Synthesis of $[Mo(\eta\text{-}C_5H_4Pr^i)(PR_3)_2H_3][R_3 = Me_3$ or $Me_2Ph)$, $[Mo(\eta\text{-}C_5H_4Pr^i)(Pr^i_2PCH_2CH_2PPr^i_2)H_3]$, and Analogues and Their Ability to catalyse the Photoinduced Hydrogen–Deuterium Exchange of Carbon–Hydrogen Bonds; Crystal Structure of $[\{Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}Cl)_2\}_2]$ *

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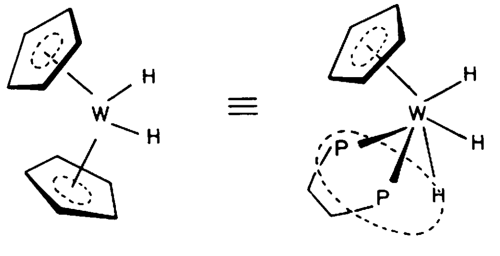
Hydrochlorination of $[Mo(\eta\text{-}C_6H_6)(\sigma,\eta^5\text{-}C_5H_4CMe_2)]$ gives $[\{Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}Cl)_2\}_2]$ for which the crystal structure has been determined. This compound is a precursor to $[Mo(\eta\text{-}C_5H_4Pr^i)(PR_3)_2Cl_2]$ ($R_3 = Me_3$ or Me_2Ph), $[Mo(\eta\text{-}C_5H_4Pr^i)(Pr^i_2PCH_2CH_2PPr^i_2)_2Cl_2]$, $[Mo(\eta\text{-}C_5H_4Pr^i)(Me_2PCH_2CH_2PMe_2)_2][PF_6]$, $[Mo(\eta\text{-}C_5H_4Pr^i)(Me_2PCH_2CH_2PMe_2)_2H][PF_6]$, $[Mo(\eta\text{-}C_5H_4Pr^i)\text{-}\mathit{trans}\text{-}(PMe_3)_2Cl\text{-}\mathit{cis}\text{-}H_2]$, $[Mo(\eta\text{-}C_5H_4Pr^i)(PR_3)_2H_3]$, and $[Mo(\eta\text{-}C_5H_4Pr^i)(PMe_3)_2O][PF_6]$. Photolysis of $[Mo(\eta\text{-}C_5H_5)(Me_2PCH_2CH_2PMe_2)H_3]$ in deuteriobenzene together with the substrates $(CH_3)_2O$, $CH_3CO_2CH_3$, toluene, mesitylene, ferrocene, bis(η-toluene)tungsten, and other organometallic compounds causes hydrogen–deuterium exchange between the C_6D_6 and some or all of the substrate hydrogens. The $[Mo(\eta\text{-}C_5H_4Pr^i)(PR_3)_2H_3]$ derivatives are less active catalysts towards photoinduced H–D exchange reactions.

The 16-electron molecule tungstenocene, $[W(\eta\text{-}C_5H_5)_2]$, has been shown to insert into carbon–hydrogen bonds of many differing compounds giving isolable hydrido compounds $[W(\eta\text{-}C_5H_5)_2(R)H]$, where R = substituted-alkyl or -aryl.[1–6] Tungstenocene can be prepared both photochemically and thermally.[4,6] However, no evidence was obtained for the insertion of tungstenocene into the C–H bonds of alkanes, although it is probable that tungstenocene is capable of such reactions. The failure to observe these reactions, or to isolate alkyl–hydride derivatives is likely to be due either to their photochemical instability, or to their instability at the temperatures required to generate tungstenocene, for example, by elimination of methane from $[W(\eta\text{-}C_5H_5)_2(Me)H]$.[4] Photolysis of tungstenocene in cyclohexane generates the tungstenocene dimer $[\{W(\eta\text{-}C_5H_5)(\mu\text{-}\sigma{:}\eta^5\text{-}C_5H_4)H\}_2]$ which is formed by attack of tungstenocene on the C–H bonds of the tungstenocene precursor, namely $[W(\eta\text{-}C_5H_5)_2H_2]$.[7]

In a continuing search for transition-metal compounds which would insert into the C–H bonds of alkanes we set out to synthesise molecules in which the metal centre would be likely to have similar properties to those of tungstenocene.

Parshall and co-workers[8] have shown that transition-metal polyhydrides such as $[Nb(\eta\text{-}C_5H_5)_2H_3]$ catalyse hydrogen–deuterium exchange between dihydrogen and deuteriobenzene, and other aromatic C–H systems. Therefore, we decided to synthesise a transition-metal trihydride where the metal centre had the potential for C–H activation. Even if it proved impossible to isolate hydrido-alkyl products formed by metal insertion into the C–H bond, evidence for this reaction occurring would arise from observation of H–D exchange on the alkane.

The molecules designed for initial study were $[M(\eta\text{-}C_5R_5)(dmpe)H_3]$, where M = Mo or W and dmpe = $Me_2PCH_2CH_2PMe_2$. The basis for this choice was that the combination of dmpe and a hydrogen ligand gives a five-electron system which has substantial electron-releasing properties coupled with a relatively compact size. In other words, the combination (dmpe)H would approximately resemble the $\eta\text{-}C_5H_5$ ligand in electronic, and to some extent, steric properties, see below.



The original synthesis of $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$, (1), is described elsewhere.[9] Only very recently have we been able to synthesise the tungsten analogue.[10] In this paper we describe the photochemically induced activation of a variety of carbon–hydrogen bonds by compounds of the type $[Mo(\eta\text{-}C_5H_4R)(PR_3)_2H_3]$. Brief communications of part of this work have been published.[11,12]

Results

Synthesis of the Compounds $[Mo(\eta\text{-}C_5H_4Pr^i)(PR_3)_2H_3]$ *and Associated Chemistry.*—Treatment of the previously described[11–13] $[Mo(\eta\text{-}C_6H_6)(\sigma,\eta^5\text{-}C_5H_4CMe_2)]$, (2), with an excess of hydrogen chloride gave a highly air-sensitive, pink-brown solid, which was soluble in toluene and light petroleum. The data in Table 1 and a crystal-structure determination show the solid to be the dimer $[\{Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}Cl)_2\}_2]$, (3).

The molecular structure of (3) is shown in Figure 1. The structure consists of dimeric units, $[\{Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}Cl)_2\}_2]$, about centres of symmetry. Each dimer contains terminal η-isopropylcyclopentadienyl moieties, four bridging Cl, and a Mo–Mo bond. The intramolecular Mo–Mo distance of 2.607(1)

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* Tetra-μ-chloro-bis[(η-isopropylcyclopentadienyl)molybdenum(III)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. units employed: G = 10^{-4} T, atm = 101 325 Pa.

Table 1. Analytical and spectroscopic data

	Compound	Colour	Analysis (%)[a]		N.m.r. data[b]
			C	H	
(3)	$[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mu\text{-}\mathrm{Cl})_2\}_2]$	Pink-brown	35.3 (35.0)	4.1[c] (4.0)	^{1}H: 6.00, 5.95 (2 H, 2 H, t, t, C_5H_4), 1.66 (1 H, spt, CH), 0.97 (6 H, d, CMe_2)[d]
(4)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\eta\text{-}\mathrm{C_6H_6})\mathrm{Cl}]$	Red[e]			^{1}H: only the signals due to (4) are given: 4.58, 4.32 (2 H, 2 H, br s, br s, C_5H_4), 4.06 (6 H, s, C_6H_6), 2.62 (1 H, c, CH), 1.19 (6 H, d, CMe_2)[d]
(5)	$[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CHPh_2})(\mu\text{-}\mathrm{Cl})_2\}_2]$	Brown	54.2 (54.3)	3.8[f] (3.7)	^{1}H: 7.55 (4 H, c, *o*-C_6H_5), 7.35 (4 H, c, *m*-C_6H_5), 7.24 (2 H, c, *p*-C_6H_5), 6.37, 6.16 (2 H, 2 H, t, t, C_5H_4), 4.08 (1 H, s, CH)[g]
(6)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{PMe_3})_2\mathrm{Cl_2}]$[h]	Red	38.9 (39.4)	6.9[i] (6.8)	
(7)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{PMe_2Ph})_2\mathrm{Cl_2}]$[j]	Red	52.0 (52.0)	6.0[k] (6.0)	
(8)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{dmpe})_2\mathrm{H}][\mathrm{PF_6}]_2$	Yellow	30.6 (30.2)	5.7 (5.8)	^{1}H: 5.42, 5.12 (2 H, 2 H, c, c, C_5H_4), 2.76 (1 H, spt, CH), 2.47—2.12 (8 H, c, PCH_2CH_2P), 1.94, 1.91 (12 H, 12 H, d, d, PMe), 1.36 (6 H, d, CMe_2), −2.16 [1 H, qnt, *J*(P–H), 47.6, Mo–H][l]
(9)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{dmpe})_2][\mathrm{PF_6}]$	Yellow	36.9 (37.0)	7.0 (6.6)	^{1}H: 4.64, 4.47 (2 H, 2 H, br s, br s, C_5H_4), 2.31 (1 H, spt, CH), 1.90 (8 H, c, PCH_2CH_2P), 1.71, 1.49 (12 H, 12 H, c, c, PMe), 1.17 [6 H, d, CMe_2][l]
(10)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{dippe})\mathrm{Cl_2}]$	Red	48.9 (49.3)	8.2[m] (8.0)	
(11)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})$-*trans*-$(\mathrm{PMe_3})_2\mathrm{Cl}$-*cis*-$\mathrm{H_2}]$	Orange	42.7 (42.8)	7.7[n] (7.9)	^{1}H at r.t.: 4.32 (2 H, br s, C_5H_4), 3.71 (2 H, qnt, C_5H_4), 2.73 (1 H, spt, CH), 1.26 (24 H, c, $2PMe_3$, CMe_2)[d] At −60 °C: 4.49 (2 H, br s, C_5H_4), 3.83 (2 H, br s, C_5H_4), 3.08 (1 H, c, CH), 2.13 [dt, part of the triplet under the PMe_3 band, *J*(P–H) 64, *J*(H–H) 12, Mo–H], 1.85 (24 H, br, $2PMe_3$, CMe_2), −6.02 [dt, *J*(P–H) 29, *J*(H–H) 12, Mo–H][o,p] At −10 °C: 4.49 (2 H, br s, C_5H_4), 3.83 (2 H, qnt, C_5H_4), 3.08 (1 H, spt, CH), 1.85 [24 H, c, $2PMe_3$, CMe_2], −6.01 [broad shoulder (hardly detectable), Mo–H] At +50 °C: 4.53 (2 H, br, C_5H_4), 3.92 (2 H, qnt, C_5H_4), 2.87 (1 H, sp, CH), −1.93 [2 H, t, *J*(P–H) 46, MoH_2][l] ^{31}P at r.t.: 9.1 (s)[o] At −20 °C: 9.1 (s)[o] At −60 °C: 10.0 (s)[o]
(12)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{PMe_3})_2\mathrm{H_3}]$	Yellow[q]			^{1}H at r.t.: 4.32, 4.15 (2 H, 2 H, br s, br s, C_5H_4), 2.64 (1 H, sp, CH), 1.28 (24 H, c, $2PMe_3$, CMe_2), −5.60 [3 H, t, *J*(P–H) 40.5, MoH_3][d,r]
(13)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{PMe_2Ph})_2\mathrm{H_3}]$	Yellow	59.4 (59.8)	7.3[s] (7.5)	^{1}H: 7.64 (4 H, c, *o*-C_6H_5), 7.15 (presence of residual C_6D_5H does not permit the integration, c, *m*-C_6H_5), 7.05 (2 H, c, *p*-C_6H_5), 4.10, 3.86 (2 H, 2 H, br s, br s, C_5H_4), 2.60 (1 H, spt, CH), 1.68 [12 H, d, *J*(P–H) 7.4, $2PMe_3$], 1.21 (6 H, d, CMe_2), −5.14 [3 H, t, *J*(P–H) 40.6, Mo–H_3][d]
(14)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{dippe})\mathrm{H_3}]$	Orange	56.3 (56.4)	9.7[t] (9.8)	^{1}H: 4.89, 4.45 (2 H, 2 H, s, s, C_5H_4), 2.76 (1 H, spt, CH), 1.73 (4 H, s, PCH), 1.33 (6 H, d, $C_5H_4CH\mathit{Me}_2$), 1.00 (28 H, c, PCH_2, $PCH\mathit{Me}_2$), −7.2 [3 H, t, *J*(P–H) 36.0, MoH_3][d]
(15)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{PMe_3})_2\mathrm{O}][\mathrm{PF_6}]$	Red	32.7 (32.6)	5.6 (5.6)	^{1}H: 6.27, 5.09 (2 H, 2 H, t, t, C_5H_4), 2.67 (1 H, spt, CH), 1.86 [18 H, d, *J*(P–H) 10.4, $2PMe_3$], 1.18 (6 H, d, CMe_2)[u]

[a] Calculated values in parentheses. [b] Given as: chemical shift (δ) [relative intensity, multiplicity (c = complex), *J*/Hz, assignment]. [c] Cl: 24.8 (25.8)%, *m*/*e* = 548 (100%), P^+. [d] In C_6D_6. [e] Not analysed, see text. [f] Cl: 17.4 (17.8)%. [g] In CD_2Cl_2. [h] E.s.r. spectrum in C_4D_8O at r.t.: *g* = 1.983; strong signal, poorly resolved triplet [$I(^{31}P) = \frac{1}{2}$]; weak signal, poorly resolved sextet of triplets, $\langle a \rangle$ = 37 G [$I(^{95,97}Mo) = \frac{5}{2}$]. [i] Cl: 16.6 (16.6)%, *m*/*e* = 427 (20), P^+; 351 (100%). P^+ −PMe_3. [j] E.s.r. spectrum in C_4D_8O at r.t.: *g* = 1.988; strong signal, triplet, $\langle a \rangle$ = 11 G [$I(^{31}P) = \frac{1}{2}$]; weak signal, sextet of triplets, $\langle a \rangle$ = 42 G [$I(^{95,97}Mo) = \frac{5}{2}$]. [k] Cl: 12.9 (12.9)%. [l] In [$^2H_6$]acetone. [m] Cl: 13.6 (13.2)%, *m*/*e* = 537 (12%), P^+. [n] Cl: 9.0 (9.0)%, *m*/*e* = 392 (61), $(P - H_2)^+$; 316 (100%), $[(P - H_2) - PMe_3]^+$; i.r. (Nujol mull, cm^{-1}): ν(Mo–H) 1 820s. [o] In [$^2H_8$] toluene. [p] The same spectrum was observed at −30 °C. [q] *m*/*e* = 354 (100%), $[P - 3H_2]^+$; i.r. (Nujol mull, cm^{-1}): ν(Mo–H) 1 700s [r] The spectrum was the same at −90 °C. [s] I.r. (Nujol mull, cm^{-1}): ν(Mo–H) 1 815s, 1 722s. [t] I.r. (Nujol mull, cm^{-1}): ν(Mo–H) 1 749s; *m*/*e* = 466 $(P - 3H_2)^+$. [u] In [$^2H_6$]Me_2SO.

Å,[14] the acute Mo–Cl(1)–Mo and Mo–Cl(2)–Mo bridging angles of 63.17(2) and 63.34(2)°, respectively, and the observed diamagnetism of the compound suggest that there is a direct Mo–Mo interaction. The crystallographic symmetry requires that the four bridging Cl atoms form a plane, the Mo atoms being 1.303 Å above and below this plane and the non-bonding Cl–Cl distance is 2.988(1) Å. This molecular structure is similar to sulphur-bridged Mo dimers such as $[\{Mo(\eta\text{-}C_5H_5)(\mu\text{-}SMe)_2\}_2]$,[15] and is the first example of such a $(\mu\text{-}Cl)_4$ bridging system. The two independent molybdenum–chlorine distances are 2.484(1) and 2.485(1) Å (average 2.485 Å), *cf.* $[PPh_4]$-$[(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2(SMe_2)]$ [mean 2.43(2) Å] and $[(Me_2S)Cl_2Mo(\mu\text{-}SMe_2)(\mu\text{-}Cl)_2MoCl_2(SMe_2)]$ (mean 2.483 Å).[16]

The η-$C_5H_4Pr^i$ ring is planar, with no atom deviating from the mean plane by more than 0.006 Å. The carbon–carbon

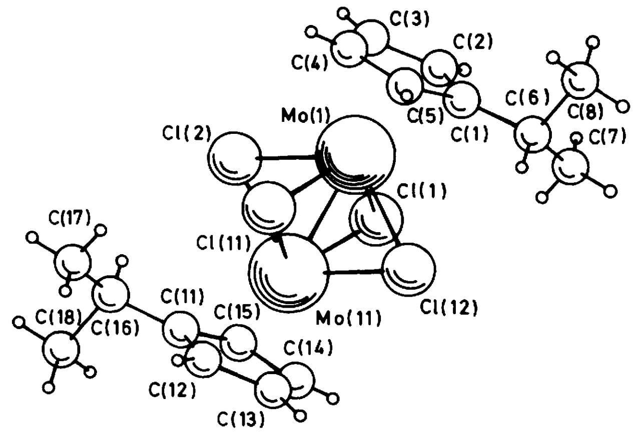


Figure 1. Molecular structure of $[\{Mo(\eta-C_5H_4Pr^i)(\mu-Cl)_2\}_2]$, (3)

distances within the $\eta-C_5H_4Pr^i$ ring lie in the range 1.399(7)—1.434(6) Å, mean 1.420 Å. The angle at the unique carbon is 106.7(4)°, while the other four angles are nearly equal with a mean value 108.3°. All these dimensions compare well with those of related compounds such as $[Mo(\eta^5-C_5H_5)_2Cl_2]$ and $[\overline{Mo(\eta-C_5H_4CH_2C}H_2)_2]$.[17]

The ^1H n.m.r. spectrum of the crude reaction product obtained when (2) was treated with hydrogen chloride for 1 min, showed the presence of (3) together with a second set of bands. The spectrum of the second product showed two broad singlets at δ 4.58 and 4.32 assignable to a C_5H_4 unit, a singlet at δ 4.06 assignable to η-benzene, and both a complex signal of integration 1 at δ 2.62 and a doublet of intensity 6 at δ 1.19 being characteristic of an isopropyl group. Attempts to separate this product from (3) by recrystallisation and chromatography were unsuccessful. The ^1H n.m.r. spectrum, together with the observation that further treatment of the mixture of compounds with HCl gas gave only (3), suggested that the second product was an intermediate in the formation of (3), namely $[Mo(\eta-C_5H_4Pr^i)(\eta-C_6H_6)Cl]$, (4).

Treatment of $[Mo(\eta-C_6H_6)(\sigma,\eta^5-C_5H_4CPh_2)]$[13] with hydrogen chloride gave a rapid reaction and brown crystals were isolated. The data in Table 1, in particular the n.m.r. spectra, suggest the compound to be $[\{Mo(\eta-C_5H_4CHPh_2)(\mu-Cl)_2\}_2]$, (5).

Compound $[\{Mo(\eta-C_5H_4Pr^i)(\mu-Cl)_2\}_2]$, (3), was treated with an excess of PMe_3 giving a crystalline red solid. The ^1H n.m.r. spectrum did not show any absorptions other than those due to residual protio solvent. This suggests that the product is paramagnetic. Microanalysis and the mass spectrum [m/e = 427 (20%)] correspond to the compound $[Mo(\eta-C_5H_4Pr^i)(PMe_3)_2Cl_2]$, (6). The e.s.r. spectrum gave a poorly resolved sextet of triplets with g = 1.983, $\langle a \rangle$ = 37 G [$I(^{95,97}Mo) = \frac{5}{2}$], plus a more intense poorly resolved triplet [$I(^{31}P) = \frac{1}{2}$]. A solution of (3) in toluene was treated with PMe_2Ph to give a crystalline red solid. The ^1H n.m.r. spectrum showed no bands. The e.s.r. spectrum gave an intense triplet, g = 1.988, $\langle a \rangle$ = 11 G [$I(^{31}P) = \frac{1}{2}$], plus a weaker sextet of triplets, $\langle a \rangle$ = 42 G [$I(^{95,97}Mo) = \frac{5}{2}$]. Microanalysis corresponds to the formulation $[Mo(\eta-C_5H_4Pr^i)(PMe_2Ph)_2Cl_2]$, (7). Compounds (6) and (7) are moderately air-sensitive and were stored under argon at room temperature.

Treatment of (3) with dmpe gave a yellow solid. After addition of NH_4PF_6 bright yellow needle crystals were obtained. The i.r. and ^1H n.m.r. spectra showed bands assignable to Mo–H at 1 713 cm^{-1} and δ −2.16 (quintet, qnt), respectively. The quintet was assigned to a Mo–H coupled to four equivalent ^{31}P nuclei [J(P–H) 47.6 Hz]. The ^1H n.m.r. spectrum also showed a pair of complex signals at δ 5.42 and 5.12, assignable to a $\eta-C_5H_4$ group, and a septet (spt) at δ 2.76 and a doublet at 1.36 characteristic of an isopropyl group. There was also a broad complex band at δ 2.47—2.12 attributable to two $-PCH_2CH_2P-$ groups and, correspondingly, two doublets at δ 1.94 and 1.91 due to the two sets of equivalent methyls on the dmpe ligand. The data (Table 1) show the compound to be $[Mo(\eta-C_5H_4Pr^i)(dmpe)_2H][PF_6]_2$, (8). When acetone rather than acetone–water was used to crystallise the product, a different product was obtained, namely $[Mo(\eta-C_5H_4Pr^i)(dmpe)_2][PF_6]$, (9). This compound readily protonates giving the dicationic hydride (8) which implies that (9), although cationic, has a high-energy (electron-rich) metal centre.

When $[\{Mo(\eta-C_5H_4Pr^i)(\mu-Cl)_2\}_2]$ was treated with dmpe, with the former in excess, the product after addition of NH_4PF_6 was (8), together with starting material. Treatment of the dimer (3) with dmpe and $NaBH_4$ in thf followed by addition of NH_4PF_6 also gave (8).

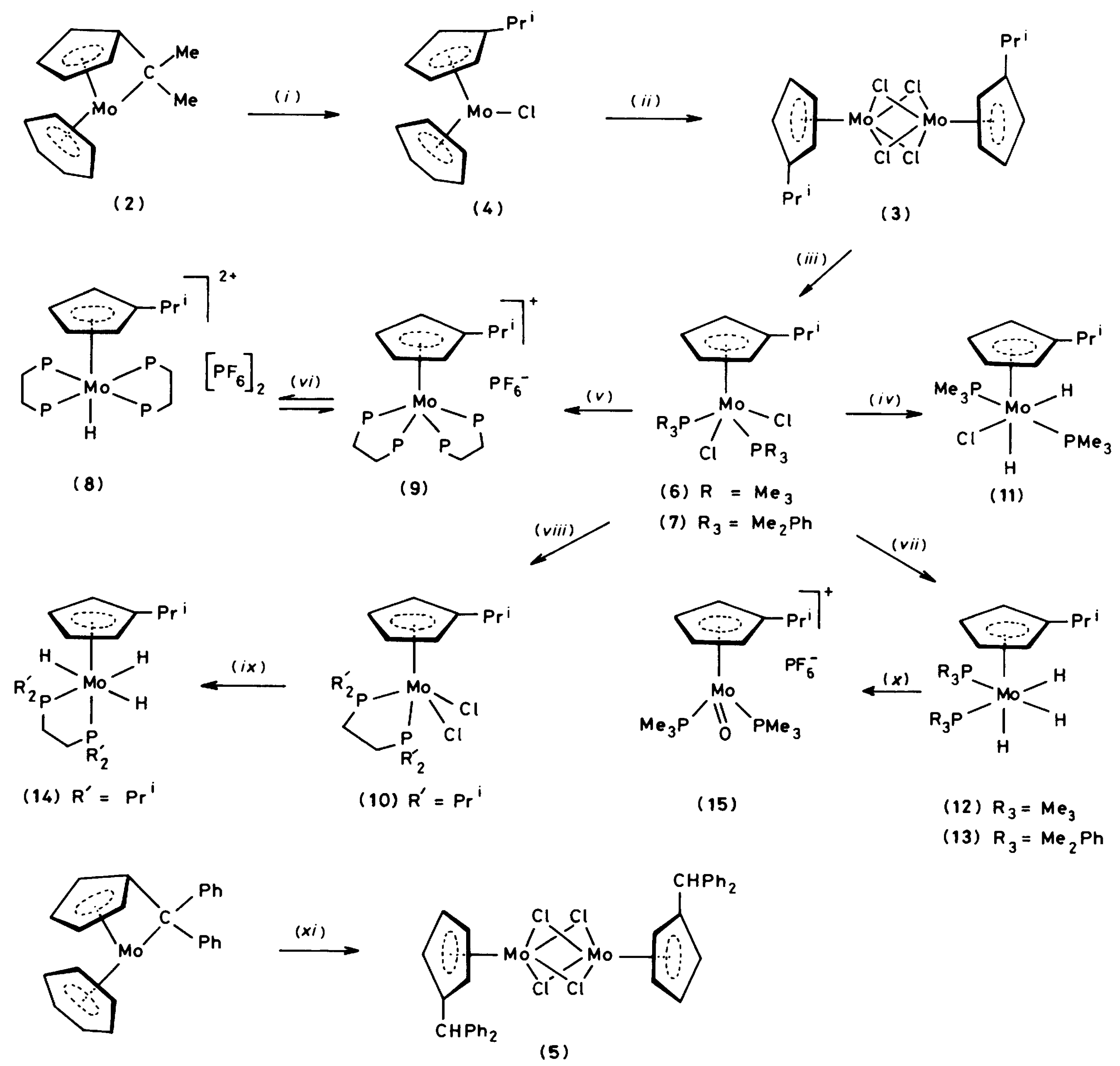
In a further attempt to prepare $[Mo(\eta-C_5H_4Pr^i)(dmpe)Cl_2]$, $[Mo(\eta-C_5H_4Pr^i)(PMe_2Ph)_2Cl_2]$, (7), was treated with one equivalent of dmpe. However, the only product that could be isolated, after addition of aqueous NH_4PF_6 was $[Mo(\eta-C_5H_4Pr^i)(dmpe)_2][PF_6]$, (9).

Compound (3) was treated with $Pr^i_2PCH_2CH_2PPr^i_2$ (dippe) giving a crystalline red solid. The ^1H n.m.r. spectrum showed only residual protio solvent. The mass spectrum exhibited a parent ion at m/e = 537 (12%), assignable to $[Mo(\eta-C_5H_4Pr^i)(dippe)Cl_2]^+$; the base peak was at 305. We propose the product to be $[Mo(\eta-C_5H_4Pr^i)(dippe)Cl_2]$, (10).

The different reactivity of the dimer (3) towards dmpe and the monodentate phosphines may relate in part to the smaller size of the former compared to two of the latter (the cone angles are: PMe_3 118, dmpe 107, PMe_2Ph 122, and $Et_2PCH_2CH_2PEt_2$ 115°).[18] It was for this reason that the reaction between (3) and the bulky dippe ligands was studied. As anticipated, the paramagnetic monomer (10) was formed.

The compound $[Mo(\eta-C_5H_4Pr^i)(PMe_3)_2Cl_2]$, (6), in thf was treated with sodium amalgam and dihydrogen (10 atm) to give orange crystals of $[Mo(\eta-C_5H_4Pr^i)(PMe_3)_2ClH_2]$, (11). The i.r. spectrum showed a band at 1 820 cm^{-1} assignable to ν(Mo–H). The ^1H n.m.r. spectrum at room temperature did not have a high-field signal. However, at −60 °C the spectrum showed a doublet of triplets centred at δ −6.02. At 50 °C there was a triplet at δ −1.93. The substantial change in chemical shift of these high-field bands suggested some averaging process was occurring. Closer re-examination of the spectrum at −60 °C revealed a doublet of triplets centred at δ 2.13 which was partially obscured by methyl resonances. The remainder of the spectrum does not change significantly with temperature. Variable-temperature ^{31}P n.m.r. spectra showed the two ^{31}P nuclei to be equivalent. We assign the doublets of triplets to two inequivalent Mo–hydrogens coupled to two equivalent phosphorus nuclei with J(P–H) 64 (low field Mo–H) and 29 Hz (high field Mo–H) and which are further coupled to each other [J(H–H) 12 Hz]. At 50 °C the Mo–hydrogens are equivalent and the averaged value of the P–H coupling constant is 46 Hz. The data show that the two tertiary phosphines are *trans* to each other and that one Mo–hydrogen lies in the P_2Mo plane. The second Mo–hydrogen must be *cis* to the two phosphorus atoms. The structure proposed for (11) is shown in the Scheme; H_a is assigned to the higher field band, *i.e. trans* to a Cl ligand. A possible mechanism for this reaction could be reduction of $[Mo(\eta-C_5H_4Pr^i)(PMe_3)_2Cl_2]$, (6), to a 16-electron monochloro intermediate which adds the dihydrogen in an oxidative-addition reaction.

Treatment of complex (6) with $LiAlH_4$ gave yellow air-



Scheme. (*i*) HCl gas at −78 °C for 20 s, not isolated; (*ii*) HCl gas at r.t. for 7 min, >95%; (*iii*) PR_3 in toluene at r.t. for 1—2 d, >90%; (*iv*) Na–Hg in thf under H_2 (10 atm) for 2 h, 69%; (*v*) dmpe in acetone–thf then NH_4PF_6 in acetone, >33%; (*vi*) NH_4PF_6 in water–acetone, >90%; (*vii*) $LiAlH_4$ in toluene at r.t. for 2 d, 33% (R_3 = Me_3), 64% (R_3 = Me_2Ph); (*viii*) dippe in toluene at r.t. for 12 h, 92%; (*ix*) $LiAlH_4$ in toluene at r.t. for 1 d, 51%; (*x*) HCl gas in toluene, then aqueous NH_4PF_6, 43%; (*xi*) HCl gas in toluene for 5 min, 87%

sensitive $[Mo(\eta\text{-}C_5H_4Pr^i)(PMe_3)_2H_3]$, (**12**). Due to the high sensitivity of this compound, consistent microanalysis could not be obtained. The highest peak in the mass spectrum was observed at *m*/*e* = 354 (100%) and is assigned to $[Mo(\eta\text{-}C_5H_4Pr^i)(PMe_3)_2H_3 - 6\ H]^+$. The i.r. spectrum showed a band at 1 700 cm^{-1} assignable to ν(Mo–H). The ^1H n.m.r. spectrum shows *inter alia* a triplet at δ −5.60 of relative intensity 3, assignable to three equivalent fluxional Mo–hydrogens coupled to two ^{31}P nuclei [*J*(P–H) 40.5 Hz].

The ^1H n.m.r. spectrum (in $[^2H_8]$toluene) at −90 °C did not show any noticeable change from that at room temperature. Therefore, the compound (**12**) can be formulated as shown in the Scheme, or an isomer thereof.

Treatment of $[Mo(\eta\text{-}C_5H_4Pr^i)(PMe_2Ph)_2Cl_2]$, (**7**), with $LiAlH_4$ in the dark gave yellow, air-sensitive crystalline $[Mo(\eta\text{-}C_5H_4Pr^i)(PMe_2Ph)_2H_3]$ (**13**). The data and assignments are given in Table 1. Similarly, $[Mo(\eta\text{-}C_5H_4Pr^i)(dippe)Cl_2]$, (**10**), reacted with $LiAlH_4$ giving orange $[Mo(\eta\text{-}C_5H_4Pr^i)(dippe)H_3]$, (**14**). The structure proposed for (**14**), by analogy with $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$, (**1**), which has four equivalent P-methyl groups, is shown in the Scheme.

Treatment of (**12**) with hydrogen chloride and then aqueous NH_4PF_6 gives red crystals of the oxo compound $[Mo(\eta\text{-}C_5H_4Pr^i)(PMe_3)_2O][PF_6]$, (**15**). The i.r. spectrum showed an absorption at 968 cm^{-1} assignable to ν(Mo=O), a value typical of other Mo=O stretching frequencies in η-cyclopentadienyl-oxo-molybdenum compounds.[19]

The Photoinduced Activation of C–H *Bonds by Compounds of the Class* $[Mo(\eta\text{-}C_5H_4R)L_2H_3]$ (L_2 = 2 *phosphine or a*

Table 2. Results of H–D exchange experiments

Substrate	Deuteriated product	Approximate rates and degree of deuteriation *
(*a*) Aromatic hydrocarbon substrates		
$C_6H_5CH_3$	$C_6D_5CD_3$	CH_3: 4 d (80%) C_6H_5: obscured by solvent
$C_6H_5CH_2CH_3$	$C_6D_5CH_2CH_3$	C_6H_5: 6 h (88%)
1,4-$C_6H_4(CH_3)_2$	1,4-$C_6D_4(CD_3)_2$	C_6H_4: 2 d (90%) CH_3: 4 d (85%)
1,3,5-$C_6H_3(CH_3)_3$	1,3,5-$C_6H_3(CD_3)_3$	CH_3: 7 d (85%)
1,2,4,5-$C_6H_2(CH_3)_4$	—	—
$C_6(CH_3)_6$	—	—
$CH_3OC_6H_5$	$CD_3OC_6D_5$	CH_3O: 8 h (100%) C_6H_5: 6 h (100%)
1,4-$CH_3C_6H_4OCH_3$	1,4-$CD_3C_6D_4OCD_3$	CH_3: 10 d (65%) C_6H_4: 6 h (100%) OCH_3: 6 h (100%)
(*b*) Non-aromatic substrates		
$(CH_3)_2O$	CD_3OCD_3	CH_3: 7 d (95%)
$(CH_3CH_2)_2O$	—	—
$(CH_3OCH_2)_2$	$(CD_3OCH_2)_2$	CH_3: 14 d (91%)
$CH_3CO_2CH_2CH_3$	$CD_3CO_2CD_2CD_3$	CH_3CO_2: 1 d (75%) CH_2: 15 d (75%) CH_3: 5 d; integration obscured by dmpe
Cyclohexane	—	—
Cyclopentane	—	—
Cyclo-octane	—	—
1,3-$(CH_3)_2C_6H_{10}$	—	—
$Si(CH_3)_4$	—	—
$PhCH_2CO_2NHCH[CH_2CH(CH_3)_2]CONHCH(CH_2Ph)CO_2CH_3$		Reacted
(*c*) Organometallic substrates		
$[Fe(\eta\text{-}C_5H_5)_2]$	$[Fe(\eta\text{-}C_5D_5)_2]$	C_5H_5: 12 h (100%)
$[W(\eta\text{-}C_6H_5CH_3)_2]$	$[W(\eta\text{-}C_6D_5CD_3)_2]$	C_6H_5: 2 h (95%) CH_3: 3 d (95%)
$[Mo(\eta\text{-}C_5H_5)_2H_2]$	$[Mo(\eta\text{-}C_5D_5)_2D_2]$	Mo–H: 8 h (100%) C_5H_5: 2 d (100%)
$[Mo(\eta\text{-}C_6H_6)_2]$	$[Mo(\eta\text{-}C_6D_6)_2]$	C_6H_6: 12 h (100%)
$[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$	$[W(\eta\text{-}C_5D_5)_2(CH_3)_2]$	C_5H_5: 3 h (100%)
$[W(\eta\text{-}C_6H_5CH_3)(\eta\text{-}C_5H_5)(O_2CCH_3)]$	$[W(\eta\text{-}C_6D_5CD_3)(\eta\text{-}C_3H_5)(O_2CCD_3)]$	C_6H_5: 6 h (72%) CH_3: 4 d (70%) O_2CCH_3: 20 d (74%)

* The times given are the times required to achieve statistical equilibrium with deuteriobenzene, *i.e.* no further change in relative intensities in the ^1H n.m.r. spectrum. Reacted indicates there was a rapid loss of bands (n.m.r.) assignable to the catalyst.

diphosphine).—Photolysis of an initially pale yellow solution of $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$, (**1**), in C_6D_6 caused a rapid colour change to red. If the red solution was placed in the dark the yellow colour reappeared after 15 min. However, heating the yellow solution to 70 °C for several hours did not result in a colour change.

A deuteriobenzene solution of (**1**) in a sealed n.m.r. tube was photolysed using a 100-W mercury lamp and the spectral changes were monitored. A rapid increase in the intensity due to protiobenzene was observed. After 1 h the $\eta\text{-}C_5H_5$ and hydride absorbances had an intensity of approximately 2—3% that of the original spectrum and the PMe_2 band was *ca.* 30% of the initial intensity. After irradiation for 6 h no bands assignable to hydride or cyclopentadienyl protons could be observed in the spectrum.

The mass spectrum of the solid product obtained from the irradiated sample showed the highest peak at $m/e = 328$ which corresponds to the ion $[Mo(\eta\text{-}C_5D_5)\{(CD_3)_2PCD_2CD_2P(CD_2)_2\}D_3 - 6\ D]^+$: the corresponding band for pure (**1**) was at $m/e = 310$. Thus all the hydrogen atoms of (**1**) undergo deuterium exchange, even the methylene hydrogens of the $Me_2PCH_2CH_2PMe_2$ ligand. No H–D exchange could be thermally induced in (**1**). Further, if irradiation of a sample was interrupted there were no further changes in the n.m.r. spectrum until irradiation was recommenced.

By analogy with the photochemistry of $[W(\eta\text{-}C_5H_5)_2H_2]$[20—22] we propose that irradiation of (**1**) induces a concerted elimination of dihydrogen, giving the unsaturated highly-reactive 16-electron intermediate $[Mo(\eta\text{-}C_5H_5)(dmpe)H]$. Subsequently the molybdenum centre could insert into all available C–H bonds *via* inter- or intra-molecular processes. Mass spectral analysis of non-condensible gases above irradiated perdeuteriotoluene solutions of (**1**) showed predominantly H_2 and, since toluene is an efficient scavenger for free hydrogen atoms, the lack of an appreciable amount of HD indicates that H atoms are not produced. Thus, elimination of the hydrogen directly as H_2 is implied.

The ability of (**1**) to catalyse the exchange of the hydrogens of various C–H groups was investigated by photolysing solutions of (**1**) in deuteriobenzene in the presence of a variety of organic

Table 3. H–D exchange for complexes [Mo(η-$C_5H_4Pr^i$)$(PMe_3)_2H_3$], (**12**), [Mo(η-$C_5H_4Pr^i$)(dippe)H_3], (**14**), and [Mo(η-C_5H_5)(dmpe)H_3], (**1**)

Substrate	(**12**)	(**14**)	(**1**)
[$^2H_{12}$]Cyclohexane		No exchange	
[$^2H_6$]Benzene	Exchange	Exchange	Exchange
[$^2H_8$]Toluene	Only aromatic H exchange	Only aromatic H exchange	All exchange
Mesitylene *	No exchange	No exchange	Only methyl H exchanged
Anisole *		All exchange	All exchange
η-Butane *	No exchange	No exchange	

* In C_6D_6.

compounds. N.m.r. tubes containing C_6D_6, organic compound, and a small quantity of (**1**) were irradiated and changes in the ^1H n.m.r. spectra monitored. Typically, the samples contained *ca.* 10 mg of (**1**), 20—80 mg of the substrate dissolved in C_6D_6 (0.7 cm^3), and, as an internal standard, a sealed capillary tube containing a solution of $SiMe_4$ in C_6D_6.

Absolute intensity changes could be estimated by comparison with the separate sealed standard $SiMe_4$. Irradiation of the sample was stopped when no further changes were observed in successive n.m.r. spectra. The sample tubes were opened and the mass spectra of the volatile substrates were recorded. The results of these experiments are shown in Table 2. It can be seen that complex (**1**) catalyses the photochemically induced hydrogen–deuterium exchange between deuteriobenzene and a variety of substrates and that there is clear evidence for selectivity. Not surprisingly aromatic C–H systems closely resembling benzene are readily exchanged. Evidence for steric inhibition to exchange is clearly shown by the failure to exchange the aromatic C–H groups of mesitylene whilst at the same time the hydrogens of the methyl groups underwent exchange.

All the hydrogens of toluene undergo exchange whereas only the aromatic hydrogens of ethylbenzene are exchanged. All the hydrogens attached to sp^3 carbons that undergo exchange are adjacent to groups which have the potential to co-ordinate, albeit weakly, to a transition metal. Examples are the methyl groups of toluene, *p*-xylene, and dimethyl ether (see Table 2).

Failure to exchange the CH_2 hydrogens of the ethyl group of ethylbenzene may reflect steric inhibition. It seems likely that the methyl group of ethylbenzene is inert to exchange for the same reasons that alkanes do not undergo exchange. Likewise whilst methyl hydrogens of $(CH_3)_2O$ are exchanged none of the hydrogens of diethyl ether is exchanged. The data in Table 2 are qualitative insofar that there was not a strict control of many potential variables, for instance, the ageing of the mercury discharge lamps and the precise concentration of catalyst and organic substrates.

The failure to exchange any of the hydrogens of 1,2,4,5-tetramethylbenzene and hexamethylbenzene suggests that the methyl groups prevent pre-co-ordination of the arene system to the metal. In $(CH_3OCH_2)_2$ only the more sterically accessible methyl hydrogens underwent exchange. In the case of diethyl ether no exchange was observed, probably because the CH_2O hydrogens were not readily available and the methyl ones were not reactive enough. All the C–H bonds of methyl acetate were exchanged. The methyl group of the acetate radical possessed the most reactive C–H bond in this particular molecule due to the fact that it was sterically unrestrained (primary carbon) and next to a strong electron-withdrawing group. Unlike the results already mentioned, the other methyl hydrogens do undergo H–D exchange and at rates comparable to benzylic protons. A possible explanation could be the formation of an intermediate where the acetate co-ordinates to the 16-electron molybdenum centre which facilitates the oxidative-addition of the methyl group to the metal. Finally the secondary C–H bonds are activated also, but to a minor degree due to steric restraints.

Complex (**1**) was also able to catalyse H–D exchange between deuteriobenzene and C–H bonds of certain organotransition-metal complexes; the data are given in Table 2.

In order to avoid the competition between aliphatic hydrocarbons with the more reactive aromatic C–H systems, a H–D exchange study was attempted using C_6D_{12} as a solvent and source of deuterium. However, (**1**) is only very slightly soluble in cyclohexane and the experiments were indeterminate.

Unfortunately compound [Mo(η-$C_5H_4Pr^i$)$(PMe_3)_2H_3$], (**12**), also has only low solubility in alkanes which somewhat limited studies using cyclohexane as solvent. However, [Mo(η-$C_5H_4Pr^i$)(dippe)H_3], (**14**), is highly soluble in aliphatic hydrocarbons. A ^1H n.m.r. sample of (**14**) in C_6D_{12} was photolysed. There were no changes in the spectrum consistent with the occurrence of activation of the cyclohexane. The mass spectrum of the solid recovered after irradiation corresponded to the unexchanged starting compound (**14**).

Photolysis of (**14**), and, separately, [Mo(η-$C_5H_4Pr^i$)$(PMe_3)_2H_3$], (**12**), in deuteriobenzene was monitored using n.m.r. samples. In both cases, the band due to protiobenzene increased in intensity dramatically and Mo–H resonances disappeared. This, together with the changes of intensity in the other bands of the complexes, and the mass spectra of the solids recovered after irradiation (*see later*), indicated that H–D exchange had taken place.

The mass spectrum of the photolysed sample of (**12**) showed a highest peak at m/e = 376 (*cf.* 354 for the protio complex). The ^1H n.m.r. spectrum showed that H–D exchange had occurred at the methyl groups of the PMe_3 and η-$C_5H_4Pr^i$ ring. However, because these bands overlap, it was not possible to compare their reactivity. The hydrogens on the β carbon (with respect to the isopropyl substituent) exchange at a faster rate than those on the α-carbon. This difference can be attributed to steric effects. Finally, the methine hydrogen in the isopropyl group underwent H–D exchange but more slowly.

For the photolysed sample of (**14**), the highest peak obtained in the mass spectrum was at m/e = 498 and this is 32 mass units higher than the highest peak for the protio complex, m/e = 466, assignable to [Mo(η-$C_5H_4Pr^i$)(dippe)H_3 – 6 H]$^+$. Unlike [Mo(η-C_5H_5)(dmpe)H_3] (**1**), where the η-C_5H_5 hydrogens undergo exchange much faster than the PMe_2 hydrogens, for (**14**) these rates are comparable. Presumably the larger phosphine in (**14**) makes the molybdenum centre less susceptible to attack.

Semi-quantitative experiments show that the rate of H–D exchange for (**1**) (several hours) is faster than for (**12**) and (**14**) (3—4 d). Table 3 shows the outcome of several H–D experiments with (**12**), (**14**), and, for comparison, (**1**). It can be seen that the isopropylcyclopentadienyl complexes are generally *less* active as catalysts for H–D exchange than their η-C_5H_5 analogues, *e.g.*, catalysis by (**12**) is slower than [Mo(η-C_5H_5)(dmpe)H_3], (**1**). This may be due to steric factors and, generally, this work illustrates that quite small changes of substituents on the molybdenum can strongly affect the ability of the molybdenum centre to activate C–H bonds.

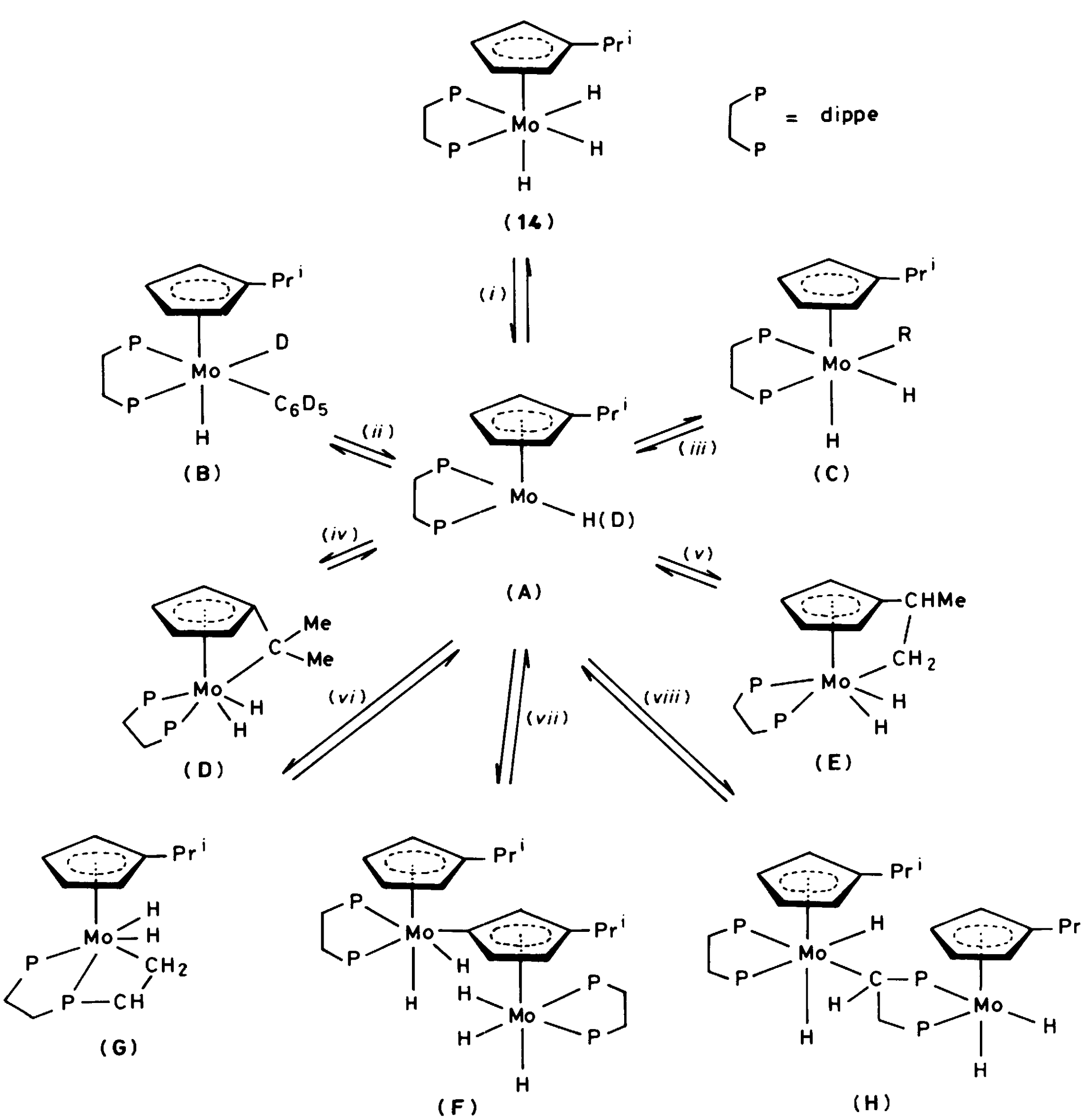


Figure 2. (*i*) Reversible photoinduced elimination of dihydrogen creating key 16-electron intermediate (**A**); (*ii*) reversible insertion of (**A**) into the C–D bonds of C_6D_6 which results in exchange of MoH of (**A**) giving MoD; (*iii*) reversible addition of C–H of organic substrate, resulting in exchange of C–H of substrate giving C–D of substrate; (*iv*), (*v*), and (*vi*) possible reversible, intramolecular C–H oxidative-addition reactions; (*vii*) and (*viii*) possible reversible, intermolecular C–H oxidative-addition reactions. The oxidative-addition reactions of (**A**) are likely to be thermal whilst the reverse reductive-elimination reactions may be either thermal, or, photoinduced

Discussion

The structures proposed for the new compounds are shown in the Scheme. Compounds (**1**), (**12**), and (**14**) act as catalysts for photoinduced H–D exchange for a variety of substrates, as shown in Table 2. The exchange presumably proceeds *via* a combination of inter- and intra-molecular steps as indicated in Figure 2 for (**14**). When the substrates are aromatic then pre-co-ordination of the arene ring by η^2-bonding may be presumed to occur. There is strong evidence for the intermediacy of an η^2-arene complex in the activation of aromatic C–H bonds involving the rhodium complex $[Rh(\eta\text{-}C_5Me_5)(PMe_3)H(C_6H_5)]$.[23–25]

The H–D exchange in the methyl groups of the $Me_2PCH_2CH_2PMe_2$ ligand can occur *via* an intra- or inter-molecular process. The H–D exchange in the η-cyclopentadienyl ring probably occurs by an intermolecular process, where the 16-electron intermediate, *e.g.*, (**A**) in Figure 2, undergoes oxidative-addition of a C–H group of the η-cyclopentadienyl ring of another molecule, *e.g.*, step (*vii*) in Figure 2. This process must occur in the H–D exchange reactions of the η-cyclopentadienyl compounds shown in Table 2, section (*c*).

No activation of alkanes was observed. However, since this work was done, alkane activation has been found for many organometallic compounds, *e.g.*, derivatives of iridium,[26] rhenium,[27] iridium,[28] rhodium,[29] lutetium,[30] thorium,[31] and scandium,[32] some of which, *e.g.* $[M(\eta\text{-}C_5R_5)(L)H_2]$ (M = Rh, L = CO; M = Ir, L = PMe_3), are closely similar to the above molybdenum compounds. A detailed theoretical discussion of activation of C–H bonds by transition metals has been published by Saillard and Hoffmann.[33]

In this search for compounds which would add to the C–H bonds of alkanes we have used tungstenocene as a model. Tungstenocene has been characterised under matrix isolation conditions as having a triplet, d^4 electronic configuration[20,21] and photoelectron studies on tungstenocene derivatives [W(η-

$(C_5H_5)_2X_2]$ (X = H, Me, or Cl) or $[W(\eta\text{-}C_5H_5)_2L]$ (L = CO or $\eta\text{-}C_2H_4$) show them to have low first ionisation energies which conform to the classification that the tungstenocene centre is high-energy (electron-rich).[34] An advantage of high-energy d^n electrons on a metal centre is that oxidation of the metal centre will be favoured and hence the oxidative-addition of C–H enhanced. In other words we see a high-energy highest occupied molecular orbital (h.o.m.o.) as a thermodynamic advantage with respect to C–H activation. However, it is correspondingly more difficult to create the required unsaturated metal centre by thermal- or photo-induced elimination of a ligand from a stable precursor compound.

The addition of C–H bonds of arenes is assisted by pre-co-ordination of the arene to the metal *via* an η^2-arene interaction. It seems reasonable that similar pre-co-ordination of alkane C–H bonds, by formation of an agostic $M \leftharpoondown H\text{–}C$ bond [35,36] also occurs and that this similarly assists towards the final oxidative-addition step. Such pre-co-ordination may be described in terms of donation of the electrons of the C–H bond into an empty *d* orbital on the metal centre and can seen to be related to the bonding of dihydrogen compounds such as $[Mo(CO)_3(PPr^i_3)_2(\eta^2\text{-}H_2)]$.[37] The lower the energy of the empty metal orbital [the lowest unoccupied molecular orbital (l.u.m.o.)] then the greater the kinetic advantage towards C–H activation as a consequence of a pre-equilibrium co-ordination of the C–H substrate to the metal centre. These arguments suppose, therefore, that the metal centre should have a high h.o.m.o. and low l.u.m.o. and this will be maximised in the triplet state (*i.e.* when they have the same energy).

The ability of the d^0 centre in the lutetium compound $[Lu(\eta\text{-}C_5Me_5)_2Me]$ to activate methane can be understood in terms of there being a favourable l.u.m.o. for pre-co-ordination. The transition state for the methane-exchange reaction of this compound, namely the electron-deficient $[Lu(\eta\text{-}C_5Me_5)_2(H)Me_2]$,[30] may have a bonding scheme formally the same as for the stable compounds $[Ta(\eta\text{-}C_5R_5)_2H_3]$ and $[W(\eta\text{-}C_5H_5)_2H_3]^+$.[38] However, there would be only four, rather than six, electrons to be placed in the three bonding molecular orbitals involved in the $Lu(H)Me_2$ fragment. We conclude that the electronic requirements for a metal centre to cause activation of C–H bonds are not very rigorous. However, such metal centres are highly reactive and the problem of achieving the desired C–H activation products is mainly one of limiting alternative reactions, *e.g.* intramolecular C–H activation, as witnessed above, or loss of the metal centre by dimerisation, as noted earlier for tungstenocene. Further, the hydrogen–deuterium exchange observed for most of the hydrogens of the tertiary phosphine ligands in the compounds (**1**), (**12**), and (**14**) suggests that activation of alkanes by these compounds is restricted in part by competition from other intra-and inter-molecular C–H addition processes.

Experimental

All manipulations were carried out under argon or dinitrogen. Argon was purified by passage through 4A molecular sieves and Fluka BTS catalyst. Schlenk vessels were flamed out under vacuum prior to use. Hydrocarbon solvents and tetrahydrofuran (thf) were dried by refluxing over sodium–potassium alloy. Dichloromethane was dried over activated 4A molecular sieves. N.m.r. solvents were stored over Na-K alloy or molecular sieves, where appropriate. ^1H N.m.r. spectra were measured using JNM PMX-60 (60 MHz), JNM FX-100 (100 MHz), Bruker WH-300 (300 MHz), or Bruker WH-400 (400 MHz) instruments. ^{13}C N.m.r. spectra were obtained on Bruker WH-300 (75.4 MHz) and AM 250 (62.9 MHz) spectrometers. ^{31}P N.m.r. spectra were obtained using a Bruker WH-90 instrument. Chemical shifts for ^1H and ^{13}C n.m.r. were referenced to $\delta(SiMe_4) = 0$ p.p.m. and for ^{31}P to $\delta[P(O)(OMe)_3$ in $D_2O] = 0$ p.p.m. Mass spectra were measured on a AEI MS 902 spectrometer. I.r. spectra were measured as Nujol mulls on a Pye-Unicam SP 2000 spectrometer. Analytical data were obtained in this laboratory or by A. Bernhardt, Germany.

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*trichloro*(η-*cyclopentadienyl*)*molybdenum*.—The preparation was slightly modified from the published procedure.[6] The compound $[Mo(\eta\text{-}C_5H_5)_2(dmpe)]PF_6$[6] was suspended in thf (200 cm^3), treated with a 3.5 mol dm^{-3} benzene solution of $Na[Al(OCH_2CH_2OMe)_2H_2]$ (20 cm^3), and the mixture stirred at room temperature (r.t.) for 12 h to give an orange solution. The solvent was removed under reduced pressure and the oily residue dissolved in toluene (100 cm^3). This solution was cooled in a water-ice bath and water (10 cm^3) was added slowly to destroy excess of the reducing agent. The resulting suspension was filtered through Celite and the solvent removed under reduced pressure. The solid residue was dried *in vacuo* and then extracted with toluene (100 cm^3). HCl gas was bubbled through the extract for 5 min to give an immediate red precipitate. The mother-liquor was decanted off and the red solid was washed twice with light petroleum (b.p. 40—60 °C, 40 cm^3) and dried *in vacuo*. Yield: 2.7 g, 45%.

1,2-*Bis*(*dimethylphosphino*)*ethane*(η-*cyclopentadienyl*)*trihydridomolybdenum*, (**1**).—The preparation was slightly modified from the published procedure.[6,9] The compound $[Mo(\eta\text{-}C_5H_5)(dmpe)Cl_3]$ was suspended in toluene (100 cm^3) and treated with a 3.5 mol dm^{-3} benzene solution of $Na[Al(OCH_2CH_2OMe)_2H_2]$ (10 cm^3). The mixture was stirred for 12 h at r.t. giving a yellow solution. This was cooled in a water-ice bath and water (10 cm^3) was added in a dropwise manner. The resulting suspension was filtered through Celite and the filtrate concentrated and cooled to −20 °C. A yellow powder separated which was washed with cold (−20 °C) light petroleum (b.p. 40—60 °C). Yield: 1.1 g, 54%.

Tetra-μ-*chloro*-*bis*[(η-*isopropylcyclopentadienyl*)*molybdenum*], (**3**).—Hydrogen chloride gas was passed through a solution of $[Mo(\eta\text{-}C_6H_5)(\sigma,\eta^5\text{-}C_5H_4CMe_2)]$ (1.90 g, 6.8 mmol) in light petroleum (b.p. 40—60 °C, 100 cm^3) for 7 min. A pink solid precipitated immediately. The solvent was decanted off and the solid recrystallised from hot (80 °C) light petroleum (100—120 °C). The crystalline solid obtained was washed with cold (−20 °C) light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield: 1.77 g, 95%.

(η-*Benzene*)*chloro*(η-*isopropylcyclopentadienyl*)*molybdenum*, (**4**).—When the above reaction was carried out without excess HCl gas, a mixture of $[Mo(\eta\text{-}C_5H_4Pr^i)(\eta\text{-}C_6H_6)Cl]$, (**4**), and $[\{Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}Cl)_2\}_2]$, (**3**), was obtained, as demonstrated by the ^1H n.m.r. spectrum. Attempts to isolate the former by recrystallisation, sublimation, and chromatography failed. Reaction of this mixture with HCl gas gives only the dimer (**3**). When the reaction was carried out at −78 °C and HCl gas was bubbled through for a few seconds a mixture of the dimer, starting material, and $[Mo(\eta\text{-}C_5H_4Pr^i)(\eta\text{-}C_6H_6)Cl]$ was obtained.

Tetra-μ-*chloro*-*bis*{[η-(*diphenylmethyl*)*cyclopentadienyl*]-*molybdenum*}, (**5**).—Hydrogen chloride gas was passed through $[Mo(\eta\text{-}C_6H_6)(\sigma,\eta^5\text{-}C_5H_4CPh_2)]$ (2.1 g, 5.2 mmol) in toluene (100 cm^3) for 5 min. A pink solid precipitated from the solution. The solvent was removed under reduced pressure and the residue extracted with thf. The resulting solution was concentrated by removal of solvent under reduced pressure and cooled overnight to − 20 °C giving a brown crystalline solid. This was washed twice with light petroleum (b.p. 40—60 °C). Yield: 1.8 g, 87%.

Dichloro(η-*isopropylcyclopentadienyl*)*bis*(*trimethylphosphine*)*molybdenum*, (**6**).—Compound (**3**) (0.48 g, 0.88 mmol) in toluene (50 cm^3) was treated with PMe$_3$ (0.31 g, 4.1 mmol) in toluene (10 cm^3), After 5 min the colour had changed from yellow-red to red. The mixture was stirred at r.t. for 1 d. The solvent was removed under reduced pressure to give a red oily solid which was extracted with a 1:1 mixture of toluene–light petroleum (b.p. 100—120 °C, 60 cm^3). Reduction of the volume under reduced pressure gradually precipitated a crystalline red solid. The suspension was cooled to -30 °C overnight, the mother-liquor was decanted off, and the solid washed with light petroleum (b.p. 40—60 °C). Yield: 0.69 g, 92%.

Dichlorobis(*dimethylphenylphosphine*)(η-*isopropylcyclopentadienyl*)*molybdenum*, (**7**).—Compound (**3**) (0.42 g, 0.77 mmol) in toluene (50 cm^3) was treated with a solution of PMe$_2$Ph (1.00 g, 7.2 mmol) in toluene (10 cm^3) and left standing at r.t. for 2 d. Reduction of the volume under reduced pressure gradually precipitated a red crystalline solid. Light petroleum (b.p. 100—120 °C, 15 cm^3) was added, more solvent was removed, and the suspension allowed to cool overnight to -20 °C. The mother-liquor was decanted off and the solid washed twice with light petroleum (b.p. 40—60 °C). Yield: 0.8 g, 95%.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*hydrido*(η-*isopropylcyclopentadienyl*)*molybdenum Bis*(*hexafluorophosphate*), (**8**).—Compound (**3**) (0.52 g, 0.95 mmol) in toluene was treated with dmpe (0.31 g, 2.07 mmol) and a yellow solid immediately precipitated. The solvent was decanted off and the solid dissolved in a mixture of acetone–water. Aqueous NH$_4$PF$_6$ was added to this solution and after removal of the acetone *in vacuo*, a yellow precipitate was obtained. This was recrystallised from acetone–water to give bright yellow needles which were washed with water. Yield: 0.5 g, 33%.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*](η-*isopropylcyclopentadienyl*)*molybdenum Hexafluorophosphate*, (**9**).—*Method A*. The reaction was carried out as above. The yellow solid obtained from the reaction mixture was treated with a solution of NH$_4$PF$_6$ in acetone and then recrystallised from acetone.

Method B. Compound (**7**) (0.60 g, 1.1 mmol) in toluene (50 cm^3) was treated with a solution of dmpe (0.14 g, 0.93 mmol) in toluene (20 cm^3). After several minutes a yellow solid started to precipitate out of solution. The mixture was stirred overnight and then filtered. The yellow solid residue was washed with toluene and recrystallised from acetone–thf. Comparison of the ^{1}H n.m.r. spectrum with that of [Mo(η-C$_5$H$_4$Pr^i)(dmpe)$_2$]PF$_6$, (**9**), showed it to contain the same cation. Yield: 0.3 g, 50%.

Method C. Compound (**3**) (0.28 g, 0.51 mmol) in thf (50 cm^3) was treated with a solution of dmpe (0.16 g, 1.1 mmol) in thf (20 cm^3) in the presence of an excess of NaBH$_4$. The mixture was stirred for 2 h and then filtered. The solvent was removed under reduced pressure and the solid obtained washed with toluene. The solid was extracted with acetone–water and the extract treated with aqueous NH$_4$PF$_6$. The acetone was removed under reduced pressure and a yellow solid precipitated which was subsequently recrystallised from acetone–water. Comparison of the ^{1}H n.m.r. spectrum with that of an authentic sample showed the product to be [Mo(η-C$_5$H$_4$Pr^i)(dmpe)$_2$][PF$_6$], (**9**).

[1,2-*Bis*(*di-isopropylphosphino*)*ethane*]*dichloro*(η-*isopropylcyclopentadienyl*)*molybdenum*, (**10**).—Compound (**3**) (0.62 g, 1.13 mmol) in toluene (50 cm^3) was treated with dippe (0.70 g, 2.67 mmol) in toluene (20 cm^3). The solution was stirred overnight at r.t. Reduction of the volume under reduced pressure gradually precipitated a red crystalline solid. The mother-liquor was decanted off and the residue recrystallised from toluene and then washed twice with light petroleum (b.p. 40—60 °C). Yield: 1.1 g, 92%.

Chloro-cis-*dihydro*(η-*isopropylcyclopentadienyl*)-trans-*bis*(*trimethylphosphine*)*molybdenum*, (**11**).—Sodium amalgam (1%, 10 g) was placed in a medium-pressure reactor (80 cm^3 capacity). A red solution of [Mo(η-C$_5$H$_4$Pr^i)(PMe$_3$)$_2$Cl$_2$], (**6**) (0.44 g, 1.0 mmol), in thf (20 cm^3) was transferred to the reactor and H$_2$ (10 atm) introduced. The mixture was left stirring overnight and then filtered through Celite giving an orange solution. Solvent was removed under reduced pressure and the solid residue was recrystallised twice from light petroleum (b.p. 40—60 °C). An orange crystalline solid was obtained after cooling to -20 °C for 12 h. The solid was collected and washed with light petroleum (b.p. 40—60 °C). Yield: 0.25 g, 62%.

Trihydrido(η-*isopropylcyclopentadienyl*)*bis*(*trimethylphosphine*)*molybdenum*, (**12**).—Compound (**6**) (1.45 g, 3.4 mmol) in toluene (100 cm^3) was transferred to a suspension of LiAlH$_4$ (1.0 g, 26.3 mmol) in toluene (30 cm^3). The reaction vessel was covered with aluminium foil and stirred at r.t. for 2 d. The colour changed from red to orange and then the reaction mixture was filtered through Celite. Reduction of the volume under reduced pressure gradually precipitated a yellow solid. The mother-liquor was decanted off and the residue was washed twice with cold (-20 °C) light petroleum (b.p. 40—60 °C). Yield: 0.4 g, 33%.

Bis(*dimethylphenylphosphine*)*trihydrido*(η-*isopropylcyclopentadienyl*)*molybdenum*, (**13**).—Compound (**7**) (0.5 g, 0.91 mmol) in toluene (70 cm^3) was transferred to a suspension of LiAlH$_4$ (0.5 g, 13.3 mmol) in toluene (30 cm^3). The reaction vessel was covered with aluminium foil and stirred at r.t. for 2 d. The colour changed from red to orange and the reaction mixture was filtered through Celite. Solvent was removed under reduced pressure. The solid residue was extracted with toluene and then light petroleum (b.p. 100—120 °C) was added. The solution was concentrated and left overnight at -60 °C giving a yellow crystalline solid. The mother-liquor was removed and the crystals were washed with cold (-20 °C) light petroleum (b.p. 40—60 °C). Yield: 0.28 g, 64%.

[1,2-*Bis*(*di-isopropylphosphino*)*ethane*]*trihydrido*(η-*isopropylcyclopentadienyl*)*molybdenum*, (**14**).—Compound (**10**) (0.40 g, 0.75 mmol) in toluene (80 cm^3) was added to a suspension of LiAlH$_4$ (0.3 g, 7.9 mmol) in toluene (20 cm^3). The reaction vessel was covered with aluminium foil and stirred at r.t. for 1 d. The colour changed from red to yellow. The resulting suspension was filtered through Celite and the solvent removed under reduced pressure. The solid residue was extracted with light petroleum (b.p. 40—60 °C). The resulting solution was filtered, concentrated, and cooled to -40 °C giving yellow crystals which were collected and dried *in vacuo*. Yield: 0.18 g, 51%.

(η-*Isopropylcyclopentadienyl*)*oxobis*(*trimethylphosphine*)*molybdenum Hexafluorophosphate*. (**15**).—HCl gas was passed through compound (**12**) (0.2 g, 0.56 mmol) in toluene (30 cm^3) and a red solid was immediately precipitated. The solid was separated and dissolved in acetone–water (1:1). Aqueous NH$_4$PF$_6$ was added and after removal of the acetone under reduced pressure a precipitate was obtained. This was recrystallised from acetone–water to give a red crystalline solid

Table 4. Fractional atomic co-ordinates with e.s.d.s in parentheses for **(3)**

Atom	*X*/*a*	*X*/*b*	*Z*/*c*
Mo(1)	0.572 6	0.023 1	0.612 7
Cl(1)	0.396 4(1)	0.161 2(1)	0.490 7(1)
Cl(2)	0.274 5(1)	0.054 0(3)	0.595 5(1)
C(1)	0.794 9(5)	0.114 4(3)	0.723 8(1)
C(2)	0.637 7(5)	0.153 1(4)	0.777 2(4)
C(3)	0.544 6(6)	0.063 4(4)	0.827 7(4)
C(4)	0.642 3(6)	−0.032 2(4)	0.830 3(4)
C(5)	0.798 4(5)	−0.001 4(4)	0.745 2(4)
C(6)	0.937 9(6)	0.180 7(4)	0.665 8(4)
C(7)	0.876 8(8)	0.288 6(5)	0.607 7(5)
C(8)	1.079 0(7)	0.199 4(5)	0.770 8(6)
H(2)	0.611 3(65)	0.221 6(44)	0.775 3(50)
H(3)	0.436 2(65)	0.073 3(41)	0.871 8(48)
H(4)	0.626 3(67)	−0.097 5(45)	0.837 3(50)
H(5)	0.889 9(64)	−0.050 7(43)	0.727 0(48)
H(6)	0.985 3(64)	0.137 9(44)	0.604 6(49)
H(71)	0.973 7(67)	0.327 0(43)	0.566 6(48)
H(72)	0.791 9(67)	0.279 8(43)	0.536 4(51)
H(73)	0.830 5(68)	0.329 0(45)	0.662 0(53)
H(81)	1.108 8(66)	0.329 0(45)	0.662 0(53)
H(82)	1.033 3(65)	0.245 60(45)	0.839 5(52)
H(83)	1.173 5(68)	0.229 0(45)	0.730 5(50)

Table 5. Bond lengths (Å) and interbond angles (°) with e.s.d.s in parentheses for **(3)**

Mo(1)–Mo(1^i)	2.607(1)	C(1)–C(2)	1.414(5)
Mo(1)–Cl(1)	2.484(1)	C(2)–C(3)	1.409(6)
Mo(1)–Cl(1^i)	2.493(1)	C(3)–C(4)	1.399(7)
Mo(1)–Cl(2)	2.485(1)	C(4)–C(5)	1.434(6)
Mo(1)–Cl(2^i)	2.479(1)	C(5)–C(1)	1.426(6)
Mo(1)–C(1)	2.329(4)		
Mo(1)–C(2)	2.357(4)	C(6)–C(1)	1.501(6)
Mo(1)–C(3)	2.267(4)	C(6)–C(7)	1.514(8)
Mo(1)–C(4)	2.186(4)	C(6)–C(8)	1.533(7)
Mo(1)–C(5)	2.208(4)		
Cl(1)–Mo(1)–Cl(1^i)	116.83(2)	C(1)–C(2)–C(3)	109.0(4)
Cl(2)–Mo(1)–Cl(2^i)	116.66(2)	C(2)–C(3)–C(4)	108.6(4)
Mo(1)–Cl(1)–Mo(1^i)	63.17(2)	C(3)–C(4)–C(5)	107.4(4)
Mo(1)–Cl(2)–Mo(1^i)	63.34(2)	C(4)–C(5)–C(1)	108.2(4)
		C(5)–C(1)–C(2)	106.7(4)
C(1)–C(6)–C(7)	113.5(4)	C(7)–C(6)–C(8)	111.0(4)
C(1)–C(6)–C(8)	108.4(4)		

Symmetry code i = 1 − *x*, −*y*, 1 − *z*.

which was washed with thf and dried *in vacuo*. Yield: 0.12 g, 43%.

Hydrogen–Deuterium Exchange Experiments.—Sealed n.m.r. samples containing *ca.* 10 mg of [Mo(η-C_5H_5)(dmpe)H_3], **(1)**, and 20—80 mg of the substrate dissolved in C_6D_6 (0.7 cm^3), and a sealed capillary tube with a solution of $SiMe_4$ in benzene, were irradiated using a 100-W medium-pressure mercury lamp. The reaction was monitored by recording the ^1H n.m.r. spectrum at intervals. When no further changes in the intensity of the bands were observed, the n.m.r. sample tubes were opened and the mass spectrum of the volatile substrate recorded. If the latter was a solid, the solvent was removed first under reduced pressure. In the case of liquids, these were distilled, and in the cases of highly volatile samples the mass spectra were obtained directly from the initial sample.

Crystal Structure Determination.—The structure was determined by heavy-atom Patterson and electron-density methods. Solution and refinement was carried out with the Oxford CRYSTALS package[39] on the VAX 11/750 computer in the Chemical Crystallography Laboratory, Oxford University. Isotropic and then anisotropic full-matrix refinement of positional and thermal parameters of a model without hydrogen atoms converged with $R = 0.0357$ ($R' = 0.0439$). The hydrogens were then located from a difference map and were given fixed isotropic thermal parameters, 0.06 Å^2, and only their positional parameters were refined. All non-hydrogen atoms were refined anisotropically to give the final residuals of $R = 0.0284$ ($R = 0.0299$).* The Mo atom was corrected for anomalous dispersion. The final difference map was featureless. The final atomic parameters are given in Table 4. Bond lengths and angles are given in Table 5. The molecular structure is shown, together with atomic numbering, in Figure 1.

Crystal data. $C_{16}H_{22}Cl_4Mo_2$, $M = 548.04$, monoclinic, $a = 7.709(2)$, $b = 12.174(1)$, $c = 10.226(1)$ Å, $\beta = 90.97(2)°$, $U = 959.53$ Å^3, space group $P2_1/c$ (no. 14), $Z = 2$, $D_c = 1.90$ g cm^{-3}, μ(Mo-K_α) = 18.25 cm^{-1}, $F(000) = 540$, crystal size 0.6 × 0.4 × 0.2 mm. Preliminary cell dimensions and space-group symmetry were determined from oscillation and Weissenberg photographs. The crystal was then mounted on a CAD4-F diffractometer. 25 High-order reflections were accurately centred and used to calculate the orientation matrix and cell dimensions. After averaging equivalent reflections, 2 082 independent reflections were corrected for Lorentz, polarisation, and absorption effects.

Acknowledgements

We thank the Venezuelan Government for financial support (to A. I.), the British Council for a Scholarship (to V. S. B. M.), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

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* $R' = [\Sigma w(|F_o| - |F_c|)^2]/[\Sigma w(|F_o|)^2]$.

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Received 13*th December* 1985; *Paper* 5/2187