Synthesis and Properties of Some Cyclohexadienylrhenium Polyhydride Complexes

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The heptahydride $[ReH_7(PPh_3)_2]$ (**1**) reacts in the presence of 3,3-dimethylbutene with benzene, toluene, *p*-xylene, and mesitylene to give dihydridocyclohexadienyl complexes. Treatment of these complexes with acid afforded the corresponding trihydridocyclohexadienyl cations, which were isolated and characterised in the case of the benzene and mesitylene derivatives. The cyclohexadienyl complexes prepared all exhibited fluxionality. The most stable conformations of these complexes and the relative energy barriers for cyclohexadienyl-ligand rotation in the neutral complexes were explained by steric interactions between the ring substituents and the bulky phosphine ligands, as was the selectivity of their formation from the heptahydride (**1**). The reversible migration of a hydrogen atom between the metal and the cyclohexadienyl ligand implied in the observed isomerisation of the latter was detected using spin-saturation-transfer n.m.r. experiments.

Cyclohexadienyl transition-metal complexes are generally prepared by nucleophilic addition to arene complexes.[1-3] Several other methods, including hydride abstraction from cyclohexadiene complexes,[4,5] have been described.[6] The reaction of benzene with the heptahydride complex $[ReH_7(PPh_3)_2]$ (**1**) in the presence of 3,3-dimethylbutene afforded the dihydridocyclohexadienyl complex $[Re(\eta\text{-}C_6H_7)H_2(PPh_3)_2]$ (**2**). This work, along with the *X*-ray crystal structure of (**2**), was reported in a preliminary communication.[7] In order to investigate the fluxionality of this compound a series of substituted analogues of complex (**2**) were prepared by the reaction of (**1**) with toluene, *p*-xylene, and mesitylene. The hydride ligands were expected to be useful in n.m.r. studies of the conformational behaviour of these complexes. Furthermore, it has been reported that in other complexes the cyclohexadienyl ligand can isomerise.[3,8,9] We were interested to find out whether such an isomerisation could be brought about in the polyhydridocyclohexadienyl complexes synthesised from (**1**), and if so to elucidate its mechanism.

Results

Synthesis.—The reactions of the heptahydride $[ReH_7(PPh_3)_2]$ (**1**) with benzene, toluene, *p*-xylene, and mesitylene (10 min at 75 °C in the aromatic hydrocarbon with 10 equivalents of 3,3-dimethylbutene) yielded complex (**2**), a mixture of complexes (**3**) and (**4**), complex (**5**), and (**6**), respectively. In the reaction of (**1**) with benzene, 1 mol of dihydrogen was evolved and 1.1 mol of 2,2-dimethylbutane (identified by g.c.) was formed. The compounds (**2**), (**5**), and (**6**), and the mixture of (**3**) and (**4**) were isolated as yellow air-stable crystals, and characterised by mass spectroscopy, elemental analysis (Table 1) and, in particular, n.m.r. spectroscopy (Tables 2 and 3).

The ^1H n.m.r. spectrum of the crude product of the reaction between (**1**) and toluene showed that the complexes (**3**) and (**4**) were formed in the ratio *ca.* 27:73, and that the other possible isomers were not present. Successive recrystallisations of mixtures of (**3**) and (**4**) from either acetone or diethyl ether led to enrichment in the complex (**4**). On heating a mixture of (**3**) and (**4**) in the proportions *ca.* 9:91 obtained in this way in benzene for 10 min at 75 °C, the ratio of (**3**) to (**4**) returned to *ca.* 27:73 and did not change on further heating. The reactions of complex (**1**) with toluene and *p*-xylene led only to 3- and/or 6-substituted products, (**3**)—(**5**); that with mesitylene led exclusively to the 2,4,6-*exo*-trimethylcyclohexadienyl complex (**6**). Treatment of an ether solution of either (**2**) or (**6**) with a slight excess of HBF_4–Et_2O led to the formation of white air-stable precipitates which were shown to be the salts $[Re(\eta\text{-}C_6H_7)H_3(PPh_3)_2][BF_4]$ (**7**) and $[Re(\eta\text{-}2,4,6\text{-}exo\text{-}Me_3C_6H_4)H_3(PPh_3)_2][BF_4]$ (**8**). Treatment of (**8**) with methanolic KOH gave back (**6**). The compounds (**7**) and (**8**) were characterised by their mass spectra, elemental analysis and, in particular, their ^1H n.m.r. spectra (Tables 2 and 3).

Complex (**2**) and the mixture of (**3**) and (**4**) were dehydrogenated by heating in vacuum[7] and in toluene, respectively, to the arene complexes $[Re(\eta\text{-}C_6H_6)H(PPh_3)_2]$ (**9**)[10] and $[Re(\eta\text{-}C_6H_5Me)H(PPh_3)_2]$ (**10**), obtained in the form of a bright yellow oil and crystals, respectively.

Dynamic Behaviour.—All of the cyclohexadienyl complexes (**2**)—(**8**) exhibited fluxional behaviour, which was studied by

Table 1. Analytical and physical data for complexes (**2**)—(**8**) and (**10**)

Complex	$\tilde{\nu}$(Re–H)[a]/cm^{-1}	*m/z*	Analysis[b]/% C	H	P
(**2**)	1 995m, 1 905w	790 (*M* − 2)	63.5 (63.7)	5.0 (5.0)	7.6 (7.8)
(**3**) + (**4**)	1 985w, 1 930m, 1 895(sh)[c]	804 (*M* − 2)	63.9 (64.1)	5.2 (5.1)	7.9 (7.7)
(**5**)	1 925w	818 (*M* − 2)	64.3 (64.5)	5.2 (5.3)	7.4 (7.6)
(**6**)	2 000w, 1 965w	832 (*M* − 2)	64.7 (64.8)	5.5 (5.4)	7.7 (7.4)
(**7**)	2 085vw, 2 035w, 1 945w	791 (*M* − 2)	57.3 (57.1)	4.6 (4.6)	7.1 (7.0)
(**8**)	2 120w, 2 065w, 2 040w	833 (*M* − 2)	58.7 (58.6)	5.2 (5.1)	6.8 (6.7)
(**10**)	1 950m	804 (*M*)	64.4 (64.2)	4.9 (4.9)	7.8 (7.7)

[a] In Nujol. [b] Required values are given in parentheses. [c] Ratio (**3**):(**4**) = 15:85.

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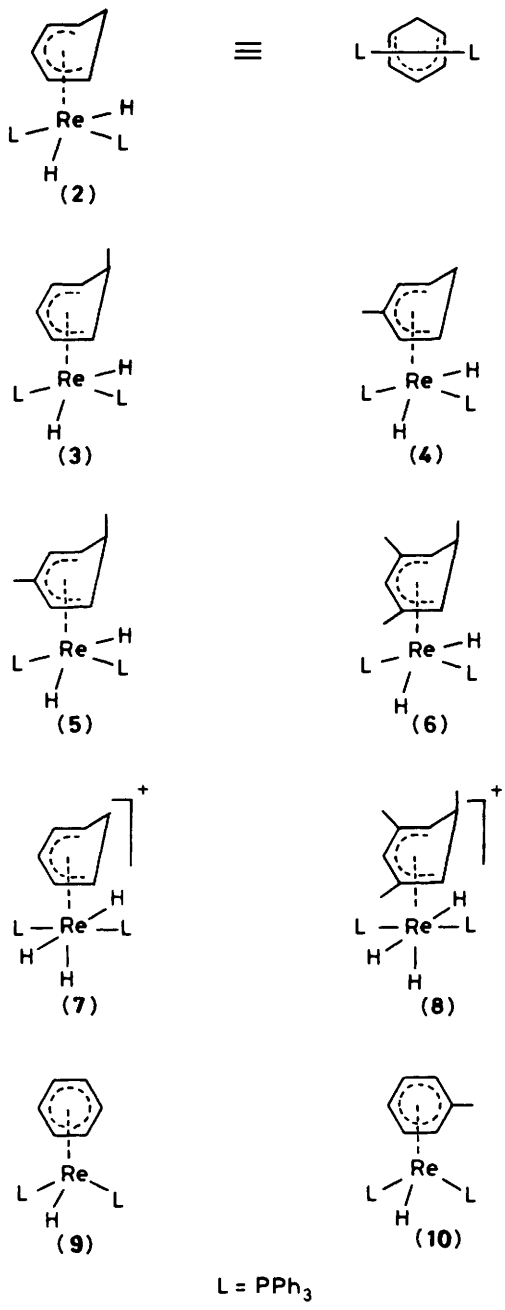


n.m.r. spectroscopy [variable-temperature and spin-saturation-transfer (s.s.t.) experiments].[11] The symmetries of complexes (2)—(6) could be deduced from the hydride signals without reference to the region 0—10 p.p.m. The hydride signals in the slow-limit ^{1}H n.m.r. spectrum are given in Table 3. These consist of two triplets for complexes (2)—(5) and three triplets for complex (6). The fast-limit spectra were not observed even at 75 °C, except in the case of (6) where it was observed at 25 °C. In contrast to complexes (2), (3), and (6), the slow-limit spectra of (4) and (5) are observed at temperatures up to 25 °C.

Two separate coalescences were observed in the ^{1}H n.m.r. spectra of the cations (7) and (8). At room temperature, only broad resonances were observed apart from those due to triphenylphosphine; the ring signals were not resolved. However, at −2 °C (7) and −40 °C (8) the ring signals were well resolved, and the hydride ligands gave rise to a single triplet (Table 3). On cooling further to −72 °C (7) and −90 °C (8), the hydride signals first coalesced then appeared as two broad signals of relative intensity 2:1.

S.s.t. experiments were performed on complexes (2), (5)—(8), and the mixture of (3) and (4); the clearest results were obtained with (2) and (8). In the ^{1}H n.m.r. spectrum of complex (2) in [$^2H_6$]benzene at 80 °C the two hydride triplets observed at

Table 2. Proton n.m.r. spectra of the cyclohexadienyl complexes (2)—(8)[a]

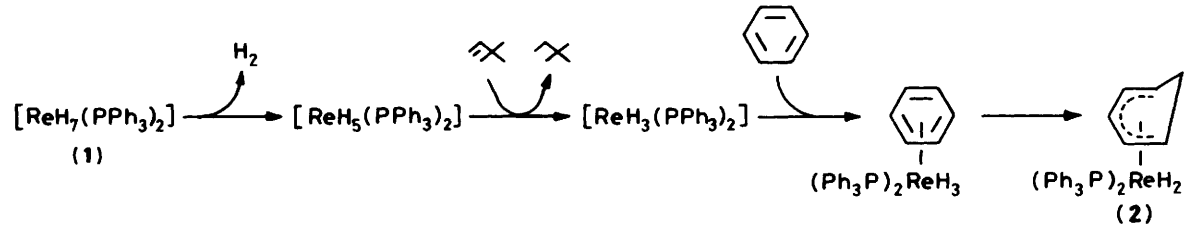
Complex	Position 1,5	2,4	3	6-*exo*	6-*endo*
(2)[b]	1.95 (2 H, br t, *J* 5)	3.45[c]	6.35 (1 H, br t, *J* 5)	3.40[c]	2.35 (1 H, dt, *J* 10, 5)
(3)[d]	*ca.* 2.8[e,f]	3.61 (2 H, t, *J* 6)	6.32 (1 H, t, *J* 6)	0.50 (3 H, d, *J* 6, Me)	2.66 (m)[f]
(4)[d]	2.42 (2 H, m)	3.80 (2 H, d, *J* 6)	2.76 (s, Me)[f]	4.04 (1 H, m)	2.80 (dt, *J*, 10, 5)[f]
(5)[g]	2.72[h,i]	3.65 (2 H, d, *J* 6)	2.72 (s, Me)[h]	0.49 (3 H, d, *J* 5, Me)	2.72[h,i]
(6)[g]	2.85 (2 H, d, *J* 5)	1.89 (6 H, s, Me)	5.44 (1 H, s)	0.54 (3 H, d, *J* 5, Me)	1.59 (1 H, m)
(7)[j]	3.05 (2 H, br)	4.86 (2 H, br)	5.47[k]	3.46 (1 H, br)	1.15 (1 H, m)
(8)[l]	3.05 (2 H, d, *J* 5)	1.92 (6 H, s, Me)	5.41 (1 H, s)	−0.02 (3 H, d, *J* 6, Me)	0.96 (1 H, m)

[a] Given as δ/p.p.m., intensity, multiplicity, H–H coupling constant in Hz, substituent. All complexes gave multiplets between 6.8 and 7.8 p.p.m. of intensity 30 H due to PPh_3; for Re–H signals see Table 3. [b] In [$^2H_2$]dichloromethane, 250 MHz, 25 °C. [c] Total intensity 3 H. [d] In [$^2H_6$]benzene, 400 MHz, 25 °C; mixture of (3) and (4) in the proportions 15:85. [e] Masked by 3-Me of complex (4). [f] Total intensity: 4 H of complex (4) + 3 H of (3). [g] In [$^2H_6$]benzene, 80 MHz, 25 °C. [h] Total intensity 6 H. [i] Masked by 3-Me. [j] In [$^2H_2$]dichloromethane, 80 MHz, −2 °C. [k] Masked by $CHDCl_2$. [l] In [$^2H_2$]dichloromethane, 80 MHz, −40 °C.

Table 3. Temperature dependence of hydride signals in the ^{1}H n.m.r. spectra (80 MHz) of complexes (2)—(8)

Complex	θ$_c$/°C	Solvent	Hydride signals[a]
(2)	−40	CD_2Cl_2	−3.10, 1 H, t, *J* 36; −12.71, 1 H, t, *J* 38
	25	CD_2Cl_2	vbr
	80	C_6D_6	−6.9, 2 H, br
(3)	−40[b]	$C_6D_5CD_3$	*ca.* −3.1; −12.06, t, *J* 35
	30	$C_6D_5CD_3$	Not visible
	90[c]	$C_6D_5CD_3$	−7.1, br
(4)	−40[b]	$C_6D_5CD_3$	*ca.* −3.2, 1 H, t, *J* 35; −11.61, 1 H, t, *J* 35
	30	$C_6D_5CD_3$	*ca.* −3.2, 1 H, t, *J* 35; −11.61, 1 H, t, *J* 35
	90[c]	$C_6D_5CD_3$	−7.1, br
(5)	25	C_6D_6	−3.76, 1 H, t, *J* 33; −11.46, 1 H, t, *J* 35
	75	C_6D_6	−7.6, br
(6)	−70	CD_2Cl_2	−3.46, 0.6 H, t, *J* 35; −8.48, 0.8 H, t, *J* 42; −11.85, 0.6 H, t, *J* 35
	25	C_6D_6	−7.25, 2 H, t, *J* 39
(7)	−72	CD_2Cl_2	−2.2, 1 H, br; −6.0, 2 H, br
	−2	CD_2Cl_2	−4.54, *d*, t, *J* 29
(8)	−90	CD_2Cl_2	−2.7, 1 H, br; −6.1, 2 H, br
	−40	CD_2Cl_2	−5.00, 3 H, t, *J* 30

[a] Given as δ/p.p.m., intensity, multiplicity, P–H coupling constant in Hz. [b] Deduced from the spectrum of the mixture of complexes (3) + (4) (*ca.* 36:64); each of the two signals at *ca.* −3.2 and −11.8 p.p.m. appears to result from the superposition of two similar triplets separated by *ca.* 17 Hz (*J*/2) and *ca.* 35 Hz (*J*) respectively. The relative abundance of (3) in this mixture with respect to the equilibrium proportions (*ca.* 27:73) probably arises from preferential crystallisation of (4) at low temperature. [c] Spectrum of the mixture of complexes (3) + (4) (*ca.* 27:73). [d] Integration varied from 2 to 3.5 H (*cf.* ref. 11).



Scheme 1. Postulated mechanism for the formation of complex (2) from the heptahydride (1) and benzene in the presence of 3,3-dimethylbutene

Table 4. S.s.t. experiments on cation (8)

Signal irradiated δ/p.p.m.	Signal perturbed δ/p.p.m.
5.5 (3-H)	3.0 (1,5-H)
3.0 (1,5-H)	5.5 (3-H)
1.9 (2,4-Me)	0.0 (6-*exo*-Me)
0.0 (6-*exo*-Me)	1.9 (2,4-Me)
−5.0 (Re–H)	1.0 (6-*endo*-H)

−40 °C were replaced by a broad signal at −6.9 p.p.m. Irradiation of this signal caused that at 2.85 p.p.m. (6-*endo*-H) to diminish by 25%, and irradiation of the signal at 2.85 p.p.m. caused that at −6.9 p.p.m. to diminish by 15%. The results of s.s.t. experiments on cation (8) at 11 °C are in Table 4. The diminutions of intensity induced were from 50 to 95%.

Discussion

Synthesis.—The reactions of the heptahydride (1) with benzene and its derivatives constitute an original synthesis of cyclohexadienyl complexes. The mechanism of the reaction of (1) with benzene presumably involves co-ordination of a molecule of benzene to the co-ordinatively unsaturated intermediate $[ReH_3(PPh_3)_2]$ to give (2) after migration of a hydrogen atom from the metal to the ring (Scheme 1). The detection of *ca.* 1 mol each of dihydrogen and 2,2-dimethylbutane is in agreement with this mechanism. The species $[ReH_3(PPh_3)_2]$ has been invoked as a reactive intermediate in the syntheses of trihydridodiene complexes [10] and the activation of alkane C–H bonds.[12] The migration of a hydrogen atom from the metal onto the ring precludes the possibility of obtaining 6-*endo*-methylcyclohexadienyl complexes, which were indeed not observed. The formation of complexes (3) and (4) is remarkable in view of the observation that the tricarbonyl-(1- and -(2-methylcyclohexadienyl)manganese complexes are more stable than their 3- and 6-*exo*-methyl isomers.[9] Similarly, to our knowledge, no reactions have previously been reported which afford 3,6-*exo*-dimethyl- or 2,4,6-*exo*-trimethyl-cyclohexadienyl complexes as the major product. The selectivity of the reactions of complex (1) with methyl-substituted benzene derivatives and the unusual nature of the products will be discussed below.

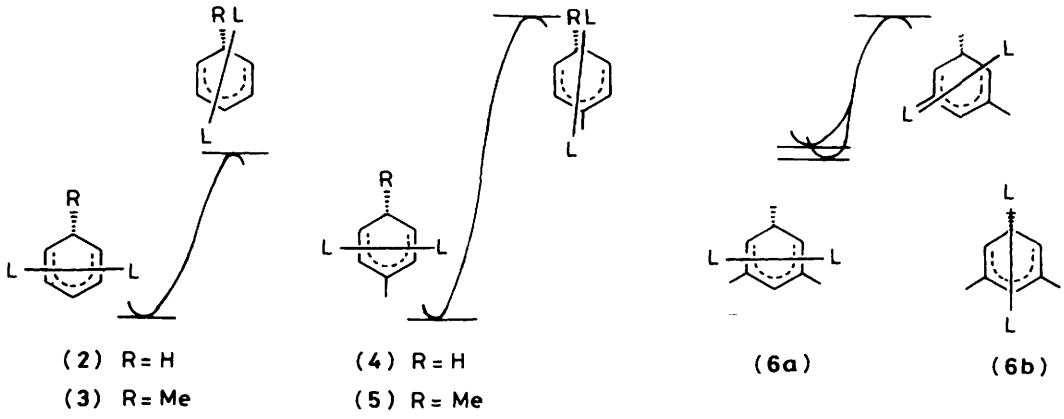
Dynamic Behaviour.—Proton n.m.r. studies of the fluxional complexes (2)—(6) enabled us to determine their most stable conformations, and to observe two distinct fluxional processes: exchange between the hydride ligands, which we interpret in terms of a rotation of the cyclohexadienyl ligand, and isomerisation of the cyclohexadienyl ligand accompanied by exchange between the 6-*endo*-hydrogen and the hydride ligands. The slow-limit spectra of complexes (2)—(5) show that the most stable conformation in solution is that in which the hydride ligands lie in the plane of symmetry of the cyclohexadienyl ring. This conformation was shown by *X*-ray crystallography [7] to be that favoured by (2) in the solid state as well (Scheme 2). In these conformations, the steric interactions in complexes (3)—(5) between the phosphine ligands and the methyl groups are minimised, and do not oppose the (presumably electronic) factors which determine the most stable conformation of (2).

In contrast to (2)—(5), the slow-limit spectrum of complex (6) shows that it adopts two conformations of similar stability: (6a) (in which the hydride ligands lie in the plane of symmetry of the ring) and (6b) (in which the phosphine ligands lie in that plane) (Scheme 2). Of the complexes that we prepared, (6) is the only one to adopt a conformation in which the hydrides are equivalent, for, unlike complexes (2)—(5), the conformation (6a) is not that in which the steric interactions between the phosphines and methyl groups on the ring are least.

The temperature dependence of the ^1H n.m.r. spectra of cations (7) and (8) closely resembles that of the complex $[Re(\eta\text{-}C_6H_8)H_3(PPh_3)_2]$.[10] The latter was shown to have a deformed pentagonal-bipyramidal structure [13] with the phosphine ligands at the apexes, and presumably the structures of cations (7) and (8) are analogous.

The evolution of the spectrum of complex (2) shows that the hydride ligands exchange. This phenomenon appears to be due to the rotation of the cyclohexadienyl ligand, and we will use this model to explain the differences in the behaviour of the complexes (2)—(6). The coalescence temperature of (2) (36 ± 1 °C) allows us to make a crude estimate of the activation energy for rotation (E_a = 56 ± 4 kJ mol^{-1}). This value is comparable with those found for other transition-metal cyclohexadienyl complexes.[2,5,14] The coalescence temperatures of complexes (4) and (5) (both methylated in the 3 position) are higher than those of complexes (2) and (3) (not substituted in the 3 position). On the other hand, the coalescence temperature of complex (6), the most substituted complex, is well below those of (2) and (3). We may thus establish a qualitative order of activation energies for the cyclohexadienyl ligand rotation: (6) < (2) ≈ (3) < (4) ≈ (5). This order can easily be explained by considering the energy profile of the rotation process (Scheme 2). In complexes (2) and (3), with no methyl group on the dienyl system, there is no methyl–phosphine interaction in the transition state. However, there is such an interaction in complexes (4)—(6), where in the transition state a methyl group is eclipsed with respect to a phosphine ligand. Thus the energies of the transition state for rotation of (2) and (3) are lower than those in complexes (4) and (5). The ground states (6a) and (6b) of complex (6) are destabilised with respect to those of complexes (2)—(5) by a methyl–phosphine interaction. This destabilisation explains the low activation energy for rotation in (6) compared to those in (4) and (5).

Isomerisation of the cyclohexadienyl ligand was shown to occur in the equilibrating complexes (3) and (4). Two mechanisms have been proposed to explain the isomerisation of cyclohexadienyl complexes. That put forward by Lamanna and



Scheme 2. Activation energies for rotation of the cyclohexadienyl ligands in complexes (**2**)—(**6**)

Brookhart[3] (applicable to any cyclohexadienyl complex) invokes the initial migration of the 6-*endo*-hydrogen onto the metal giving a η^4-arene intermediate, while the first step of the mechanism suggested by Werner and Werner[8] (only applicable to hydridocyclohexadienyl complexes) is the migration of a hydride ligand onto the ring giving a cyclohexadiene intermediate. Experiments undertaken to determine which of these two mechanisms might be relevant to the compounds (**2**)—(**8**) are described in the following paper.[15] Whatever the mechanism, isomerisation of the cyclohexadienyl ligand implies reversible migration of a hydrogen atom between the metal and the ring which would be observed as exchange between the hydride ligands and the 6-*endo*-hydrogen. This exchange was observed in complexes (**2**) and (**8**) by use of spin-saturation transfer. The s.s.t. experiments conducted on cation (**8**) also revealed the degenerate isomerisation of the cyclohexadienyl ligand. Exchange was found to take place within the three sets of protons of complex (**8**) shown below.

$$\text{1-H} \rightleftharpoons \text{3-H} \rightleftharpoons \text{5-H}$$

$$\text{2-Me} \rightleftharpoons \text{4-Me} \rightleftharpoons \text{6-}exo\text{-Me}$$

$$\text{Re–H} \rightleftharpoons \text{6-}endo\text{-H}$$

Having seen that the cyclohexadienyl ligands of compounds (**2**)—(**6**) can isomerise, it remains to explain the absence of the isomers of (**3**)—(**6**). In these isomers of the toluene and *p*-xylene derivatives (**3**)—(**5**) the presence of methyl groups in the 1 or 2 positions would engender an interaction with the phosphine ligands which could be avoided only by the adoption of an electronically unfavourable conformation. While in complex (**6**) the 2,4-methyl groups are probably approximately coplanar with the dienyl system, in its 1,3,5-trimethylcyclohexadienyl isomer the 1,5-methyl groups would be bent towards the metal,[16] leading to a greater steric interaction with the phosphine ligands than in (**6**).

Experimental

All experiments were carried out under nitrogen using standard Schlenk techniques. Evaporations were done under reduced pressure. Solvents were distilled before use, ether and benzene from sodium–benzophenone, and CH_2Cl_2, after treatment with P_2O_5, from CaH_2. Benzene (Fluka, 'thiophen-free'), *p*-xylene (Fluka puriss), mesitylene and 3,3-dimethylbutene (Fluka 'purum'), $LiAlH_4$ (Prolabo), and HBF_4 (Ega Chemie) were used without purification. Potassium t-butoxide[17] and $[ReH_7(PPh_3)_2]$ (**1**)[10] were prepared by literature methods.

I.r. spectra were recorded on a Perkin-Elmer 297 instrument and n.m.r. spectra on Perkin-Elmer R12B, Bruker WP-80/CW, WP-200/SY, and WM/400 instruments. Chemical shifts were calculated using $SiMe_4$ (0.00 p.p.m.), C_6D_5H (7.20 p.p.m.), $C_6D_5CD_2H$ (2.06 p.p.m.), or $CDHCl_2$ (5.25 p.p.m.) as internal references. The mass spectra of cationic complexes were recorded on an AEI MS-80 instrument equipped with a fast-atom-bombardment source, and those of neutral complexes on an AEI MS-50 (the masses given are for ^{187}Re). The elemental analyses were performed by the Service Central d'Analyse of the Centre National de la Recherche Scientifique.

Syntheses.—$[Re(\eta\text{-}C_6H_7)H_2(PPh_3)_2]$ (**2**). The compound $[ReH_7(PPh_3)_2]$ (287 mg, 0.40 mmol) was dissolved in benzene (40 cm^3). 3,3-Dimethylbutene (0.51 cm^3, 3.95 mmol) was added, and the solution refluxed for 10 min. The solvent was evaporated from the beige solution obtained. Acetone (3 cm^3) was added to the residue, and the resulting solution rapidly deposited beige crystals of complex (**2**). The crystals were washed with acetone and dried under vacuum (232 mg, 73%). An analytically pure sample of pale yellow crystals of (**2**) was prepared by recrystallisation from CH_2Cl_2–acetone. After a similar reaction, the amount of non-condensable material in the reaction vessel was shown to correspond to 1 mol H_2 per mol Re. The solvent was analysed by gas chromatography (SE 30 column on a Perkin-Elmer F11 instrument) and found to contain 1.1 mol 2,2-dimethylbutane per mol Re.

Substituted analogues of (**2**). Complexes (**3**) + (**4**), (**5**), and (**6**) were prepared by a similar method using toluene, *p*-xylene, and mesitylene, respectively, instead of benzene. The heptahydride was initially insoluble; after heating at 75 °C for 10 min, pale yellow solutions were obtained from which the products were isolated as for (**2**) (yields 62, 41, and 71% respectively). Recrystallisation of the mixture of (**3**) and (**4**) from acetone or ether allowed us to obtain mixtures enriched in (**4**) up to a ratio of *ca.* 9:91. Such a mixture (ratio *ca.* 9:91) (88 mg, 0.109 mmol) was dissolved in benzene (*ca.* 0.5 cm^3) in an n.m.r. tube. The solution was heated to 75 °C for 10 min whereupon the ratio of (**3**) to (**4**) was *ca.* 27:73. Prolonged heating had no further effect on the ratio.

Complex (**6**) *by deprotonation of* (**8**). To a colourless solution of complex (**8**) (47 mg, 0.051 mmol) in CH_2Cl_2 (*ca.* 0.5 cm^3) was added 0.83 mol dm^{-3} KOH in methanol (70 μl, 0.058 mmol). The n.m.r. spectrum of the resulting yellow suspension indicated the quantitative formation of (**6**). Dichloromethane (3 cm^3) was added and the inorganic salt extracted with water (2 × 3 cm^3).

The organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated. Acetone (0.5 cm^3) was added to the residue, and the resulting solution rapidly deposited yellow crystals of complex (**6**) (23 mg, yield 54%).

$[Re(\eta\text{-}C_6H_7)H_3(PPh_3)_2][BF_4]$ (**7**). Complex (**2**) (119 mg, 0.150 mmol) was dissolved in ether (25 cm^3). Fluoroboric acid (54% in diethyl ether, 22 μl, 0.159 mmol) was added. The white suspension obtained was filtered and the residue washed with ether (2 × 5 cm^3) to give an analytically pure white powder of complex (**7**) (82 mg, 62%).

The complex $[Re(\eta\text{-}2,4,6\text{-}exo\text{-}Me_3C_6H_4)H_3(PPh_3)_2][BF_4]$ (**8**) was prepared in the same way from (**6**). Recrystallisation of the resulting white powder (crude yield 84%) from CH_2Cl_2–methanol gave analytically pure colourless crystals of (**8**).

$[Re(\eta\text{-}C_6H_6)H(PPh_3)_2]$ (**9**). Complex (**2**) (200 mg, 0.253 mmol) was heated under vacuum with a flame. The yellow crystals melted to give a dark residue which was extracted with C_6D_6. The ^1H n.m.r. spectrum of this solution indicated the formation of complex (**9**) (79%).

$[Re(\eta\text{-}C_6H_5Me)H(PPh_3)_2]$ (**10**). This was prepared by thermolysis of a mixture of complexes (**3**) and (**4**) prepared *in situ* from (**1**) (500 mg, 0.697 mmol) as described above. A portion of the solvent (*ca.* 20%) of the pale yellow solution obtained was evaporated to remove most of the 3,3-dimethyl-butane and -butene. After heating the remainder at reflux for 6.5 h a yellow solution was obtained. The solvent was evaporated and the yellow oil obtained was consolidated by treatment with hexane (2 × 20 cm^3). The yellow powder obtained was extracted with hot hexane (100 cm^3), and 15 h after cooling to room temperature analytically pure yellow crystals of complex (**10**) were obtained. The crystals were washed with hexane and dried under vacuum (210 mg, 37%). N.m.r. ($[^2H_6]$benzene): δ 7.60 (12 H, m, *o*-Ph), 6.95 (m, *m,p*-Ph and C_6D_5H), 5.05 (1 H, t, *J* 5, 4-H), 3.90 (2 H, t, *J* 5, 3,5-H), 3.60 (2 H, d, *J* 5, 2,6-H), 2.60 (3 H, s, Me), and −7.00 [1 H, t, *J*(PH) 34 Hz, Re–H].

N.M.R. Studies.—All variable-temperature work and s.s.t. experiments were conducted on a Bruker WP 80/CW instrument. The instrument and its dedicated temperature-control unit were calibrated at 36 °C using a methanol–$[^2H_4]$methanol–trace of acid standard. The temperature indicated was found to be correct to ± 1 °C.

Variable-temperature experiments. The slow-limit spectra and those recorded at high temperature are shown in Table 3. The coalescence temperature of the hydride signals of complex (**2**) in $[^2H_2]$dichloromethane was found to lie between 36 and 38 °C, indicating a value of 56 ± 4 kJ mol^{-1} for $\Delta G^{\ddagger}$.[18] Coalescence of the hydride signal of complex (**6**) took place between −30 and −40 °C.

Spin-saturation-transfer experiments. For complex (**2**) at 80 °C in $[^2H_6]$benzene, irradiation of the signal at −6.9 p.p.m. caused the intensity of the signal at 2.85 p.p.m. to diminish by 25%; irradiation of the signal at 2.85 p.p.m. caused the intensity of that at −6.9 p.p.m. to decrease by 15%. The results of s.s.t. experiments on cation (**8**) in $[^2H_2]$dichloromethane at 11 °C are in Table 4.

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Received 22nd April 1985; *Paper* 5/663