulated spectrum. [s] All these are assignable to $P(CH_3)_3$ or $P(CH_3)_2$ of dmpe. A cluster of peaks (t) near or under the solvent resonance could not be assigned unambiguously but presumably belong to the central dmpe carbons (PCH_2CH_2P) and to the ethylene carbons of compound (**24**). [t] I.r. (KBr): ν(C–H) 2 755m cm^{-1}. [u] The fourth tertiary C could not be detected; it presumably coincides with a peak due to compound (**31**). The quaternary C atoms were too weak to detect. [v] The other dmpe ^{31}P band appeared only as an indistinct shoulder on a peak due to compound (**31**). [w] These signals were buried, and their presence was deduced from a two-dimensional ^{1}H–^{1}H COSY spectrum.

$[Mo(\eta\text{-}C_6H_6)\{P(OMe)_3\}_2(\eta\text{-}C_3H_5)]PF_6$, **(12)**, respectively. Reduction of compounds **(10)** and **(11)** with sodium amalgam in the presence of ethylene gives the neutral η-ethylene derivatives $[Mo(\eta\text{-}C_6H_6)(pdmp)(\eta\text{-}C_2H_4)]$, **(13)**, and $[Mo(\eta\text{-}C_6H_6)(pdma)(\eta\text{-}C_2H_4)]$, **(14)**, respectively. These are readily protonated by tetrafluoroboric acid; addition of aqueous NH_4PF_6 then gives the hydrido compounds $[Mo(\eta\text{-}C_6H_6)(pdmp)(\eta\text{-}C_2H_4)H]PF_6$, **(15)**, and $[Mo(\eta\text{-}C_6H_6)(pdma)(\eta\text{-}C_2H_4)H]PF_6$, **(16)**. Treatment of compound **(15)** with PMe_3 gives the η-ethylbenzene derivative $[Mo(\eta\text{-}C_6H_5Et)(pdmp)(PMe_3)H]PF_6$, **(17)**, in high yield. Similarly, $[Mo(\eta\text{-}C_6H_5Et)(pdma)(PMe_3)H]PF_6$, **(18)**, can be prepared from **(16)** and trimethylphosphine. Addition of pdmp to **(15)** gives the *endo*-η-ethylcyclohexadienyl compound $[Mo(\eta\text{-}C_6H_6Et\text{-}endo)(pdmp)_2]PF_6$, **(19)**.

Spectroscopic evidence strongly supports the assignment of a *cis*-ethylenehydride structure to the ground state of the cations **(15)** and **(16)**, as well as to the previously described $[Mo(\eta\text{-}C_6H_6)(dmpe)(\eta\text{-}C_2H_4)H]PF_6$, **(1)**. For example, the isomeric structural alternative for **(1)** bearing an $Mo\text{–}CH_2CH_2\text{–}H$ group with an agostic hydrogen,[7] *i.e.* structure **(A)** in Scheme 1, is ruled out both by the absence of coupling between the high-field proton and any of the ethylene protons, by the observation of large hydride–phosphine coupling constants, and by the appearance of a band in the i.r. spectrum of **(1)** (as its PF_6^- salt) assignable to a Mo–H stretching frequency (1 798w cm^{-1}). For



Scheme 1. (*i*) Dilute HCl(aq), then NH_4PF_6(aq), yield >80%; (*ii*) and (*iii*), CF_3SO_2OMe in CH_2Cl_2, then NH_4PF_6(aq), *ca.* 30%; (*iv*)—(*vi*) and (*ix*), $[OEt_3]BF_4$ in CH_2Cl_2 at −30 °C, warm, add NH_4PF_6; (*vii*) DBF_4 in D_2O, >90%; (*viii*) PMe_3 in acetone, 84%; (*ix*) intermolecular H^+ addition step, see text; (*x*) Dilute HBF_4, >90%; (*xi*) KH in thf, >80%; (*xii*) PMe_3 in acetone; (*xiii*) PMe_3 at −45 °C, see text; (*xiv*) dmpe in acetone at r.t.

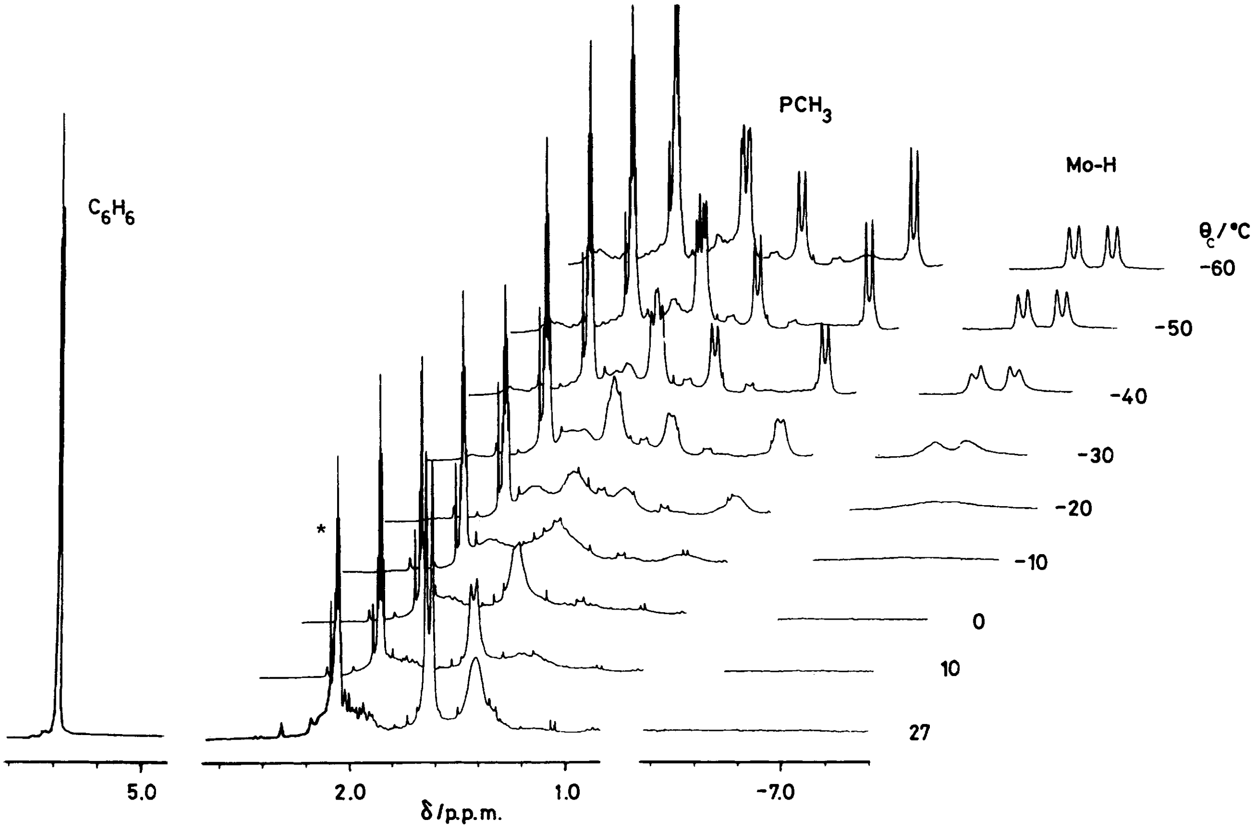
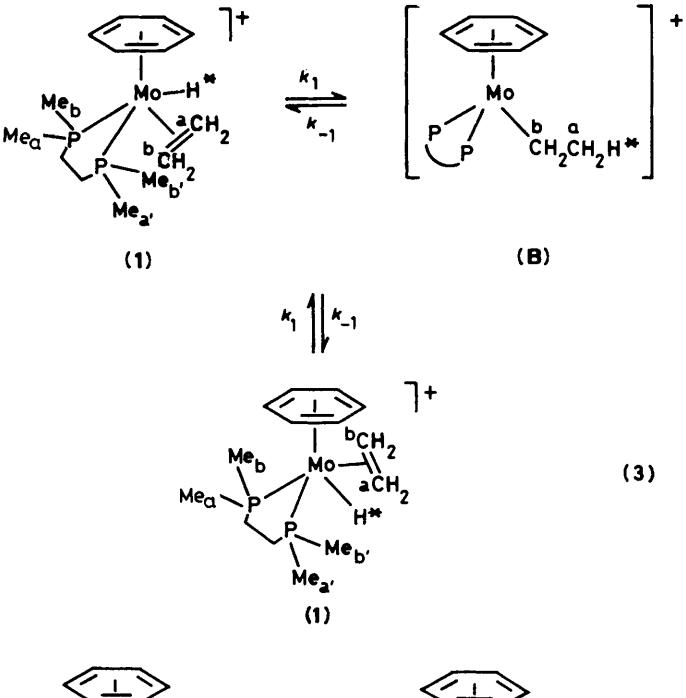


Figure 1. Variable-temperature ^{1}H n.m.r. spectra of compound (**1**) (300 MHz) in [^{2}H$_6$]acetone. The η-arene peak at δ 5.4 p.p.m. is temperature invariant. Asterisk denotes solvent peak

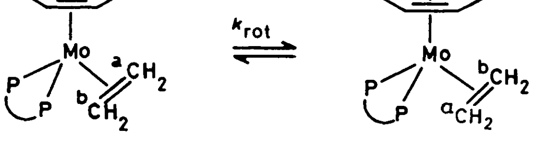
the η-toluene analogue [Mo(η-C_6H_5Me)(dmpe)(η-C_2H_4)H]-PF_6, (**4**), the corresponding band also appears at 1 798w cm^{-1}.

Variable-temperature ^{1}H *N.M.R. Studies on Compound* (**1**).—The spectra shown in Figure 1 demonstrate that compound (**1**) is fluxional. There are four doublets corresponding to the dmpe-methyl groups which coalesce in a pairwise fashion and a 60-MHz spectrum shows that in the high-temperature limit the methyl groups occur as a pair of virual triplets. The hydride and all four ethylene-proton signals merge to give a broad, five-proton singlet at the mean position of their chemical shifts, 0.2 p.p.m. The combined behaviour of the dmpe-methyl groups and of the ethylene and hydride protons is best accounted for by the operation of the insertion equilibrium (3) coupled with olefin rotation [equation (4)]. We assume that (**B**) is symmetrical, or that there is a rapid equilibrium between less symmetrical structures for (**B**). The olefin rotation [equation (4)] must be at least as fast as insertion because all four ethylene protons are involved in the scrambling process with the hydride. This conclusion is supported by the observation that the ethylene carbons give rise to a sextet ($J_{obs.}$ = 61 Hz) in the fully ^{1}H-coupled ^{13}C n.m.r. spectrum at room temperature (r.t.): each carbon experiences only an average coupling of [2/5(155) + 3/5(*ca.* 0 Hz)] to the five scrambling protons that are indicated by the signal multiplicity.

The observations are less readily explained in terms of an equilibrium between compound (**1**) an an agostic-ethyl species, such as (**A**) in Scheme 1. Even when coupled with olefin rotation, this process would not directly give the molecule the quasi-plane of symmetry required by the behaviour of the dmpe-



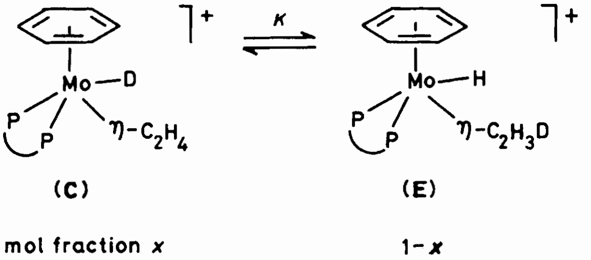
(3)



(4)

methyl groups in the fast-exchange limit. However, the agostic species (**A**) is quite conceivably an intermediate on the path between the ethylenehydride and the ethyl tautomer, (**B**) [equation (3)]. The absence of detectable equilibrium amounts of (**B**) in solutions of (**1**) establishes a lower relative limit, $k_{-1} > 100k_1$, for the rate constant for the de-insertion process.

Treatment of [Mo(η-C_6H_6)(dmpe)(η-C_2H_4)], (**20**), with [^{2}H]tetrafluoroboric acid gives [Mo(η-C_6H_6)(dmpe)(C_2H_4)-D]BF_4, (**1D**), the ^{2}H n.m.r. spectrum of which, at r.t., shows a single broad peak at 1.1 p.p.m. Essentially no deuterium is incorporated by this route into the η-arene or dmpe ligands; the resonance at δ 1.1 p.p.m. represents the exchange-averaged position of the single deuterium among the ethylene and hydride sites. The shift of this signal downfield when compared with the corresponding signal in the protio-compound (at 0.2 p.p.m.) reflects the thermodynamically preferred arrangement of hydrogen isotopes in these sites arising from differences in zero-point energies. If deuterium site preferences among individual positions in the bound olefin can be neglected, as seems reasonable, then the isotope effect can be discussed simply in terms of the equilibrium (5) between (η-C_2H_4)D and (η-C_2H_3D)H species.



(5)

Let δ(Mo–D) represent the chemical shift, in the absence of exchange of a metal-bound deuterium in (**1D**), and δ(C–D) that of an ethylenic deuterium. These parameters are equal to those obtained from the low-temperature ^{1}H n.m.r. spectrum of compound (**1**): δ(Mo–D) = -6.8 ± 0.1 and δ(C–D) = *ca.* 2.0 p.p.m.; the latter is a reasonable estimate of the mean ethylene-proton shift, given that the four individual signals are not clearly distinguishable. Let x be the proportion of (**C**) and $(1 - x)$ the proportion of (**E**) in the sample of (**1D**). The exchange-averaged chemical shift, δ, in the ^{2}H n.m.r. spectrum is then given by the expression (6). From the observed value, δ = 1.1 p.p.m. and the

$$\delta = x\delta(\mathrm{Mo{-}D}) + (1 - x)\delta(\mathrm{C{-}D}) \qquad (6)$$

estimates for δ(Mo–D) and δ(C–D) we calculate that $x = 0.10 \pm 0.01$. A statistically corrected equilibrium constant, K, for equilibrium (5) can be defined as $K = [(\mathbf{E})]/4[(\mathbf{C})] = (1 - x)/4x$. In the absence of an isotope effect, $x = \frac{1}{5}$ and $K = 1$. In the present case, $K = 2.2 + 0.3$, which corresponds to an energy difference, ΔG, of 2.0 ± 0.4 kJ mol^{-1} in favour of (**E**). This is of the magnitude and direction expected from zero-point-energy differences: the lighter isotope (H) prefers the site of lower vibrational energy (Mo–H), the heavier isotope (D) the site of higher vibrational energy (C–D).

Table 2. Ethylene-insertion rates for compound (**1**) obtained by the coalescence method

	$\Delta\nu$/Hz	T_c/°C	$k_{ins} = 2k_{ex}$/s^{-1}
$Me_a/Me_{a'}$	231 ± 5	$+3 \pm 2$	$(1.03 \pm 0.14) \times 10^3$
$Me_b/Me_{b'}$	75 ± 5	-10 ± 2	$(3.3 \pm 0.2) \times 10^2$

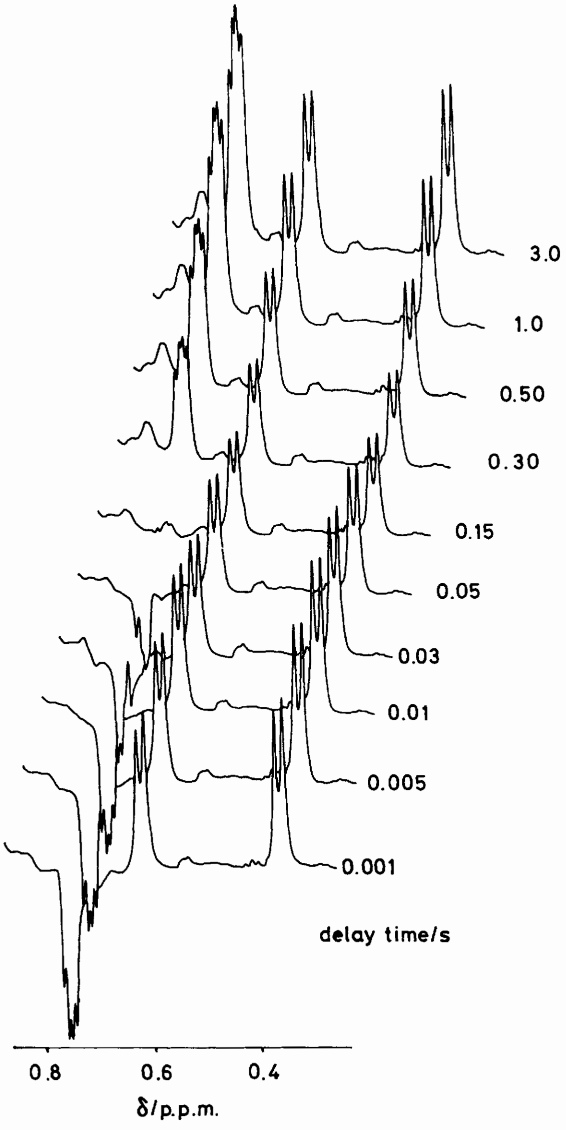


Figure 2. Magnetisation-transfer experiments for compound (**2**) at −45 °C

Kinetic Examination of Ethylene-insertion Reactions of Compounds (**1**) *and* (**13**).—The observation of coalescence and line-broadening effects in the n.m.r. spectra of [Mo(η-C_6H_6)(dmpe)(η-C_2H_4)H]$^+$, (**1**), provides qualitative information about the barriers to olefin insertion into a molybdenum–hydrogen bond. The relative complexity of the spectra and the concurrence of rotation and insertion processes precluded the use of complete line-shape analysis. However, the exchange between the dmpe-methyl groups that accompanies ethylene insertion [equation (3)] is clearly independent of olefin rotation, as is shown in equation (3) (where $k_1 = k_{\mathrm{insertion}}$), and therefore leads directly to insertion data, *i.e.* for $\mathrm{Me_a} \overset{k_{ex}}{\rightleftharpoons} \mathrm{Me_{a'}}$ and $\mathrm{Me_b} \overset{k_{ex}}{\rightleftharpoons} \mathrm{Me_{b'}}$, $k_{\mathrm{insertion}} = 2k_{ex}$. The four methyl groups form two equally populated, uncoupled systems (Me_a and $Me_{a'}$ and Me_b and $Me_{b'}$), the coalescence temperatures for which can be gauged quite accurately. Measurement of the respective slow-exchange chemical-shift separations led to two satisfactory rate estimates (Table 2).

Magnetisation-transfer (m.t.) experiments at temperatures considerably lower than the coalescence points were undertaken in order to obtain a more extensive data set. These experiments

Table 3. Rate data for ethylene insertion in compound (**1**) obtained by magnetisation transfer experiments ([$^2H_6$]acetone)

θ_c/°C (±1)	T_1(av.)*/s	$k_{ins} = 2k_{ex}/s^{-1}$
−30	0.56 ± 0.04	37.3 ± 2.2
−35	0.56 ± 0.05	22.4 ± 2.2
−45	0.47 ± 0.04	6.2 ± 0.8

* Average longitudinal relaxation time obtained from m.t. analysis.

involved the selective inversion of the two overlapping doublets (assigned arbitrarily the labels Me_a and Me_b) at δ 1.72 p.p.m., followed by observation of the system's recovery to equilibrium. The intensity perturbation of the protons at δ 0.96 ($Me_{a'}$) and 1.47 p.p.m. ($Me_{b'}$) results from their exchange with the spin-inverted protons, concurrent with longitudinal relaxation, which tends to bring all magnetisations back to equilibrium values. Figure 2 shows spectra from the m.t. experiment at −45 °C, analysis of which, as outlined below, gives the exchange rate constant, k_{ex}. The insertion rate is obtained from the relation, $k_{ins} = 2k_{ex}$, the factor of two arising because insertion leads to exchange only half of the time.

The dmpe-methyl groups form two kinetically identical pairs, analysis of either of which yields k_{ex}, so the exchange can be treated as a simple two-site problem (either $Me_a/Me_{a'}$ or $Me_b/Me_{b'}$). Let I be the normalized intensity of the inverted peak and S that of the perturbed peak at time t. Since the exchange is a redundant process, the equilibrium intensities I_∞ and S_∞ are equal. Within the validity of the approximation that the values of the relaxation time T_1 are also equal for the two nuclei, the appropriate differential equations are (7) and (8). These lead

$$dI/dt = T_1^{-1}(I - I_\infty) - k_{ex}(I - S) \quad (7)$$

$$dS/dt = T_1^{-1}(S - I_\infty) + k_{ex}(I - S) \quad (8)$$

readily to expressions (9) and (10), which, upon integration,

$$d(I + S)/dt = T_1^{-1}(I + S) + 2T_1^{-1}I_\infty \quad (9)$$

$$d(I - S)/dt = -(T_1^{-1} + 2k_{ex})(I - S) \quad (10)$$

predict that a plot of $\ln[2I_\infty - (I + S)]$ *vs.* t should be linear with slope $-T_1^{-1}$, that a plot of $\ln(S - I)$ *vs.* t should be linear with slope $-(T_1^{-1} + 2k_{ex})$, and the rate constant for exchange, k_{ex}, can be obtained.

It was observed that Me_a and Me_b have very nearly equal values of T_1 (0.45 ± 0.05 s) and therefore recover synchronously. The measured relaxation times, T_1, for Me_a and $Me_{a'}$ are equal, within experimental error, so that the approximations inherent in the development of expressions (9) and (10) are valid. These then give $T_1(\text{av}) = 0.48 \pm 0.02$ s and $k_{ex} = 3.1 \pm 0.4\ s^{-1}$. The measured rates were the same, within experimental error, from analysis of the pair $Me_b/Me_{b'}$. Table 3 summarizes the rate data derived from the m.t. experiments at three temperatures. The Arrhenius plot shown in Figure 3 uses the combined data from the coalescence and m.t. measurements, giving the parameters $E_a = 55.9 \pm 1.8$ kJ mol^{-1} and $\ln(A/s^{-1}) = 31.3 \pm 1.1$, whence $\Delta H^\ddagger = 53.6 \pm 1.8$ kJ mol^{-1}, $\Delta S^\ddagger = 6 \pm 5$ J K^{-1} mol^{-1}, and $\Delta G^\ddagger = 51.9 \pm 2.4$ kJ mol^{-1} at 276 K. The primary experimental data for these experiments and for all other kinetic measurements are given in ref. 8.

Entropies of activation for intramolecular migration reactions are usually small and negative, as they are for ethylene insertion in the complexes [$Nb(\eta\text{-}C_5Me_5)_2(\eta\text{-}C_2H_4)H$][9] and *trans*-[$Rh(PPr^i_3)_2(\eta\text{-}C_2H_4)H$], (**21**).[10] The positive value in the present system is surprising, but because the error limits are so large little significance can be made of this result.

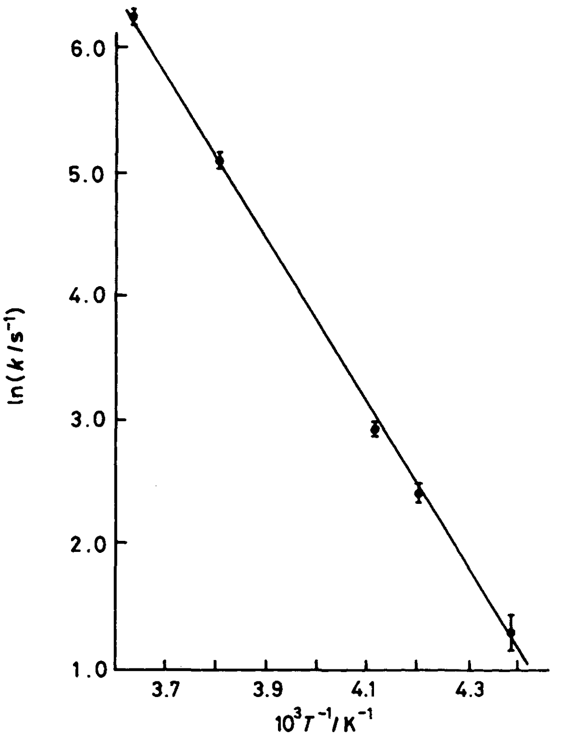


Figure 3. Arrhenius plot of rate data for ethylene insertion in compound (**1**) from coalescence and magnetisation-transfer measurements; $E_a = 55.9 \pm 1.8$ kJ mol^{-1}, $\ln(A/s^{-1}) = 31.3 \pm 1.1$

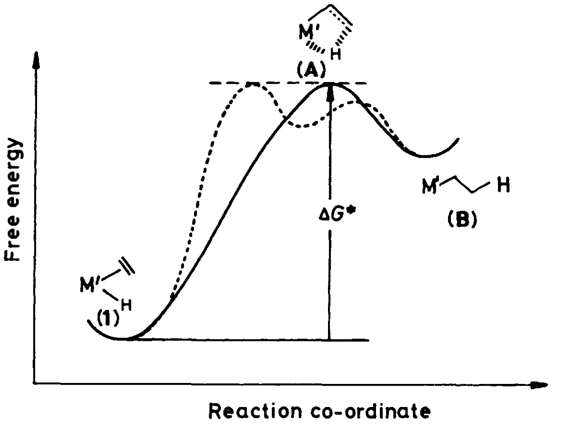


Figure 4. Free energy profile for olefin insertion; M' = Mo(η-C_6H_6)(dmpe)$^+$

The activation energy derived from this kinetic study on [$Mo(\eta\text{-}C_6H_6)(dmpe)(C_2H_4)H$]$^+$ can be interpreted as a gauge of the energy separation between the terminal- and bridged-hydride formulations of the complex [(**1**) and (**A**) respectively] (Figure 4). This conclusion is valid even if, as is possibly the case, the agostic structure, (**A**), is not merely the transition state for insertion but a true intermediate, because, by Hammond's postulate, its energy will be close to that of the actual transition state, measured by $\Delta G^\ddagger$, see Figure 4. The situation is, then, to be contrasted with that for the cobalt complex [$Co(CH_2CH_2\text{-}H)(\eta\text{-}C_5Me_5)(\eta\text{-}C_2H_4)$], (**22**), whose agostic ground state is *ca.* 30 kJ mol^{-1} more stable than the corresponding terminal bis(ethylene) hydride.[11]

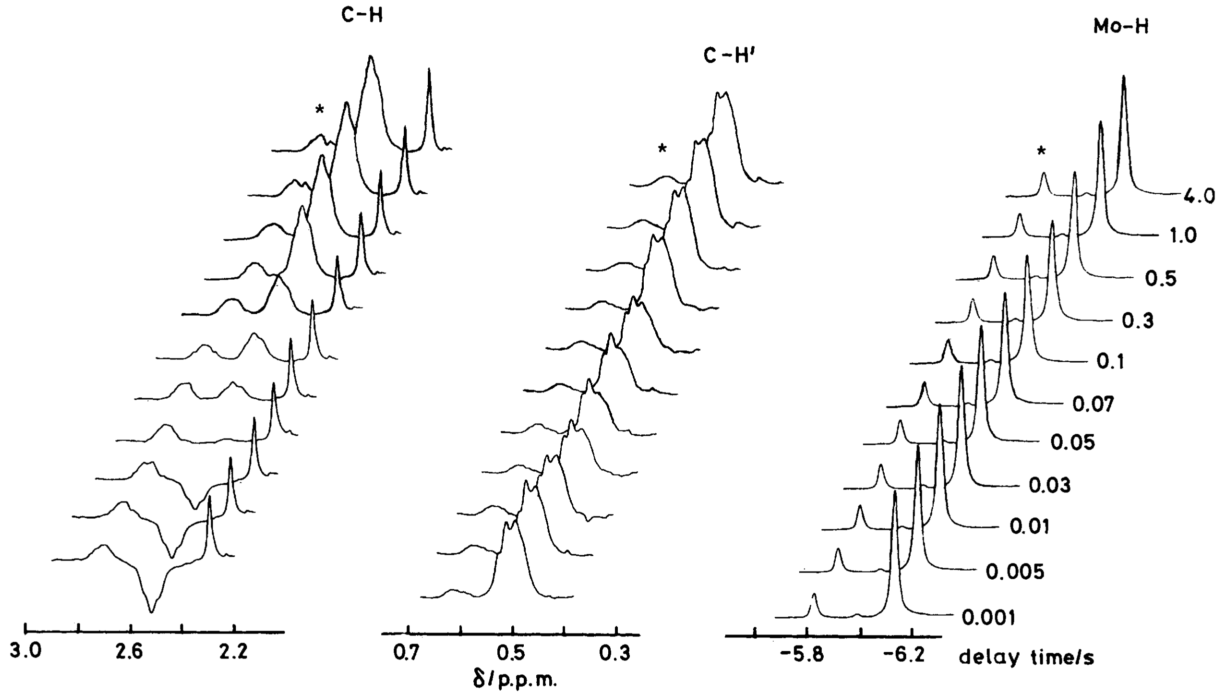


Figure 5. Magnetisation-transfer experiment for compound (**16**) involving inversion of the signal at δ 2.52 p.p.m. (C–H) and observation of those at δ 0.54 (C–H′) and −6.14 (Mo–H). Asterisk denotes impurity

The relative rate of olefin rotation in compound (**1**) must be at least as fast as insertion to account for the fact that the scrambling process involves all five of the ethylene and hydride protons.

M.t. experiments were made on the cation $[Mo(\eta-C_6H_6)(pdma)(\eta-C_2H_4)H]^+$, (**16**), which was chosen because the low-temperature-limiting ^1H n.m.r. spectrum is considerably simpler than that of (**1**): the four inequivalent pdma-methyl groups appear as singlets, as does the hydride; and three of the four ethylene protons are clearly distinguishable as complex multiplets (δ 0.54, 1.90, and 2.52). The rates of exchange between the two olefinic protons at δ 2.52 and 0.54 p.p.m. and the hydride at δ −6.14 p.p.m. were estimated by m.t. experiments at −35 °C. These involved the selective inversion of either one of the olefinic signals, followed by observation of the rate at which the inverted magnetisation was incorporated into both the hydride and the other olefinic site, as the system re-equilibrated. The spectra obtained from the experiment in which the effect of inversion of the ethylene proton (CH) at δ 2.52 was monitored are shown in Figure 5.

The data show that transfer of magnetisation from CH to CH′ is considerably faster than it is to Mo–H. The inference is that, by some process faster than ethylene insertion, site exchange between the ethylenic protons is taking place. The deduction that this process is indeed ethylene rotation about the metal–ligand axis requires the reasonable supposition that CH and CH′ are in a *trans* vicinal disposition in the ethylene ligand, *i.e.* H_a/H_b' or H_b/H_a' as shown for compound (**1**) in Scheme 2.

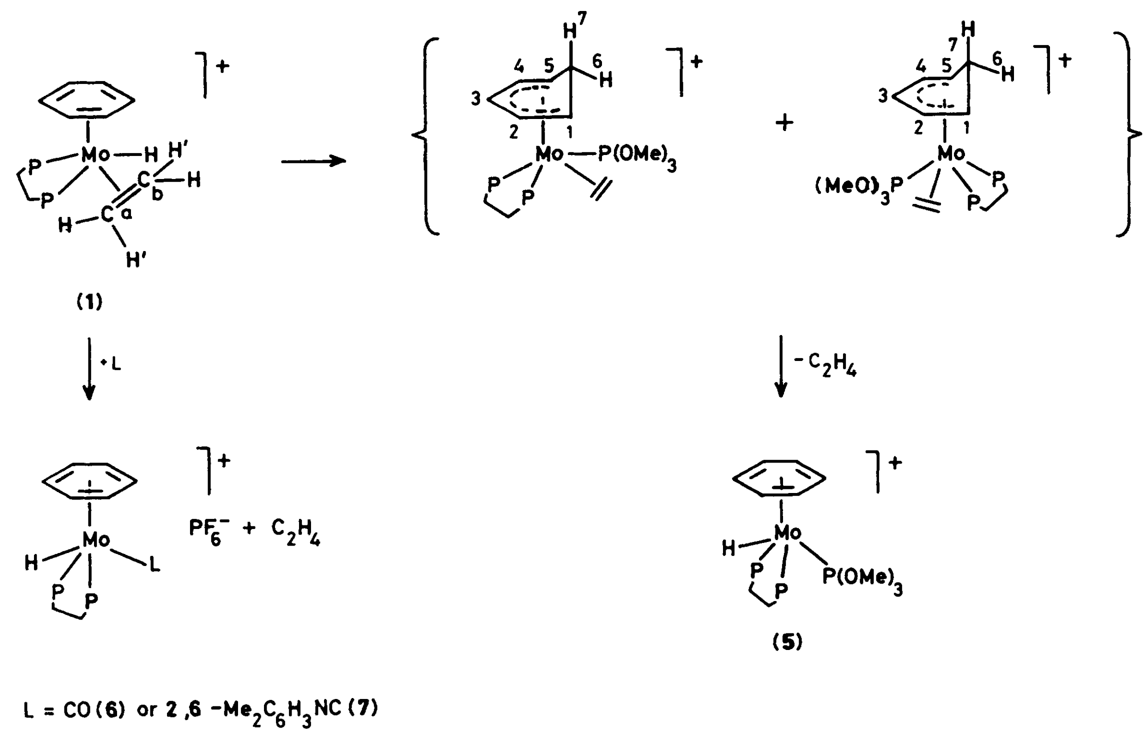
Quantitative estimation of relative rates from these spectra is made difficult by the complexity of the three-site exchange. If it is assumed, to a first approximation, that the values of T_1 are equal for the three nuclei, and using the method of initial rates which provides only a semi-quantitative estimate, then the data show that the rate of ethylene rotation in $[Mo(\eta-C_6H_6)(pdma)(\eta-C_2H_4)H]^+$, (**16**), exceeds that of insertion by a factor of *ca.* 4 at −35 °C, as is deduced also for the dmpe analogue.[8]

A Kinetic Study of the Reaction between Compound (**1**) *and* PMe_3.—Treatment of compound (**1**) with trimethylphosphine gives near-quantitative formation of (**2**) [equation (2)]. The *trans* stereochemistry originally assigned[6] to (**2**) is strongly suggested by the magnitude of the P–H coupling constant between hydride and PMe_3 (55 Hz). Also, the ^1H n.m.r. spectrum of (**2**) is essentially invariant down to −80 °C, which militates against a fluxional *cis* geometry.

We note that the product of reaction (2), $R_3 = Me_3$, appears by n.m.r. spectroscopy to contain, in addition to compound (**2**) a minor component giving rise to a second metal–hydride multiplet. It has been proposed[6] that this corresponds to the *cis* isomer of (**2**), and as the proportion is typically only *ca.* 5% it is consequently ignored in subsequent discussions.

The overall transformation, (**1**) to (**2**), takes place at r.t. over a period of hours, as judged from the brown-to-red colour change. Figure 6 shows the ^1H n.m.r. spectrum of the reaction solution obtained by allowing compound (**1**) to react for 3 min at r.t. with a five-fold excess of PMe_3, then introducing the sample into the spectrometer probe maintained at −30 °C. It is apparent that the reaction has been halted at a stage at which practically all of (**1**) has been consumed, but none of the final product, (**2**), has been generated. This mixture reacts further at room temperature, over several hours, giving (**2**) quantitatively, but is stable indefinitely below −30 °C.

The relative integrations show that there are two new compounds present in the molar ratio *ca.* 3:1. In the phosphine-methyl region (0.9—1.9 p.p.m.) two sets of peaks can be distinguished, corresponding to the major and minor components (**23**) and (**24**), respectively. For each compound there is a single nine-proton doublet, indicating a molecule of bound PMe_3, and four three-proton doublets indicating bound dmpe. The fact that the four dmpe-methyl groups are in both cases inequivalent implies that neither (**23**) nor (**24**) has a plane of symmetry. This conclusion is also reached on the basis of the ^{31}P n.m.r. spectrum of this mixture in which each component



Scheme 2. Proposed mechanism for the reaction of compound (**1**) with $P(OMe)_3$ giving (**5**) and structures proposed for (**6**) and (**7**)

gives rise to three distinct one-phosphorus doublets of doublets, as would be expected of the three mutually coupled phosphorus nuclei in a Mo(dmpe)(PMe_3) moiety.

The series of one-proton multiplets in the region 3.0—6.2 p.p.m. of the ^1H spectrum suggests immediately, by comparison with similar features in the spectrum of the complex [Mo(η-C_6H_7)(dmpe)(η-C_3H_5)],[12] that both (**23**) and (**24**) are η-cyclohexadienyl species. Further, decoupling experiments establish, for both the major and minor species, a partial connectivity pattern for the η-cyclohexadienyl ring protons and the similarity of the spectra of the two species suggests that they have closely related structures.

The substituents at the tetrahedral carbon, C^6, of the η-cyclohexadienyl rings are more difficult to identify. The broad-band-decoupled ^{13}C n.m.r. spectrum of the mixture is shown in Figure 7, along with the *J*-modulated spectrum. In the latter, primary and tertiary carbons (CH_3 and CH) appear with negative intensities, secondary and quaternary carbons (CH_2 and C), positive. Resonances are assignable on the basis of intensity and multiplicity to the major or minor component as indicated.

The C–H coupling-constant data for the non-phosphine carbons, derived from a fully ^1H-coupled ^{13}C n.m.r. spectrum, are given in Table 1.

For both compounds, all five dienyl carbons are observable, in the region δ 40—105 p.p.m. From a comparison with data for the complex [Mn(η-C_6H_6Me-*endo*)$(CO)_2(PPh_3)$],[13] the upfield signals (40—60 p.p.m.) are assignable to the terminal carbons C^1 and C^5, and the downfield signals (75—105 p.p.m.) to the internal carbons C^2, C^3, and C^4.

The cluster of quartets in the region 0—20 p.p.m. are readily assignable to phosphine-methyl groups (dmpe + PMe_3), since they all show substantial phosphorus coupling. There are, however, no signals in this region that would indicate the presence of an ethyl group, for which reason possible structures for (**23**) or (**24**), namely isomers of [Mo(η-C_6H_6Et-*endo*)(dmpe)(PMe_3)]$^+$, can be ruled out. Most strongly diagnostic, in the case of the major component (**23**), are the signals at 26.9, 32.0, and 40.9 p.p.m., all of which are triplets, the respective values of *J*(C–H) being 131, 155, and 152 Hz. The coupling-constant values show that the first signal corresponds to an aliphatic (sp^3) carbon and the other two to olefinic (sp^2) carbons.[14] The structure that accords most successfully with these features, and with all the above evidence, is the cation [Mo(η^5-C_6H_7)(dmpe)(PMe_3)(η-C_2H_4)]$^+$: the triplet at δ 26.9 is assignable to the tetrahedral carbon of the cyclohexadienyl ring, and those at δ 32.0 and 40.9 to the inequivalent ends of the olefin. We presume that, in the ^1H n.m.r. spectrum of the mixture of (**23**) and (**24**), some of the olefinic protons are in the complex region, δ 0.8—2.2 p.p.m. and a broad, one-proton band at 0.62 p.p.m. may be assigned to one of the ethylene hydrogens of (**23**).

When the ethylenehydride (**1**) is allowed to react with PMe_3, at −25 °C, the initial and only species present is the minor compound (**24**), which at *ca.* −10 °C reacts further to give (**23**) until equilibrium is reached at the ratio of *ca.* 1:3. This equilibrium ratio of (**23**) to (**24**) is essentially the same as that observed in the mixture formed at r.t., and implies that (**23**) is thermodynamically slightly more stable (by *ca.* 2.5 kJ mol^{-1}) than the kinetic product (**24**). At temperatures above 0 °C decomposition of the mixture of (**23**) and (**24**) into the final, ethyl-migrated product, (**2**), becomes kinetically significant. The rate of disappearance of compound (**1**) was found, by monitoring the peak height of its C_6H_6 resonance at 5.37 p.p.m., to be kinetically first order, under the conditions of the run, $[(\mathbf{2})]_0 = 0.070$, $[PMe_3]_0 = 0.31$ mol dm^{-3}, with $k_{-25\,°C} = (4.42 \times 0.02) \times 10^{-4}\ s^{-1}$.

From relative integrals in the final (equilibrium) spectrum, the ratio of (**23**) to (**24**) was determined to be 3.2 ± 0.2, and the concentration of PMe_3 to be 1.02 mol dm^{-3}. The equilibrium ratios [(**23**)]/[(**24**)] are independent of [PMe_3] and also of temperature and this shows that PMe_3 is not involved

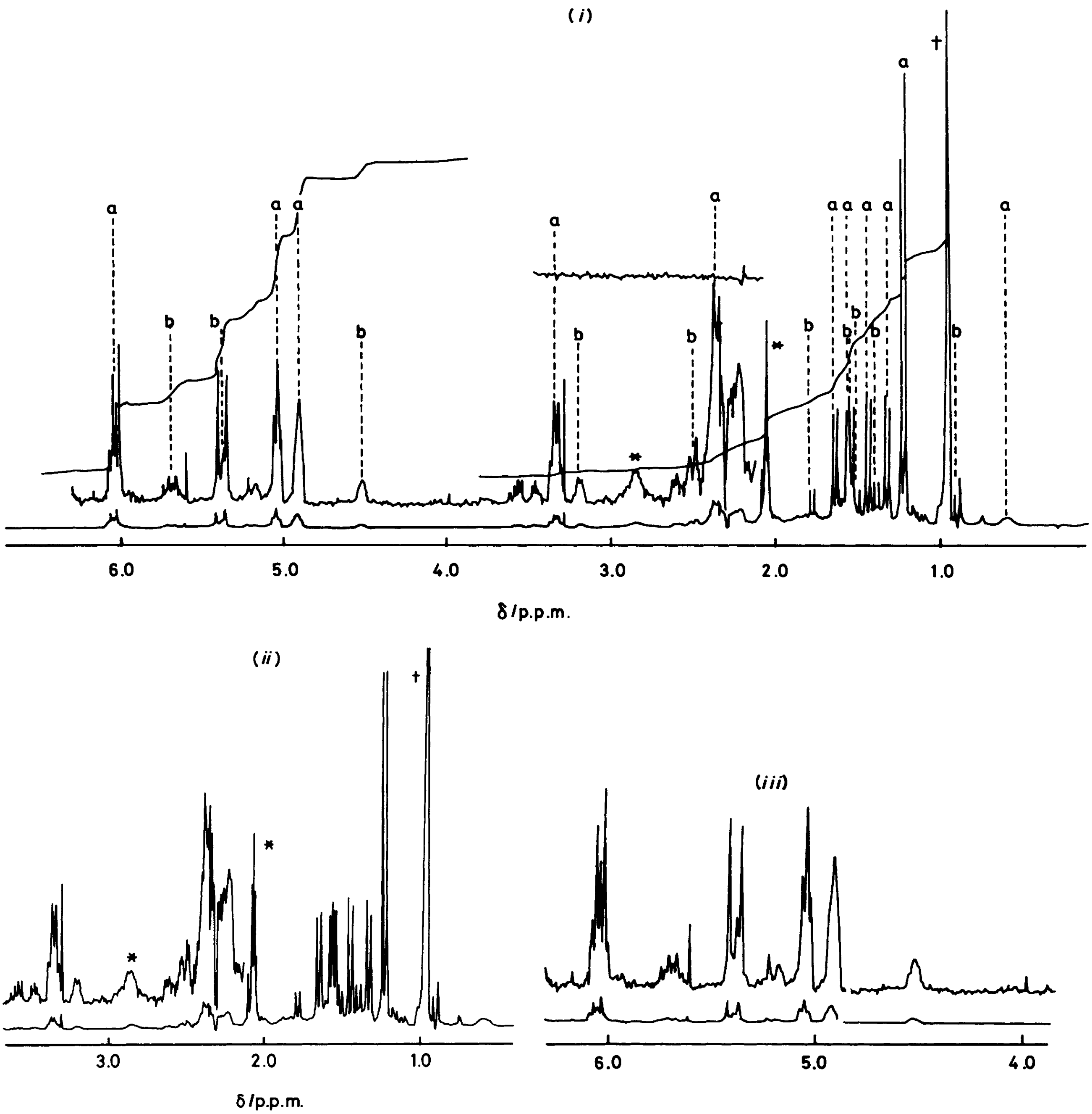


Figure 6. (*i*) Proton n.m.r. spectrum of the compounds (**23**) (major isomer a) and (**24**) (minor isomer b) formed from (**1**) and PMe_3 at −30 °C. Dagger denotes free PMe_3, asterisk denotes solvent. (*ii*) Expansion of the phosphine region. (*iii*) Expansion of the cyclohexadienyl region

(stoicheiometrically) in the interconversion of (**23**) and (**24**), and that the ratios represent the true equilibrium constant, K, for the reaction.

The rate of approach to equilibrium was measured by monitoring the growth of the (PMe_3) doublet of (**23**) at δ 1.22 p.p.m. The kinetics was found to be first order with $k_{obs.} = k_f + k_r = (4.72 \pm 0.13) \times 10^{-4}\ s^{-1}$ but $K = k_f/k_r = 3.2 \pm 0.2$ therefore $k_f = (3.67 \pm 0.33) \times 10^{-4}\ s^{-1}$ and $k_r = (1.12 \pm 0.1) \times 10^{-3}\ s^{-1}$ at −10 °C.

The combination of facts that the spectroscopic features of the complexes (**23**) and (**24**) are so similar, that the species are energetically so close to one another ($\Delta G = 2.5\ kJ\ mol^{-1}$) and that an equilibrium interconverting the two exists argues strongly in favour of the hypothesis that they are in fact isomers. The process most likely to lead to isomerism in this system is rotation of the η-cyclohexadienyl ring about the metal–ligand axis.

The data do not allow distinction between the conformational possibilities of the η-C_6H_7 ring relative to the basal plane, so that the structural assignments for (**23**) and (**24**) indicated in Scheme 1 are arbitrary; all that is required is that neither structure should have a plane of symmetry. Intuitively it seems entirely reasonable that phosphine-induced metal-to-ring transfer of hydrogen, *i.e.* the process that must occur when (**24**) is formed from (**1**), should lead stereospecifically to a particular conformational isomer, which need not be the most stable one.

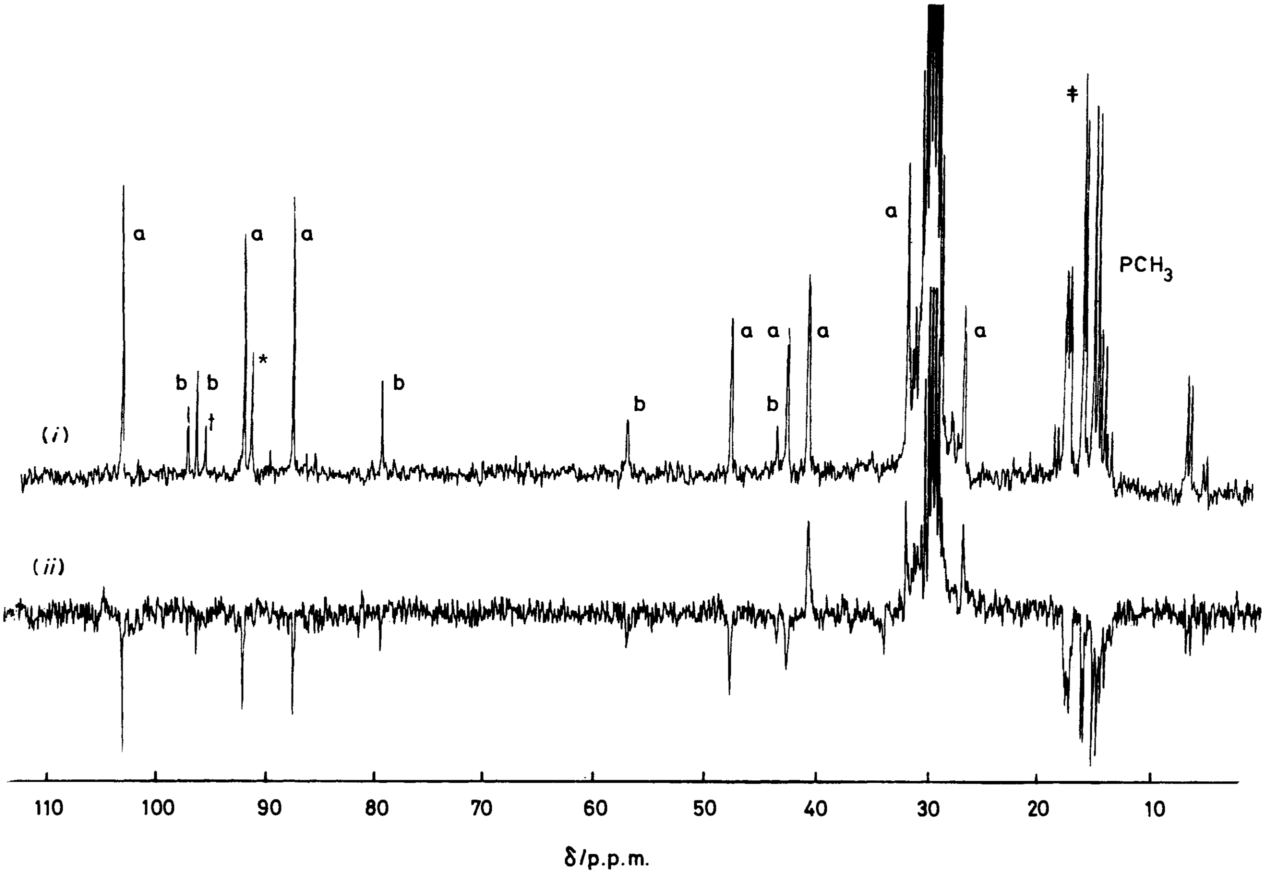


Figure 7. ^{13}C N.m.r. spectra of the mixture of compounds (**23**) and (**24**) (*i*) noise decoupled and (*ii*) *J*-modulated. Asterisk denotes residual compound (**2**), dagger an impurity, and double dagger free PMe_3

Equilibration between such isomers can be relatively slow and, indeed, high barriers to rotation of the dienyl rings must certainly exist in the previously described compounds $[Mo(\eta\text{-}C_6H_7)(dmpe)(\eta\text{-}C_3H_5)]$[12] and $[Mo(\eta\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(dmpe)]$,[15] because neither molecule appears to have a plane of symmetry on the n.m.r. time-scale, even though the basal moieties are themselves symmetrical. The barrier, ΔG, to rotation implied by the value for k_f of $3.67 \times 10^{-4}\ s^{-1}$ for (**23**) and (**24**) is *ca.* 81 kJ mol^{-1}.

The unexpected conclusion of this low-temperature n.m.r. study of the reaction between the ethylenehydride, (**1**), and PMe_3 is that the first-formed product arises by hydrogen migration from the metal to the aromatic ring. This is evidently faster than the other metal-to-ligand migration reaction presumably accessible to (**1**), namely the formation of the ethyl adduct $[Mo(\eta\text{-}C_6H_6)(dmpe)(PMe_3)Et]^+$, a process more usual for an ethylenehydride complex. Intramolecular metal-to-ring shift of hydrogen has been reported elsewhere.[16]

The interconversion of compounds (**23**) and (**24**) to (**2**) at 30 °C is first order, and the rate constants are the same, within experimental error, whether the appearance of the product or the disappearance of the starting compounds is followed. No other species are detected by n.m.r. spectroscopy and, in particular, only one hydride band, that of the product, is evident as the reaction proceeds. The ratio of (**23**) to (**24**) remains constant during the reaction, since the kinetic process that interconverts the two would be relatively fast at 30 °C. Rates were independent of the concentration of excess of PMe_3 (see Table 4).

Table 4. Rate constants for the conversion of compounds (**23**) and (**24**) into (**2**) at 30 °C in $[^2H_6]$acetone, gauged by monitoring the decrease in peak height of the (PMe_3) doublet of (**23**) at 1.22 p.p.m.

$[PMe_3]$/mol l^{-1}	$10^2\ k$/min^{-1}
0.26 ± 0.04	1.59 ± 0.06
0.80 ± 0.10	1.64 ± 0.08
1.15 ± 0.08	1.60 ± 0.08

The question of whether or not the complexes (**23**) and (**24**) are true intermediates on the pathway between (**1**) and (**2**) is not a straightforward one, they are structurally more remote from the final product (**2**) than is the starting compound itself. We propose, based on the evidence given below, that compounds (**23**) and (**24**) are formed merely in a redundant side-equilibrium with (**1**) which must lie well over to the side of (**23**) and (**24**).

The kinetic dependencies indicated in equation (11) are hypothetical but demonstrate that the proposal of a side-equilibrium need not conflict with the observation that the overall rate of conversion of (**23**) and (**24**) into (**2**) is independent

$$(23) + (24) \underset{k_1[PMe_3]}{\overset{k_{-1}}{\rightleftharpoons}} (1) \xrightarrow{k_2[PMe_3]} (2) \qquad (11)$$

of $[PMe_3]$. By applying the steady-state approximation to the concentration of (**1**) we obtain expression (12) for the observed rate where $k_{obs.} = k_2k_{-1}/k_1 + k_2$; as required empirically, it contains no terms in $[PMe_3]$.

$$d[(2)]/dt = k_{obs.}\{[(23)] + [(24)]\} \qquad (12)$$

We have provided an alternative entry into the sequence of steps between (**1**) and (**2**) by treatment of the neutral compound [Mo(η-C_6H_6)(dmpe)(PMe_3)], (**8**), with 1 equivalent of [OEt_3]BF_4 at room temperature and conversion of the ionic product into its hexafluorophosphate salt. This results in formation of a mixture of the compounds (**2**) and [Mo(η-C_6H_6)(dmpe)(PMe_3)H]PF_6, (**25**), in the proportion 60:40. Compound (**25**) is assumed to arise from protonation of (**8**), by adventitious acid (see the Experimental section).

Available analogies[17,18] suggest that the electrophilic reagent would initially attack a molecule as electron-rich as (**8**) (first i.p. 5.3 eV) at the metal to give an ethyl adduct [Mo(η-C_6H_6)(dmpe)(PMe_3)Et]$^+$, (**26**) (see Scheme 1), and a metal-to-ring ethyl shift and subsequent transfer of H^+ from the ring to the metal (see below) would then lead to the ring-substituted product (**2**). In support of this proposal, treatment of (**8**) with CF_3SO_2OMe gives first the metal–methyl cation [Mo(η-C_6H_6)(dmpe)(PMe_3)Me]$^+$, (**27**), which undergoes rearrangement in solution at r.t. to give, after addition of aqueous ammonium hexafluorophosphate, the η-toluene compound [Mo(η-C_6H_5Me)(dmpe)(PMe_3)H]PF_6, (**9**) (see Scheme 1). Compound (**27**) was characterized by ^1H n.m.r. spectroscopy, as a component in a mixture also containing (**25**). In particular, in addition to the expected phosphine bands, there is a three-proton triplet of doublets at δ −0.29 p.p.m. [J(P–H) = 11.6 and 3 Hz] assignable to the Mo–Me group, and a six-proton doublet at 5.04 p.p.m. assignable to the η-benzene ring. The methyl-migrated product (**9**) is immediately identifiable because of the similarity of its spectrum to that of its η-ethylbenzene analogue (**2**). After *ca.* 3 d the peaks due to (**27**) in the spectrum of the mixture disappeared and those due to (**9**) grew correspondingly, in a clean reaction.

When these qualitative results are extended to the corresponding reaction of compound (**8**) with Et_3O^+ they rule out a mechanism that does not involve initial electrophilic attack at the metal centre. They also disfavour the possibility that the ethyl adduct (**26**) reverts first to (**1**) because, for the methyl analogue (**27**) a β-elimination pathway is not available. The conclusion that the conversion of the ethylene hydride (**1**) into the ethyl-migrated product (**2**) proceeds *via* the ethyl adduct (**26**) follows from the argument that generation of the latter by an alternative route leads also to (**2**).

The formation of compound (**26**) is presumably followed by intramolecular migration of the ethyl group to the ring, giving the *endo*-ethylcyclohexadienyl species (**28**) (see Scheme 1).

It should be noted that not all alkyl shifts are intramolecular, for example the photochemical reaction of the iron–benzyl complex [Fe(η-C_5H_5)$(CO)_2$(CH_2Ph)] with PPh_3 gives the *exo*-benzylcyclopentadiene complex [Fe(η-$C_5H_5CH_2Ph$-*exo*)$(CO)_2$(PPh_3)].[2] However, evidence to suggest that the *endo*-migration route shown in Scheme 1 is fundamentally correct is provided by the reaction of the ethylenehydride (**1**) with the chelating phosphine dmpe which gives the stable *endo*-ethylcyclohexadienyl adduct [Mo(η-C_6H_6Et-*endo*)$(dmpe)_2$]PF_6, (**29**). The *endo* stereochemistry at C^6 is established by the observation of a band in the i.r. spectrum at 2755 cm^{-1} assignable to the C–H_{exo} stretch.[19]

Further, long-range coupling in a W arrangement occurs between H_{exo} and two of the basal phosphorus nuclei; H_{exo} appears as a triplet in the ^{31}P-decoupled ^1H n.m.r. spectrum, with coupling only to the CH_2 protons of the ethyl group (J = 7.7 Hz) being observed. In the undecoupled spectrum, a triplet coupling to phosphorus of 3.8 Hz is reintroduced, so that the signal appears as a 1:2:3:4:3:2:1: septet. This criterion of long-range coupling between atoms in a W arrangement has also been established by Davies *et al.*[19] No coupling occurs between H_{exo} and the dienyl protons H^1 and H^5; H_{exo} shows homonuclear coupling only to the CH_2 protons of the ethyl group, whilst H^1 and H^5 appear as a doublet in the ^1H spectrum, showing coupling only to H^2 and H^4 respectively. This criterion, based on dihedral angle considerations, has been used definitively for a range of compounds by Brookhart and co-workers.[20]

The possibility exists that the ethyl shift of compound (**26**) is assisted by a second molecule of PMe_3, which is subsequently lost again in the rearrangement step giving (**2**). However the overall rearrangement of (**26**) to (**2**) proceeds in the absence of excess of PMe_3, *i.e.* from the reaction of [Mo(η-C_6H_6)(dmpe)(PMe_3)], (**8**), with Et_3O^+, so it would seem unnecessary to implicate the intermediacy of the compound [Mo(η-C_6H_6Et-*endo*)(dmpe)$(PMe_3)_2$]$^+$.

When the ethylenehydride (**1**) is treated with PMe_3 in [$^2H_6$]acetone containing 10% (v/v) D_2O, the product (**2**) shows >70% incorporation of deuterium into the hydride position. This was deduced from the virtual absence of a hydride signal in the ^1H n.m.r. spectrum of the product solution, and the corresponding presence, in the ^2H n.m.r. spectrum of the isolated product, of a doublet of triplets at δ −7.27 p.p.m. characteristic of the monodeuterio compound [Mo(η-C_6H_5Et)(dmpe)(PMe_3)D]$^+$. In a complementary experiment, it was found that treatment of [Mo(η-C_6D_6)(dmpe)(η-C_2H_4)H]$^+$, (**1D$_6$**) with PMe_3 in acetone containing 20% (v/v) water resulted in formation of [Mo(η-C_6D_5Et)(dmpe)(PMe_3)H]PF_6, which bore *no* deuterium in the hydride position, as gauged from the ^2H n.m.r. spectrum of the isolated product. In a separate experiment, we have shown that under the conditions of these reactions (10—20% aqueous acetone), exchange of the metal-bound hydrogen of both the starting compound, (**1**) and the product (**2**) with the solvent was negligibly slow.

On the basis of these observations we propose that the final proton transfer of H_{exo} in (**28**) giving (**2**) proceeds by an *intermolecular* path, *via* neutral [Mo(η-C_6H_5Et)(dmpe)(PMe_3)]. It is probable that the loss of the *exo*-hydrogen is assisted by the solvent. The reprotonation of the molybdenum centre of the proposed intermediate [Mo(η-C_6H_5Et)(dmpe)(PMe_3)], giving (**2**), would be expected to occur readily. Indeed we have shown that protonation of the analogous [Mo(η-C_6H_6)(dmpe)(PMe_3)] proceeds readily (Scheme 1).

It is interesting that, in the reaction of (**1**) with PMe_3 in the presence of D_2O, there is no incorporation of deuterium into the aromatic ring at any stage. This implies that, although reversible metal-to-ring hydrogen shifts are certainly taking place in the system, for example in the formation of (**1**) from (**23**) or (**24**), the transfer of hydrogen back to the metal must be intramolecular.

We note that the migration reaction (2) appears to be quite specific to tertiary phosphines (*e.g.* PMe_3 or PMe_2Ph) as the nucleophilic reagent. For example, as noted earlier, (**1**) with trimethyl phosphite, carbon monoxide, and 2,6-$Me_2C_6H_3NC$ gives the products (**5**), (**6**), and (**7**), respectively (Scheme 2).

The reaction of compound (**1**) with an excess of $P(OMe)_3$ was monitored at 30 °C by ^1H n.m.r. spectroscopy in the manner used for the corresponding reaction with PMe_3; see Experimental section and Figure 8. It is clear that the initial processes broadly parallel those observed in the reaction of (**1**) with PMe_3: the starting compound is completely consumed within the period before the first scan (t = 1.5 min), generating a mixture of two transient species roughly in the ratio 2:1. Each gives rise to a series of complex multiplets detectable in the region 3—6 p.p.m. that can be taken to indicate η-cyclohexadienyl compounds. For each there is also a doublet [J(P–H) = 13 Hz] corresponding to a molecule of bound $P(OMe)_3$ (3.76 and 3.95 p.p.m.), and four doublets in the region (0.5—2.0 p.p.m.) corresponding to inequivalent dmpe-methyl groups. The two species subsequently undergo concurrent conversion into the final product (**5**) in a first-order process

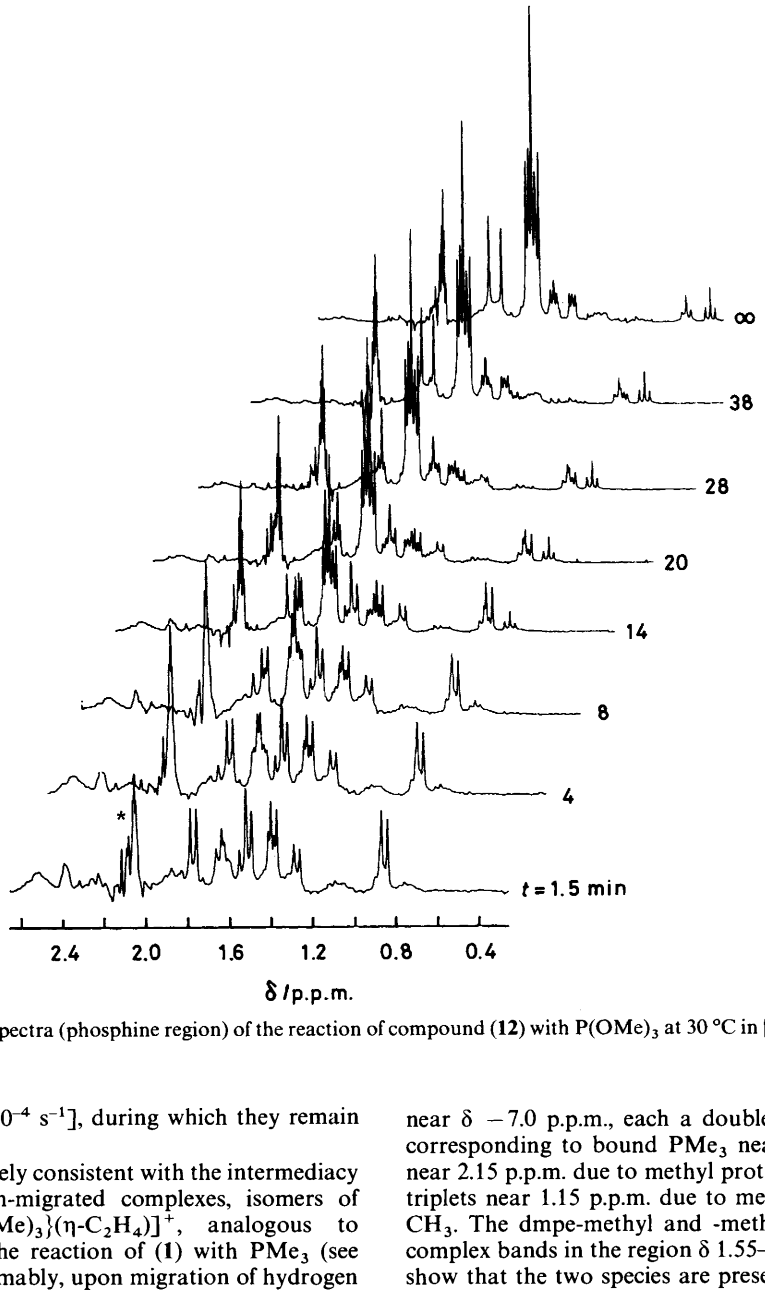


Figure 8. Successive ^1H n.m.r. spectra (phosphine region) of the reaction of compound (**12**) with $P(OMe)_3$ at 30 °C in [$^2H_6$]acetone. Asterisk denotes solvent

[$k_{30\,°C}$ = $(8.42 \pm 0.08) \times 10^{-4}\ s^{-1}$], during which they remain in constant ratio.

These details are completely consistent with the intermediacy of a mixture of hydrogen-migrated complexes, isomers of $[Mo(\eta\text{-}C_6H_7)(dmpe)\{P(OMe)_3\}(\eta\text{-}C_2H_4)]^+$, analogous to those formed initially in the reaction of (**1**) with PMe_3 (see Scheme 2). However, presumably, upon migration of hydrogen back to the metal, the molecule of ethylene is lost, generating (**5**), in preference to the molecule of $P(OMe)_3$. The mechanism of substitution is, therefore, an associative one, with a reversible hydrogen shift providing the spare co-ordination site.

The final conclusion of our examination of the mechanism of the conversion of compound (**1**) to (**2**) is that this proceeds by the sequence of transformations in Scheme 1, namely, (**1**) ⟶ (**26**) ⟶ (**28**) ⟶ $[Mo(\eta\text{-}C_6H_5Et)(dmpe)(PMe_3)]$ ⟶ (**2**).

The Regiospecificity of Ethyl Migration in Compound (**4**).—We were interested to study the directive effect of an arene-ring substituent on the course of the above ethyl-migration reaction. Accordingly, $[Mo(\eta\text{-}C_6H_5Me)(dmpe)(\eta\text{-}C_2H_4)H]PF_6$, (**4**), was treated with PMe_3 and a mixture of isomeric η-ethyltoluene complexes (**30**) and (**31**) was formed. From the ^1H n.m.r. spectra (Figure 9) of the product it is apparent that only two of the three possible regioisomers (bearing an *o*-, *m*-, or *p*-ethyltoluene ring) have been generated. For example, there are two hydride bands near δ −7.0 p.p.m., each a doublet of triplets, two doublets corresponding to bound PMe_3 near 1.5 p.p.m., two doublets near 2.15 p.p.m. due to methyl protons of $\eta\text{-}C_6H_5Me$, and two triplets near 1.15 p.p.m. due to methyl protons of $C_6H_4CH_2CH_3$. The dmpe-methyl and -methylene protons give rise to complex bands in the region δ 1.55—1.95. Relative integrations show that the two species are present in the ratio 30:70.

What reveals most about the structure of these two isomers is that for both the methylene protons of $\eta\text{-}C_6H_4CH_2CH_3$ are diastereotopic. For the major isomer, (**31**), these protons appear as a mutually coupled (AB) pair of doublets of quartets centred at δ 2.34 p.p.m. [see expansion, Figure 9(*b*)]. For the minor isomer, (**30**), both methylene protons appear also as doublets of quartets, at δ 2.18 and 2.55 p.p.m. respectively. In both cases the quartet coupling is due to the vicinal methyl protons of the ethyl group. This interpretation of these particular bands was supported by a ^1H–^1H COSY-45 spectrum (500 MHz), in which coupled protons are indicated by off-diagonal peaks in a plot of chemical shift *vs.* chemical shift.

The diastereotopic methylene protons in (**30**) and (**31**) can arise only if the molecules are chiral, and this rules out the *para* isomer, which has a plane of symmetry. Comparison with features of the n.m.r. spectra of the 1-acetyl-2- or 3-methylbenzene complexes $[Cr\{C_6H_4Me(COMe)\}(CO)_3]$ that parallel those in the present system[21] enables assignment of the *ortho* and *meta* conformations for (**30**) and (**31**). Thus, for the

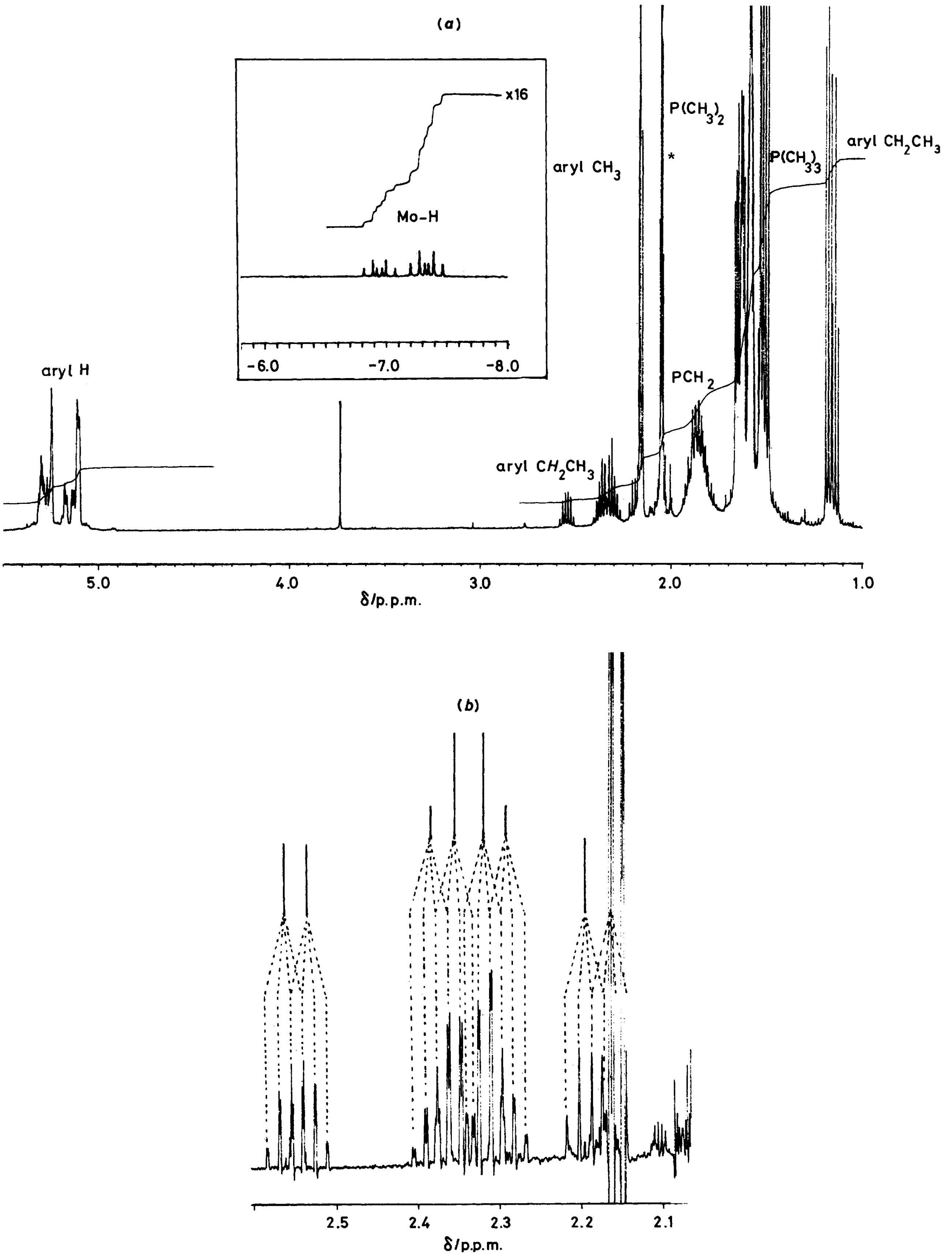
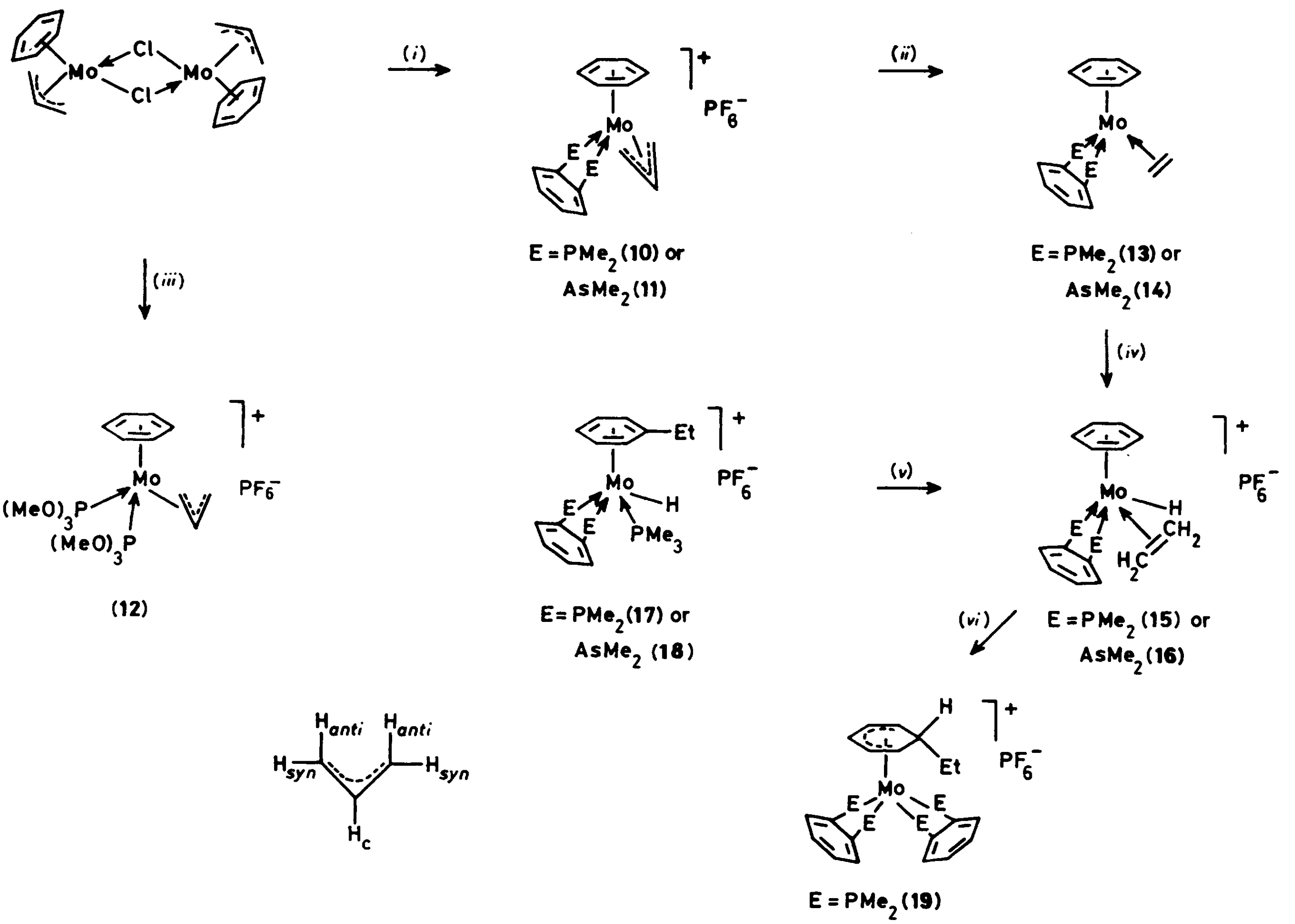
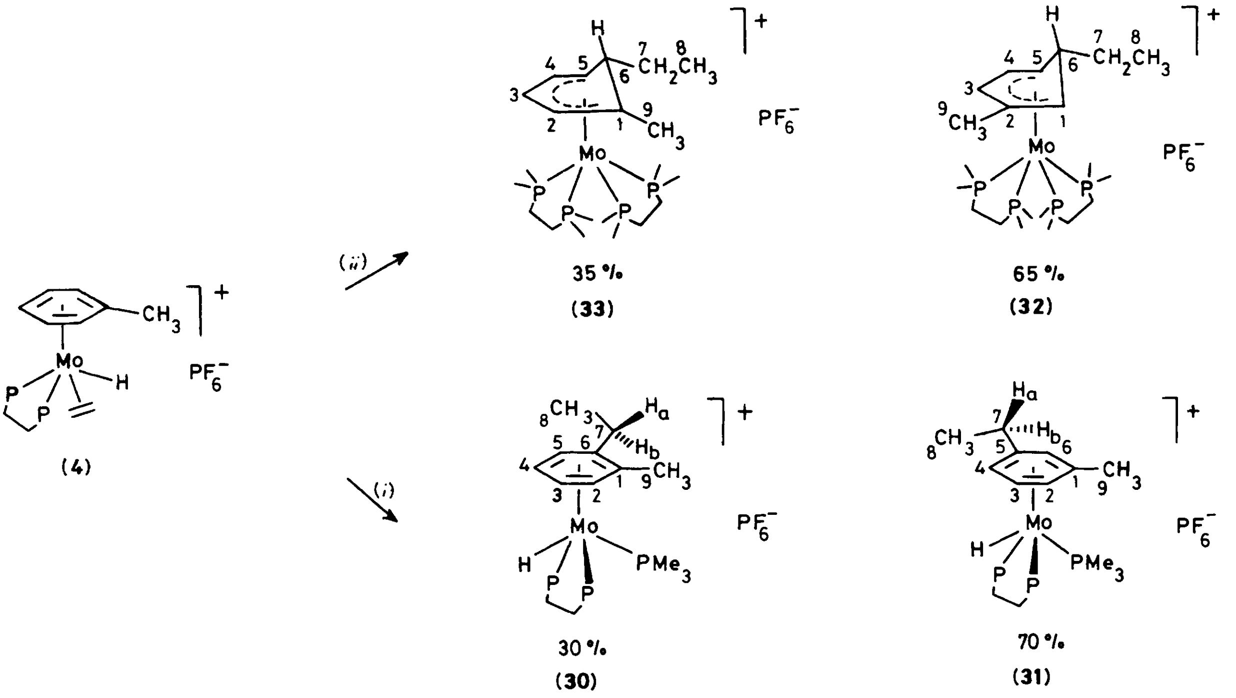


Figure 9. (*a*) Proton n.m.r. spectrum of compounds (**30**) and (**31**). (*b*) Expansion of (*a*) showing the mutually coupled diasterotopic $C_6H_4CH_2CH_3$ protons. Asterisk denotes solvent



Scheme 3. (*i*) pdmp (or pdma) in ethanol under reflux for 3 h, then NH_4PF_6(aq); (*ii*) Na–Hg in thf under ethylene (1 atm) for 18 h; (*iii*) $P(OMe)_3$ and $TlPF_6$ in ethanol, reflux for 3 h, then NH_4PF_6(aq); (*iv*) NH_4PF_6 in water; (*v*) PMe_3 in acetone at r.t.; (*vi*) pdmp in acetone at r.t.



Scheme 4. (*i*) PMe_3 in acetone, yield >80%; (*ii*) dmpe in acetone, >80%

chromium compounds the chemical shift separation of H_a and H_b in the *ortho* isomer is as great as 0.8 p.p.m. However, for the *meta* isomer the resonances for H_a and H_b are coincident. By analogy, the *ortho* isomer is that with the greater diastereotopic chemical shift separation, *viz.* the minor component, **(30)**; consequently **(31)** is the *meta* isomer. This assignment is fully consistent with the ^{13}C n.m.r. spectrum.

The somewhat surprising conclusions are, therefore, that ethyl migration to the position *meta* to a formally electron-releasing methyl group is favoured by a factor of *ca.* 2 over that to the *ortho* position, and that migration to the *para* position does not occur at all.

A similar conclusion is reached from analysis of the products of reaction between **(4)** and dmpe, which gives a mixture of 2- and 1-methyl-6-*endo*-ethylcyclohexadienyl complexes, **(32)** and **(33)** respectively, in the ratio 65:35. Figure 10 shows the ^1H n.m.r. spectrum of this mixture: one-proton multiplets characteristic of dienyl hydrogens appear in the region δ 2.2—5.6 p.p.m., whilst overlapping triplets due to methyl protons of the ethyl groups appear at 0.8 p.p.m. Dissection of this spectrum into the contributions of the individual isomers was aided by a ^1H-^1H COSY-45 spectrum [Figure 11]: off-diagonal elements in the two-dimensional plot indicate coupling, and therefore connectivity, between the associated protons. Two connectivity patterns could be distinguished, though not all the bands in the complex region, δ 1.5—2.2 p.p.m., could be assigned unambiguously. Differentiation between the two regioisomers was based upon the positions of the cyclohexadienyl protons, and upon arguments analogous to those for **(30)** and **(31)**. The diastereotopic methylene protons of the 1-methyl compound **(33)** are separated by 0.3 p.p.m., whereas the resonances of the methylene protons in compound **(32)** are apparently coincident; nevertheless, we presume **(32)** to be the 2-methyl compound.

It is known from studies on several reaction types[22] that co-ordination of an arene ring to a metal centre greatly reduces the effectiveness with which substituent electronic influences are transmitted through the ring, so that the high regioselectivity often exhibited in the chemistry of the free arene is not mirrored in that of its metal η complexes. The directive effects exerted by a ring substituent on the pattern of electrophilic substitution on η-arenetricarbonylchromium complexes have been investigated;[21,23] the results bear, at least qualitatively, on those in the present system, even though the mechanism of substitution in neutral η-arenechromium compounds is more likely to involve direct electrophilic attack at the *exo* face than co-ordination at the metal prior to *endo* migration to the ring.

The present ethylenehydride system would appear to represent an extreme case of *para* deactivation.

Experimental

All reactions and manipulations were performed under nitrogen either by standard Schlenk and vacuum-line techniques or in a glove-box.

All solvents were thoroughly deoxygenated before use by repeatedly shaking them under an active vacuum then admitting nitrogen to the vessel. Generally solvents were predried over molecular sieves and then distilled, under an atmosphere of nitrogen, from potassium (toluene, benzene, tetrahydrofuran), sodium–potassium alloy [diethyl ether, light petroleum (b.p. 40—60 °C)], or phosphorus pentoxide (dichloromethane).

Triethyloxonium tetrafluoroborate (B.D.H.) was washed with several portions of cold diethyl ether to remove acidic impurities, then dried *in vacuo*. [^2H]Tetrafluoroboric acid was prepared by adding $HBF_4{\cdot}OEt_2$ (0.5 cm^3) to D_2O (5 cm^3), then

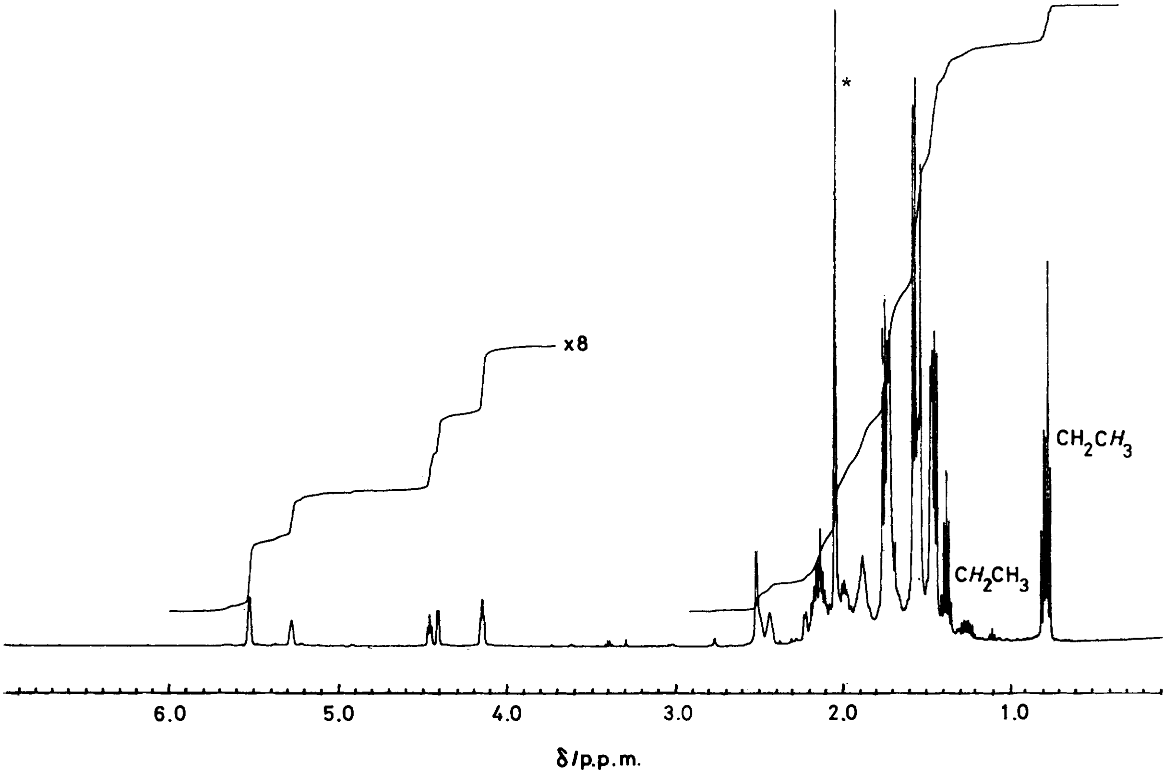


Figure 10. Proton n.m.r. spectrum of compounds **(32)** and **(33)**. Asterisk denotes solvent

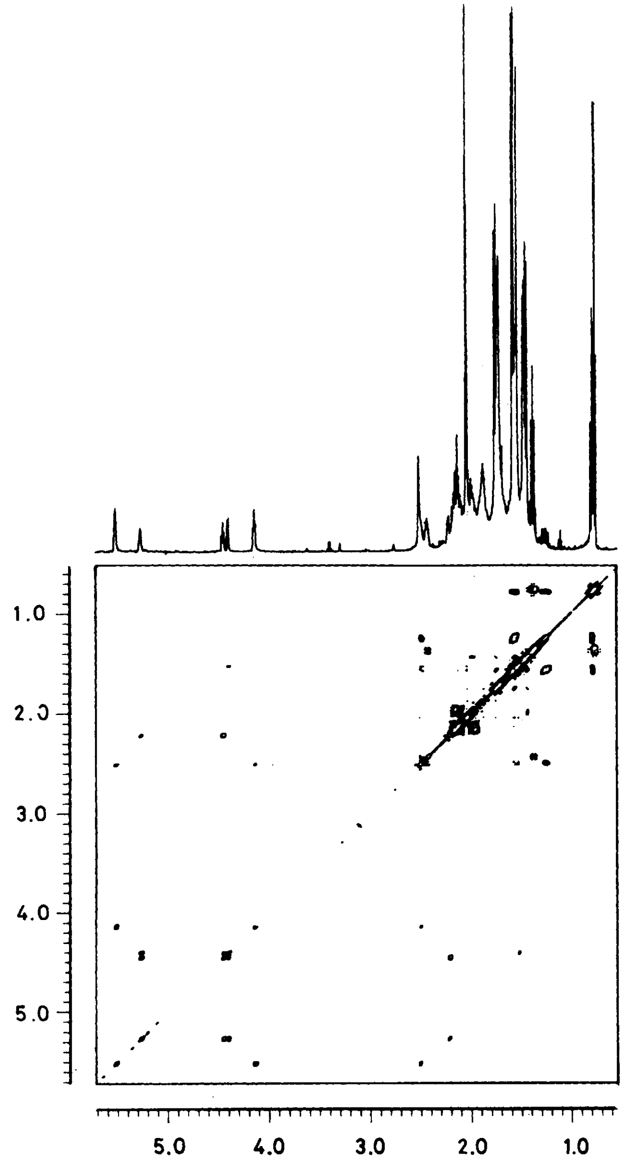


Figure 11. ^1H-^1H COSY n.m.r. spectrum of the mixture of (**32**) and (**33**)

removing the solvent under reduced pressure to give a viscous, ether-soluble liquid.

Microanalyses were performed by the Analysis Department of the Inorganic Chemistry Laboratory, Oxford. Infrared spectra were recorded on either a Pye Unicam SP2000 double-beam grating spectrometer or a Perkin-Elmer 1710 Fourier-transform interferometer. For measurement of photoelectron spectra, a PES Laboratories 0078 spectrometer with a heated inlet system was used. Spectra were calibrated against the ionisation potentials of He, Xe, and N_2. N.m.r. spectra were recorded with the following instruments: ^1H (60 MHz), JEOL PMX-60; (250 MHz), Bruker AM-250; (300 MHz), Bruker WH-300; (500 MHz), Bruker AM-500; ^{13}C (62.8 MHz), ^{31}P (101.2 MHz), and ^2H (38.4 MHz), Bruker AM-250. Spectra were referenced either internally by using the residual protio-solvent resonance (^1H) or the solvent carbon resonance (^{13}C), both relative to tetramethylsilane ($\delta = 0$ p.p.m.), or externally by using trimethyl phosphate in D_2O (^{31}P).

In kinetic experiments, probe temperatures were maintained with the WH-300 temperature controller and were constant within ±0.5 °C. Values quoted are accurate to ±1 °C, and were calibrated by using the linewidth of a standard methanol sample. All multiple-pulse experiments were acquired with standard Bruker software, and were processed by using an ASPECT 2000 or 3000 computer.

The compounds $[\{Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$,[12] $[Mo(\eta\text{-}C_6H_6)(dmpe)(\eta\text{-}C_3H_5)]PF_6$,[12] and $[Mo(\eta\text{-}C_6H_6)(dmpe)(\eta\text{-}C_2H_4)]$[6] were prepared as previously described.

(η-Benzene)[1,2-bis(dimethylphosphino)ethane](η-ethylene)hydridomolybdenum Hexafluorophosphate, (**1**).—To a solution of the compound $[Mo(\eta\text{-}C_6H_6)(dmpe)(\eta\text{-}C_2H_4)]$ (0.8 g, 2.3 mmol) in diethyl ether (40 cm^3) was added, dropwise, a solution of the adduct tetrafluoroboric acid–diethyl ether (1 cm^3) in diethyl ether (20 cm^3), until precipitation of the protonated compound was complete. The pale green solid was collected on a bed of Celite, washed with diethyl ether, and then extracted with acetone (3 × 40 cm^3). To the extract was added a solution of NH_4PF_6 (0.6 g) in water (10 cm^3). Concentration of the resulting solution under reduced pressure gave the product as a yellow powder, which was collected and recrystallized from ethanol–acetone (1:1), washed with ethanol, and finally dried *in vacuo* for 3 h at r.t., yield 0.8 g (71%).

The monodeuteriated analogue (**1D**) (Scheme 1) was prepared similarly using DBF_4 in D_2O.

[1,2-Bis(dimethylphosphino)ethane](η-ethylbenzene)hydrido(trimethylphosphine)molybdenum Hexafluorophosphate, (**2**).—The compound $[Mo(\eta\text{-}C_6H_6)(dmpe)(\eta\text{-}C_2H_4)H]PF_6$ (0.5 g, 1.0 mmol) in acetone (20 cm^3) was treated with an excess of trimethylphosphine (0.5 cm^3) at r.t. for 1 h. The solvent was removed from the resulting red solution under reduced pressure, and the red residue was recrystallized from ethanol–acetone (1:1) to give red crystals, yield 0.48 g (84%).

(η-$[^2H_6]$Benzene)[1,2-bis(dimethylphosphino)ethane](η-ethylene)hydridomolybdenum Hexafluorophosphate, (**1D$_6$**).—This compound was prepared in an overall yield of 12%, by converting $[Mo(\eta\text{-}C_6D_6)_2]$ to $[Mo(\eta\text{-}C_6D_6)(dmpe)(\eta\text{-}C_2H_4)]$ and then subsequent protonolysis. Its purity was confirmed by the ^1H n.m.r. spectrum which was identical to that of the protio-compound but for the absence of the band for bound arene at δ 5.39. The compound $[Mo(\eta\text{-}C_6D_6)_2]$ was itself synthesized by the co-condensation of molybdenum atoms and $[^2H_6]$benzene.

[1,2-Bis(dimethylphosphino)ethane](η-ethylene)hydrido(η-toluene)molybdenum Hexafluorophosphate, (**4**).—This compound was prepared from $[Mo(\eta\text{-}C_6H_5Me)_2]$ by the same route as that for the benzene analogue, (**1**). Yield >60%.

(η-Benzene)[1,2-bis(dimethylphosphino)ethane]hydrido(trimethyl phosphite)molybdenum Hexafluorophosphate, (**5**).—Compound (**1**) (0.10 g, 0.2 mmol) was dissolved in acetone and treated with an excess of trimethyl phosphite (0.3 cm^3). After 20 h at r.t. the solution had become orange; the solvent was removed under reduced pressure and the orange residue washed with diethyl ether (3 × 10 cm^3), then dried *in vacuo*. The product was recrystallized from ethanol–acetone (1:1) to give orange crystals. Yield >80%.

(η-Benzene)[1,2-bis(dimethylphosphino)ethane](carbonyl)hydridomolybdenum Hexafluorophosphate, (**6**).—A solution of compound (**1**) (100 mg) in acetone (25 cm^3) was stirred under carbon monoxide (1.5 atm) for 24 h. Over this time a small amount of a white solid separated. The brown supernatant was filtered, and to it was added ethanol (10 cm^3). Partial removal of

the solvent under reduced pressure gave the product as a yellow-brown solid. This was collected, washed with diethyl ether, and dried *in vacuo*. Yield 40%.

(η-*Benzene*)[1,2-*bis*(*dimethylphosphino*)*ethane*](2,6-*dimethylphenyl isocyanide*)*hydridomolybdenum Hexafluorophosphate*, (**7**).—A solution of compound (**1**) (0.10 g, 0.2 mmol) and 2,6-dimethylphenyl isocyanide (0.10 g, 0.76 mmol) in acetone (15 cm^3) was allowed to stand at r.t. for 3 d, over which time its colour became red. The solvent was removed under reduced pressure, and the red, glassy residue was then washed with diethyl ether (4 × 15 cm^3) and dried *in vacuo*. The product was recrystallized from ethanol to give orange-red crystals. Yield 0.09 g, 74%.

(η-*Benzene*)[1,2-*bis*(*dimethylphosphino*)*ethane*](*trimethylphosphine*)*molybdenum*, (**8**).—A suspension of the compound [Mo(η-C_6H_6)(dmpe)(η-C_3H_5)]PF_6 (0.7, 1.6 mmol) in tetrahydrofuran (50 cm^3) was treated with an excess of trimethylphosphine (0.5 cm^3) and sodium amalgam (20 g, 1%). The mixture was stirred for 12 h at r.t., during which time the suspension dissolved and the solution became orange. The solution was filtered through Celite, and the solvent was removed from the filtrate under reduced pressure giving an orange oil. The product was sublimed from the oils at 130 °C onto a liquid-nitrogen-cooled probe, where it formed as a spectroscopically pure, oily orange solid. It could be used in this form for subsequent experiments, or could be recrystallized from light petroleum (b.p. 40—60 °C) as a red-orange solid. Yield, 0.28 g (44%).

Reaction of [Mo(η-C_6H_6)(dmpe)(PMe_3)], (**8**), *with Methyl Trifluoromethanesulphonate. Formation of* [1,2-*Bis*(*dimethylphosphino*)*ethane*]*hydrido*(η-*toluene*)(*trimethylphosphine*)*molybdenum Hexafluorophosphate*, (**9**), *and Salts of the* (η-*Benzene*)[1,2-*bis*(*dimethylphosphino*)*ethane*]*methyl*(*trimethylphosphine*)*molybdenum Cation*, (**27**).—Compound (**8**) (1.10 g, 2.8 mmol) was dissolved in dichloromethane (10 cm^3) and immediately cooled to 77 K. The sulphonate (0.60 g, 3.7 mmol) was vacuum distilled onto the frozen solution, and the whole was allowed to warm to r.t., upon which the originally orange solution turned rapidly deep red. After 5 min, ethanol (5 cm^3) was added to destroy the excess of reagent, and the solvent was then removed under reduced pressure to give a red oil. This was redissolved in ethanol (10 cm^3), and to the red solution was added NH_4PF_6 (0.80 g) dissolved in water (10 cm^3), causing precipitation of a brown solid. This was collected on a glass frit, washed with water (3 × 25 cm^3), dried partially *in vacuo*, and finally recrystallized from ethanol–acetone (1:1) to give brown microcrystals (two crops, total 1.2 g).

The ^1H n.m.r. spectrum of the product mixture indicated the major components to be [Mo(η-C_6H_6)(dmpe)(PMe_3)Me]PF_6, (**27**), and [Mo(η-C_6H_5Me)(dmpe)(PMe_3)H]PF_6, (**9**), in the molar ratio 40:60.

(η-*Allyl*)(η-*benzene*)[o-*phenylenebis*(*dimethylphosphine*)]*molybdenum Hexafluorophosphate*, (**10**).—The compound [{Mo(η-C_6H_6)(η-C_3H_5)Cl}$_2$] (0.86 g, 1.7 mmol) in ethanol (50 cm^3) was treated with *o*-$C_6H_4(PPh_2)_2$ (0.86 g 3.4 mmol) and the mixture was stirred under reflux for 3 h to give a dark brown solution. The salt NH_4PF_6 (0.5 g, excess) in water (10 cm^3) was added to the filtered solution to give a pale brown precipitate which was filtered off, washed with water (3 × 20 cm^3), and dried *in vacuo* for 3 h. The precipitate was extracted with acetone (50 cm^3) giving a deep orange solution. Addition of an equal volume of ethanol, and cooling to −20 °C, afforded bright orange crystals, which were washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield 1.25 g, 65%.

(η-*Allyl*)(η-*benzene*)[o-*phenylenebis*(*dimethylarsine*)]*molybdenum Hexafluorophosphate*, (**11**).—The compound [{Mo(η-C_6H_6)(η-C_3H_5)Cl}$_2$] (0.57 g, 1.2 mmol) in ethanol (50 cm^3) was treated with *o*-$C_6H_4(AsPh_2)_2$ (0.65 g, 2.3 mmol) and the mixture was stirred under reflux for 3 h to give a dark brown solution. The salt NH_4PF_6 (0.5 g) in water (10 cm^3) was added to the filtered solution to give a pale brown precipitate which was filtered off, washed with water (3 × 20 cm^3), and dried *in vacuo* for 3 h. The precipitate was extracted into acetone (50 cm^3) to give a red solution. An equal volume of ethanol was added, and cooling to −20 °C afforded dark orange crystals which were washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield 1.25 g, 85%.

(η-*Allyl*)(η-*benzene*)*bis*(*trimethyl phosphite*)*molybdenum Hexafluorophosphate*, (**12**).—The compound [{Mo(η-C_6H_6)(η-C_3H_5)Cl}$_2$] (1.18 g, 4.8 mmol), $P(OMe)_3$ (1 g), and $TlBF_4$ (0.5 g) in ethanol (50 cm^3) were refluxed for 3 h to give a brown precipitate in a pale pink solution. The suspension was filtered, washed with hot water to remove excess $TlBF_4$, and dried *in vacuo* for 4 h. Extraction with acetone left grey insoluble TlCl and an orange solution, which was treated with NH_4PF_6 (0.5 g) in water (10 cm^3). An equal volume of ethanol was added and the solution was concentrated to half volume, giving an orange precipitate of the PF_6 salt. This was filtered off and the orange powder was washed with water (3 × 20 cm^3) and dried *in vacuo* for 4 h. It was then extracted into acetone, and an equal volume of ethanol was added; cooling to −20 °C afforded bright orange crystals, presumably [Mo(η-C_6H_6)(η-C_3H_5){$P(OMe)_3$}Cl]. Yield 2.5 g, 85%.

A suspension of these orange crystals (1.8 g, 4.8 mmol), trimethyl phosphite (1 cm^3) and thallium tetrafluoroborate (0.5 g) in ethanol (50 cm^3) was refluxed for 3 h. The resulting pink solution containing a brown precipitate was filtered and the residue was washed with hot water (2 × 10 cm^3) and dried *in vacuo*. The residue was extracted with acetone and the orange solution was filtered from the grey TlCl residues. Aqueous ammonium hexafluorophosphate (0.5 g in 10 cm^3 water) was added to the orange filtrate and the solution was concentrated under reduced pressure. Orange crystals precipitated which were collected, washed with water (3 × 20 cm^3), and dried *in vacuo*. The product was recrystallised from acetone–ethanol as bright orange crystals. Yield 2.5 g, 85%.

(η-*Benzene*)(η-*ethylene*)[o-*phenylenebis*(*dimethylphosphine*)]*molybdenum*, (**13**), *and* (η-*Benzene*)(η-*ethylene*)*hydrido*[o-*phenylenebis*(*dimethylphosphine*)]*molybdenum Hexafluorophosphate*, (**15**).—A suspension of [Mo(η-C_6H_6)(pdmp)(η-C_3H_5)]PF_6 (0.42 g, 0.81 mmol) in tetrahydrofuran (50 cm^3) was treated with 1% Na–Hg amalgam (10 g) and the mixture was stirred under an ethylene atmosphere for 18 h to give a dark brown solution. The brown solution was isolated, the solvent was removed under reduced pressure, and the residue was extracted into light petroleum (b.p. 40—60 °C) to give a cherry-red solution. Cooling to −20 °C afforded dark crimson crystals of (**13**). Yield 0.12 g, 40%. A solution of [Mo(η-C_6H_6)(pdmp)(η-C_2H_4)], (**13**), in diethyl ether (30 cm^3) was titrated with a solution of $HBF_4 \cdot Et_2O$ (1 g HBF_4 in 40 cm^3 Et_2O). The reaction was complete when a pale green powder had precipitated and the supernatant had changed from a red to a clear solution. The supernatant was decanted and the powder dried *in vacuo*. It was then extracted into acetone and treated with NH_4PF_6 (0.5 g) in water (10 cm^3). An equal volume of ethanol was added and the solution concentrated to half volume, at which point all of the pale green hexafluorophosphate salt precipitated. This suspension was filtered and the green powder washed with water (3 × 20 cm^3) and dried *in vacuo* for 4 h. It was then extracted into acetone and an equal volume of ethanol was added; cooling to −20 °C afforded a pale green powder which was washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield >80%. The powder was stable indefinitely, but $t_{\frac{1}{2}}$ in solution at r.t. was found to be *ca.* 24 h; n.m.r. samples were stored at −80 °C.

(η-*Benzene*)(η-*ethylene*)[o-*phenylenebis*(*dimethylarsine*)]-*molybdenum*, (**14**), *and* (η-*Benzene*)(η-*ethylene*)*hydrido*[o-*phenylenebis*(*dimethylarsine*)]*molybdenum Hexafluorophosphate*, (**16**).—A suspension of [Mo(η-C_6H_6)(pdma)(η-C_3H_5)]-PF_6 (0.7 g, 1.1 mmol) in thf (50 cm^3) was treated with sodium amalgam (1%, 10 g) and the mixture was stirred under an atmosphere of ethylene for 18 h. The resulting dark red solution was separated and the solvent was removed under reduced pressure. The residue was extracted with light petroleum (b.p. 40—60 °C, 25 cm^3) and, after filtration, the filtrate was concentrated and cooled to −20 °C giving brick-red crystals of compound (**14**). Yield 0.45 g, 85%. A solution of [Mo(η-C_6H_6)(pdma)(η-C_2H_4)], (**14**) (0.4 g), in diethyl ether (30 cm^3) was titrated with a solution of $HBF_4 \cdot Et_2O$ (1 g HBF_4 in 40 cm^3 ether). The reaction was complete when an olive-green powder had precipitated and the supernatant had changed from a red to a clear solution. The supernatant was decanted and the powder was dried *in vacuo*, extracted into acetone, and treated with NH_4PF_6 (0.5 g) in water (10 cm^3). An equal volume of ethanol was added and the solution concentrated to half volume, at which point all of the olive-green PF_6^- salt precipitated. This suspension was filtered and the green powder washed with water (3 × 20 cm^3) and dried *in vacuo* for several hours. It was then extracted into acetone, and an equal volume of ethanol was added; cooling to −20 °C afforded an olive-green powder which was washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield *ca.* 85%. The solid was stable indefinitely, but $t_{\frac{1}{2}}$ in solution at room temperature was *ca.* 12 h; n.m.r. samples were stored at −80 °C.

(η-*Ethylbenzene*)*hydrido*[o-*phenylenebis*(*dimethylphosphine*)]-(*trimethylphosphine*)*molybdenum Hexafluorophosphate*, (**17**).—The compound [Mo(η-C_6H_6)(pdmp)(η-C_2H_4)H]PF_6 (0.8 g, 1.5 mmol) in acetone (20 cm^3) was treated with PMe_3 (1 cm^3) at −196 °C. On warming to r.t. and shaking the mixture, the colour changed from green to yellow to orange to red over a period of *ca.* 3 min. The solvent was removed under reduced pressure, and the residue was dried *in vacuo* for 4 h. It was then washed with light petroleum (b.p. 40—60 °C) to remove excess of PMe_3, and extracted into acetone. An equal volume of ethanol was added, and cooling to −20 °C afforded a red powder which was washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield 0.7 g, 65%.

(η-*Ethylbenzene*)*hydrido*[o-*phenylenebis*(*dimethylarsine*)](*trimethylphosphine*)*molybdenum Hexafluorophosphate*, (**18**).—The compound [Mo(η-C_6H_6)(pdma)(η-C_2H_4)]PF_6 (0.15 g, 0.2 mmol) in acetone (20 cm^3) was treated with PMe_3 (1 cm^3) at −196 °C. On warming to r.t. and shaking the mixture, the colour changed from green to yellow to orange to red over a period of *ca.* 10 min. Solvent was removed under reduced pressure, and the residue was washed with light petroleum (b.p. 40—60 °C) to remove excess of PMe_3, and was then extracted into acetone. Addition of an equal volume of ethanol, and cooling to −40 °C, afforded a brown powder which was washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield 0.07 g, 55%.

(η-endo-6-*Ethylcyclohexadienyl*)*bis*[o-*phenylenebis*(*dimethylphosphine*)]*molybdenum Hexafluorophosphate*, (**19**).—The compound [Mo(η-C_6H_6)(pdmp)(η-C_2H_4)H]PF_6 (0.14 g, 0.25 mmol) in acetone (30 cm^3) was treated with pdmp (0.05 g, 0.25 mmol) to give an orange solution The solvent was removed under reduced pressure and the residue was washed with light petroleum (b.p. 40—60 °C) to remove any unreacted pdmp. Extraction of the residue into acetone gave an orange solution. An equal volume of ethanol was added, and cooling to −20 °C afforded dark orange crystals of [Mo(η^5-C_6H_6Et)$(pdmp)_2$]PF_6 which were washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield 0.07 g, 40%.

Formation of [1,2-*Bis*(*dimethylphosphino*)*ethane*](η-*cyclohexadienyl*)(η-*ethylene*)(*trimethylphosphine*)*molybdenum Hexafluorophosphate, a Mixture of Conformational Isomers*, (**23**) *and* (**24**).—A solution of compound (**1**) in [$^2H_6$]acetone (0.15 mol l^{-1}) was transferred to an n.m.r. sample tube, and chilled in liquid nitrogen. A *ca.* five-fold excess of trimethylphosphine (*ca.* 0.03 g) was transferred by vacuum distillation onto the frozen mixture. The mixture was warmed to r.t. and after 2 min it was transferred directly into the n.m.r. probe maintained at −30 °C. The spectrum showed that all the starting compound (**1**) had been consumed, to generate (**23**) and (**24**) and only a negligible amount of (**2**).

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*](η-endo-6-*ethylcyclohexadienyl*)*molybdenum Hexafluorophosphate*, (**29**).—A solution of compound (**1**) (0.40 g, 0.8 mmol) in acetone (20 cm^3) was treated with an excess of dmpe (0.25 cm^3). After 10 h at r.t. the solution had become orange; the solvent and excess of reagent were removed under reduced pressure. The residual orange solid was then washed with light petroleum (b.p. 40—60 °C, 3 × 30 cm^3), and dried *in vacuo*. It was recrystallised from ethanol–acetone (1:1) to give orange crystals, 0.45 g (86%).

[1,2-*Bis*(*dimethylphosphino*)*ethane*](η-1-*ethyl*-2-*methylbenzene*)*hydrido*(*trimethylphosphine*)*molybdenum Hexafluorophosphate*, (**30**), *and* [1,2-*Bis*(*dimethylphosphino*)*ethane*](η-1-*ethyl*-3-*methylbenzene*)*hydrido*(*trimethylphosphine*)*molybdenum Hexafluorophosphate*, (**31**).—Compound (**4**) was treated with trimethylphosphine in acetone, in the same manner as its η-benzene analogue, to give a mixture of isomeric compounds, (**30**) and (**31**), in the molar ratio 30:70.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*](η-6-endo-*ethyl*-2-*methylcyclohexadienyl*)*molybdenum Hexafluorophosphate*, (**32**), *and Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*](η-6-endo-*ethyl*-1-*methylcyclohexadienyl*)*molybdenum Hexafluorophosphate*, (**33**).—A solution of compound (**4**) in acetone was treated with dmpe in the same manner as its η-benzene analogue to give, as orange crystals, an isomeric mixture of (**32**) and (**33**).

Reaction of [Mo(η-C_6H_6)(dmpe)(η-C_2H_4)H]PF_6, (**1**), *with* D_2O: *attempted Exchange of Metal-bound Hydrogen*.—A sample of compound (**1**) was made up in [$^2H_6$]acetone–D_2O (80:20 v/v), and the relative intensity of the broad five-proton singlet at 0.20 p.p.m. ($CH_2=CH_2$ + Mo–H) was monitored by ^1H n.m.r. spectroscopy (60 MHz). Over 10 h the band decreased in intensity to about half its initial value. However, it was evident, from examination of the rest of the spectrum, that some decomposition of the compound was taking place. If exchange of the metal–bound hydrogen with the solvent occurs at all under these conditions, it is very slow ($t_{\frac{1}{2}}$ < 600 min). Similarly, (**1D**) in acetone-H_2O showed no formation of (**1**).

Reaction of [Mo(η-C_6H_5Et)(dmpe)(PMe_3)H]PF_6, (**2**), *with* D_2O: *attempted Exchange of Metal-bound Hydrogen*.—A sample of compound (**2**) was made up in [$^2H_6$]acetone–D_2O (80:20 v/v) in the presence of *ca.* 1 mol equivalent of trimethylphosphine. By monitoring the relative integral of the hydride resonance in the ^1H n.m.r. spectrum, it could be deduced that negligible exchange (<4%) of the metal-bound hydrogen with the solvent occurred over 14 h.

Reaction of [Mo(η-C_6H_6)(dmpe)(PMe_3)], (**8**), *with Triethyloxonium Tetrafluoroborate.*—All glassware for this experiment was flame-dried under vacuum to minimise the possible hydrolysis of the reagent by adventitious water. Compound (**6**) decomposes within hours in dichloromethane at r.t.; it was therefore dissolved in that solvent (0.25 g, 0.62 mmol in 10 cm^3) at -30 °C, at which temperature it is stable. To it was added a solution of [OEt_3]BF_4 (0.12 g, 0.63 mmol) in dichloromethane (10 cm^3) also chilled to -30 °C. The mixture was allowed to warm to r.t. over 15 min, during which time its colour changed from orange to red. The solvent was then removed under reduced pressure, to give a brown solid, which was washed with light petroleum (b.p. 40—60 °C, 2 × 20 cm^3) and dried *in vacuo*. The solid was redissolved in acetone (10 cm^3) and to the solution was added NH_4PF_6 (0.25 g) dissolved in water (5 cm^3). Evaporation of the solvent led to precipitation of a red-brown solid, which was filtered off and recrystallized from ethanol–acetone (1:1) to give red-brown microcrystals, 0.25 g. The ^1H n.m.r. spectrum (300 MHz in [$^2H_6$]acetone) showed that the product consisted entirely of [Mo(η-C_6H_6)(dmpe)(PMe_3)H]PF_6, (**25**), and [Mo(η-C_6H_5Et)(dmpe)(PMe_3)H]PF_6, (**2**), in the molar ratio 40:60. The proportion of the former compound, derived from protonation of (**8**), was greater in reactions in which less care was taken to exclude water.

Kinetic Procedures.—(a) *Kinetics of ethylene insertion by magnetisation transfer.* Proton n.m.r. (300 MHz) magnetisation transfer (m.t.) experiments involving [Mo(η-C_6H_6)(dmpe)(η-C_2H_4)H]PF_6, (**1**), and [Mo(η-C_6H_6)(pdma)(η-C_2H_4)H]PF_6, (**16**), were performed with a Bruker WH 300 spectrometer and associated software.

The relaxation times, T_1, for the dmpe-methyl protons in (**1**), and for the ethylene and hydride protons in (**16**), were estimated at each temperature prior to performing the m.t. experiment by using the standard inversion-recovery method.[24] It was necessary to know values of T_1 both to be able to ensure that a sufficient relaxation delay would be used in the m.t. acquisition, and to judge the validity of approximations used in subsequent calculations.

Selective peak inversion for m.t. experiments was achieved by using the low-power transmitter, suitably attenuated (typically to 20L in HG mode) to produce pulses of 0.01—0.02 s duration. Inversion was followed by a variable delay time, *t*, then a $\pi/2$ observation pulse: typically, 16 transients were accumulated for each value of *t*, which was selected automatically from the variable delay list, VD.

Nuclear magnetisations were assumed to be proportional to peak heights, which, for the purposes of calculation were normalised to their values at equilibrium (*i.e.* after $8T_1$). Graphical analyses of the variation with delay time for inverted- and exchanging-peak intensities was performed according to the magnetisation equations given in ref. 25. The justifiable assumption was made that nuclear Overhauser enhancement effects, between the exchanging nuclei in both compounds (**1**) and (**16**), were negligible.[26] Errors in rate constants extracted from the analyses were, unless otherwise stated, taken to be those propagated by varying the peak-height data within their error limits, and represent approximately one standard deviation.

(b) *Kinetics of ethylene insertion from coalescence data.* Estimates of the coalescence temperatures (T_c) for the pairs of exchanging dmpe-methyl protons in compound (**1**) were made from the variable-temperature spectra. The peak separation in the slow-exchange limit ($\Delta\nu$) was that measured at -60 °C. The equation $k_c = \pi\Delta\nu/\sqrt{2}$ was used to determine the rate constant at coalescence; the error was calculated from the estimated errors in measurement of T_c and $\Delta\nu$.

(c) *Kinetics of the reaction between compound* (**1**) *and trimethylphosphine.* Substrate concentrations were typically 0.07—0.10 mol l^{-1}, and reactions were run under pseudo-first-order conditions with a five- to ten-fold excess of PMe_3. Benzene (*ca.* 0.30 mol l^{-1}) was included as an internal standard of known concentration, from which, by using relative integrals, the concentrations of the other species present in solution could be calculated during a run. Since the kinetics was pseudo-first-order, it was in fact not necessary to know absolute concentrations for the extraction of rate constants. However the investigation of the rate dependence on the concentration of PMe_3 did require that absolute values were known.

N.m.r. samples were prepared in batches from a stock solution of compound (**1**) containing a known weight of benzene. In the preparation of the stock solution, the solvent and benzene were transferred by vacuum distillation into an ampoule containing the substrate, and were weighed by difference. The approximation was made, in the calculation of concentrations, that the density of final solution was the same as that of the solvent, [$^2H_6$]acetone. Samples were made up immediately from the stock solution to minimise the effect of differential evaporation of solvent and standard. Trimethylphosphine was vacuum distilled into the sample tube prior to the flame-sealing step; glass bulbs of known volume were used to gauge roughly the amount of PMe_3 vapour (10—20 cm^3 at 25 °C) being transferred. The samples were stored in liquid nitrogen until required.

Immediately before a kinetic run the sample was warmed in a solid CO_2–acetone slurry to -78 °C, at which temperature the reactants are still inert. The sample was allowed 2 min to equilibrate in the n.m.r. probe before the first spectrum was recorded; temperatures were in the range -30 to $+30$ °C. Successive spectra were then accumulated, each with eight transients and a relaxation delay of 2 s, and stored on disc. Since the reactions were generally relatively slow, the error introduced by the fact that spectra were not measured instantaneously was very slight.

The kinetics was followed by monitoring the heights of appropriate peaks belonging to reactants or products as the reactions proceeded. Peak heights, *h*, were standardised, before being used in rate calculations, by dividing them by the integral of the benzene standard. First-order rate constants were then obtained from plots of $\ln(h - h_\infty)$ *vs.* *t*; at least eight data points per plot were used, and the data were rejected if the correlation was poor ($r < 0.998$). Reactions were monitored for *ca.* 3 half-lives.

Estimates of the error in each rate constant had to take into account not only that propagated by varying the peak-height data within their error limits, but also the limited reliability of temperature control (± 0.5 °C). Values of 10—15% for the relative error are, we feel, generous assessments of these combined factors.

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References

1 F. W. S. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1324; G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 1974, 516; E. Cannillo and C. K. Prout, *Acta Crystallogr., Sect. B.*, 1977, **33**, 3916.

2 G. A. Sim, D. I. Woodhouse, and G. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1979, 629.

3 M. Brookhart, A. R. Pinhas, and A. Lukacs, *Organometallics.*, 1982, **1**, 1730.

4 H. Werner and W. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 794; H. Werner, *ibid.*, 1983, **22**, 927.

5 R. Barone, M. Chanon, and M. L. H. Green, *J. Organomet. Chem.*, 1980, **185**, 85.

6 M. Canestrani, M. L. H. Green, and A. Izquierdo, *J. Chem. Soc., Dalton Trans.*, 1984, 2795.

7 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.

8 P. A. Newman, D. Phil. Thesis, Oxford, 1985.

9 N. H. Doherty and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107**, 2760.

10 D. C. Roe, *J. Am. Chem. Soc.*, 1983, **105**, 7770.

11 M. Brookhart, M. L. H. Green, and R. B. A. Pardy, *J. Chem. Soc., Chem. Commun.*, 1983, 691.

12 M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 2177.

13 M. Brookhart, A. R. Pinhas, and A. Lukacs, *Organometallics*, 1982, **1**, 1730.

14 H. Gunther, 'NMR Spectroscopy—an Introduction,' Wiley, New York, 1980.

15 M. L. H. Green and P. A. Newman, unpublished work.

16 S. G. Davies, J. Hibberd, and S. J. Simpson, *J. Organomet. Chem.*, 1983, **246**, C16.

17 H. Werner and W. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 794; H. Werner and R. Feser, *J. Organomet. Chem.*, 1982, **232**, 351.

18 F. W. S. Benfield, N. J. Cooper, and M. L. H. Green, *J. Organomet. Chem.*, 1974, **76**, 49.

19 S. G. Davies, S. D. Moon, S. J. Simpson, and S. E. Thomas, *J. Chem. Soc., Dalton Trans.*, 1983, 1805.

20 M. Brookhart and W. Lamanna, *J. Am. Chem. Soc.*, 1980, **102**, 3490; C. P. Lewis, W. Kitching, A. Eisenstadt, and M. Brookhart, *ibid.*, 1979, **101**, 4896.

21 W. R. Jackson and W. B. Jennings, *J. Chem. Soc. B*, 1969, 1221.

22 W. E. Silverthorn, *Adv. Organomet. Chem.*, 1975, **13**, 47; F. van Meurs, A. J. Hoefnagel, B. M. Wepster, and H. van Bekkum, *J. Organomet. Chem.*, 1977, **142**, 299; W. E. Watts, in 'Comprehensive Organometallic Chemistry,' Pergamon, Oxford, 1982, vol. 8.

23 G. E. Herberich and E. O. Fischer, *Chem. Ber.*, 1962, **95**, 2803.

24 T. C. Farrer and E. D. Becker, 'Pulse and Fourier Transform NMR,' Academic press, New York, 1971, pp. 20—22.

25 I. D. Campbell, C. M. Dobson, R. G. Ratcliffe, and R. J. P. Williams, *J. Magn. Reson.*, 1987, **29**, 397.

26 J. Sandstrom, 'Dynamic NMR Spectroscopy,' Academic Press, New York, 1982, p. 109.

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