Synthesis of Some (η-Arene)dihydridorhenium Cations and Their Reactions with $LiAlH_4$ and $LiAlD_4$

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A series of cations $[Re(\eta\text{-arene})H_2(PPh_3)_2]^+$ (arene = benzene, toluene, *p*-xylene, or mesitylene) was prepared from the corresponding neutral dihydridocyclohexadienyl complexes by treatment with CPh_3BF_4. These cations reacted with $LiAlH_4$ and $LiAlD_4$ to form dihydridocyclohexadienyl complexes. The unusual selectivity of the hydride attack is explained by steric interactions between the ring methyl groups and the bulky phosphine ligands. The initial product of the reaction of the η-mesitylene cation with $LiAlD_4$ allows the isomerisation mechanism for the cyclohexadienyl complexes to be clarified.

Cations of the formula $[Re(\eta\text{-arene})H_2(PPh_3)_2]^+$ are readily prepared from the corresponding dihydridocyclohexadienyl complexes whose preparation is described in the preceding paper.[1] We were interested to study the regioselectivity of the attack of $LiAlH_4$ or $LiAlD_4$ on the substituted arene ligands. Furthermore, we set out to prepare isotopically labelled cyclohexadienyl complexes in order to investigate the mechanism of isomerisation of the cyclohexadienyl ligand.[2,3]

Results and Discussion

Synthesis.—The cyclohexadienyl complexes (**2**),‡ (**3**) + (**4**), (**5**), and (**6**) are easily prepared from $[ReH_7(PPh_3)_2]$ (**1**).[1] They react immediately with a small excess of triphenylmethyl (trityl) tetrafluoroborate in CH_2Cl_2 to give the (η-arene)dihydridobis-(triphenylphosphine)rhenium cations (**12**)—(**15**) [arene = benzene, toluene, *p*-xylene, or mesitylene, respectively (Scheme 1)], isolated as bright yellow air-stable crystals and characterised by mass spectrometry, elemental analysis, and ^1H n.m.r. spectroscopy (Table).

While the 6-*exo*-unsubstituted complexes (**2**) and (**4**) may react with trityl by simple loss of the *exo*-hydrogen,[4,5] the 6-*exo*-methylated complexes (**3**), (**5**), and (**6**) must either undergo prior rearrangement to 6-*exo*-H complexes[3] or react directly at 6-*endo*-H[6,7] or, more probably, at the hydride ligands. We did not attempt to elucidate the mechanism of this reaction.

The dihydrido cations may be synthesised by other methods (Scheme 1); thus the cations (**12**) and (**15**) were formed by loss of H_2 from the cyclohexadienyl cations (**7**) and (**8**) prepared *in situ*,[1] the cyclohexadiene complex (**11**) reacted with trityl to give the cation (**12**), and the arene complex (**10**) could be reversibly protonated to the cation (**13**). Treatment of (**13**) with KOH in methanol gave back (**10**).

Reactions with $LiAlH_4$ *and* $LiAlD_4$.—The reactions of the dihydrido(η-arene) cations (**12**)—(**15**) with $LiAlH_4$ and $LiAlD_4$ led, in most cases, to dihydridocyclohexadienyl complexes that had already been prepared directly from $[ReH_7(PPh_3)_2]$[1] (Scheme 2). The product of the reaction of (**12**) with $LiAlD_4$ showed no particular concentration of deuterium at any one position of the ring. Mass spectrometry confirmed the presence of one atom of deuterium in the product (**2**). The reaction of complex (**13**) with $LiAlD_4$ led only to 6-*exo*-D-(**4**). The reaction of the cation (**14**) with $LiAlH_4$ led to a mixture of the new complex (**16**) and (**5**) in the ratio 85:15.§ The ^1H n.m.r. spectrum of (**16**) at 25 °C shows two hydride triplets, indicating that rotation of the cyclohexadienyl ligand is slow. This observation is consistent with the behaviour of complexes (**4**) and (**5**) which also bear a methyl group in the 3 position.[1] No signals in the ^1H n.m.r. spectrum of the product of the reaction of (**15**) with $LiAlH_4$ were observed which might be attributed to a 6-*endo*-methyl product.

Regioselectivity.—Nucleophiles adding to η-arene ligands are invariably found in the 6-*exo* position of the initially formed cyclohexadienyl product.[8] Thus the reaction of complex (**12**) with $LiAlD_4$ must initially give 6-*exo*-D-(**2**) which rapidly isomerises to D-(**2**) with the deuterium atom distributed statistically among the 1—5 and 6-*exo* positions. The regioselectivity of nucleophilic attack on substituted arene ligands has been the subject of numerous investigations.[4,7,9] It has been shown that in most cases hydride preferentially attacks unsubstituted sites in such complexes;[4,10] however, with highly substituted ligands such as penta- or hexamethyl-benzene, hydride tends to attack a substituted site to give a 6-*endo*-methylcyclohexadienyl complex.[4]

The cations (**13**)—(**15**) react, like (**12**), with $LiAlH_4$ or $LiAlD_4$ to give products arising from *exo* attack of 'H^-' or 'D^-.' The remarkable regioselectivity of these reactions contrasts with that of analogous reactions in the literature.[4] This selectivity may be explained by steric effects; we presume, neglecting electronic factors, that the most stable conformations of cations (**13**)—(**15**) are those depicted in Scheme 2, where the steric interactions between the methyl groups and the phosphine ligands are minimised. The most stable transition states in the reaction of these cations with $LiAlH_4$ and $LiAlD_4$ will be those which most resemble the most stable conformations of the starting cation and the cyclohexadienyl product.[1] Thus attack on the 1 and 4 positions of the arene ligand will be favoured.

The nature of the products obtained in the reactions of cations (**13**)—(**15**) with $LiAlH_4$ and $LiAlD_4$ may be explained by *exo* attack of 'H^-' or 'D^-' on the less hindered of the 1 and 4 positions of the arene ligand, followed [in the cases of (**14**) and (**15**)] by isomerisation of the initial product. The fact that complex (**4**) obtained from the reaction of the η-toluene cation (**13**) with $LiAlD_4$ was almost entirely deuteriated in the 6-*exo* position shows that attack of 'D^-' takes place almost entirely at the non-substituted 4 position.

The predominant formation of (**16**) in the reaction of cation

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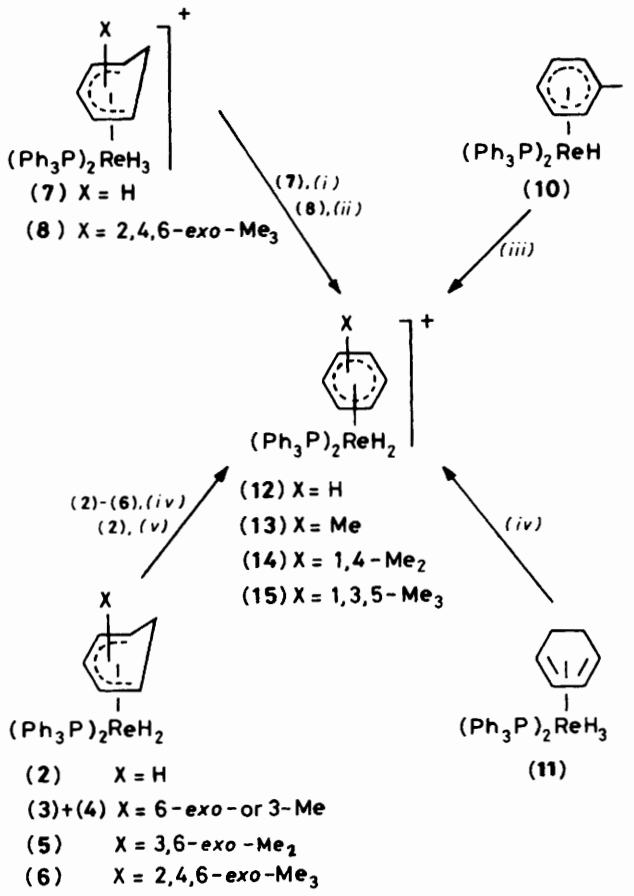
‡ The numbering of compounds is consistent with that used in the preceding paper.

§ After crystallisation: further crystallisation did not alter the ratio so we presume that it is the same as in the crude product.



Scheme 1. Preparation of the dihydrido cations (**12**)—(**15**): (*i*) MeOH–CH_2Cl_2; (*ii*) MeOH–CH_2Cl_2, reflux; (*iii*) HBF_4–Et_2O, Et_2O; (*iv*) CPh_3BF_4–CH_2Cl_2; (*v*) MeI–CH_2Cl_2

(**14**) with $LiAlH_4$ indicates that the influence of the phosphine ligands on the conformation of the transition state outweighs the preference of 'H^-' for attack on unsubstituted positions. The presence of complex (**5**) in the crude product cannot, however, be accounted for by a single-step addition of 'H^-' to the arene ligand.

Isomerisation of the Cyclohexadienyl Ligand.—Let us now turn our attention to the mechanism of isomerisation of the cyclohexadienyl ligand. The formation of complex (**5**) implies attack at an unsubstituted position followed by isomerisation, as does the formation of (**6**) from cation (**15**).

Two mechanisms have been postulated for the isomerisation of cyclohexadienyl complexes. In that suggested by Lamanna and Brookhart[2] the 6-*endo*-hydrogen migrates onto the metal to give a η^4-arene intermediate. By this mechanism, the expected product of the reaction between cation (**15**) and $LiAlD_4$ would be 3-D-(**6**) after formal 1,4 migration of the 6-*endo*-hydrogen in the intermediate (Scheme 3) [or, if migration of the η^4-arene ligand were relatively rapid, the product would be D-(**6**) with the deuterium atom statistically distributed]. Neither of these results was observed. The actual formation of 1- or 5-D-(**6**) is better accounted for by the mechanism put forward by Werner and Werner,[3] in which the initial step is the migration of a hydrogen from the metal onto the ring, leading to a formal 1,2 migration. While Brookhart's mechanism is the only one which can explain the isomerisation of cyclohexadienyl complexes without hydrides, it appears from our experiments that Werner's mechanism may be general for hydridocyclohexadienyl complexes.

Experimental

All experiments were carried out under nitrogen using standard Schlenk techniques. Evaporations were done under reduced pressure. Solvents were distilled before use, tetrahydrofuran and diethyl ether over sodium–benzophenone, and dichloromethane, after stirring over P_2O_5, from CaH_2. The compounds $LiAlH_4$ (Prolabo), $LiAlD_4$ (Fluka), and HBF_4–Et_2O (Ega-Chimie) were used without purification, CPh_3BF_4[11] and $[Re(\eta\text{-}C_6H_8)H_3(PPh_3)_2]$[12] 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 and WP-200/SY instruments. Chemical shifts were calculated with respect to $SiMe_4$ (0.00 p.p.m.), C_6D_5H (7.20 p.p.m.), and $CDHCl_2$ (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 of the (η-*Arene*) dihydridorhenium Cations.—*Complex* $[Re(\eta\text{-}C_6H_6)H_2(PPh_3)_2]BF_4$ (**12**) *from* $[Re(\eta\text{-}C_6H_7)H_2(PPh_3)_2]$ (**2**) *using* CPh_3BF_4. Complex (**2**) (238 mg, 0.301 mmol) was dissolved in CH_2Cl_2 (10 cm^3). To this pale yellow solution was added, with stirring, a solution of CPh_3BF_4 (150 mg, 0.455 mmol) in CH_2Cl_2 (10 cm^3) until the orange colour of CPh_3BF_4 persisted. The solvent was evaporated and to the orange foam remaining was added methanol (2 cm^3). The solution obtained rapidly deposited pale yellow crystals of complex (**12**), which were washed with methanol and dried under vacuum (154 mg, 54%).

The cations (**13**)—(**15**) were synthesised by similar methods from the mixture of (**3**) + (**4**) and the complexes (**5**) and (**6**). Yields were 58, 80, and 50% respectively.

Complex (**12**) *from* $[Re(\eta\text{-}C_6H_8)H_3(PPh_3)_2]$ (**11**). To a colourless solution of complex (**11**) (130 mg, 0.164 mmol) in CH_2Cl_2 (10 cm^3) was added CPh_3BF_4 (60 mg, 0.182 mmol). The solvent was evaporated. The solution obtained after addition of methanol rapidly deposited pale yellow crystals of complex (**12**) which were washed with methanol and dried under vacuum (63 mg, 44%).

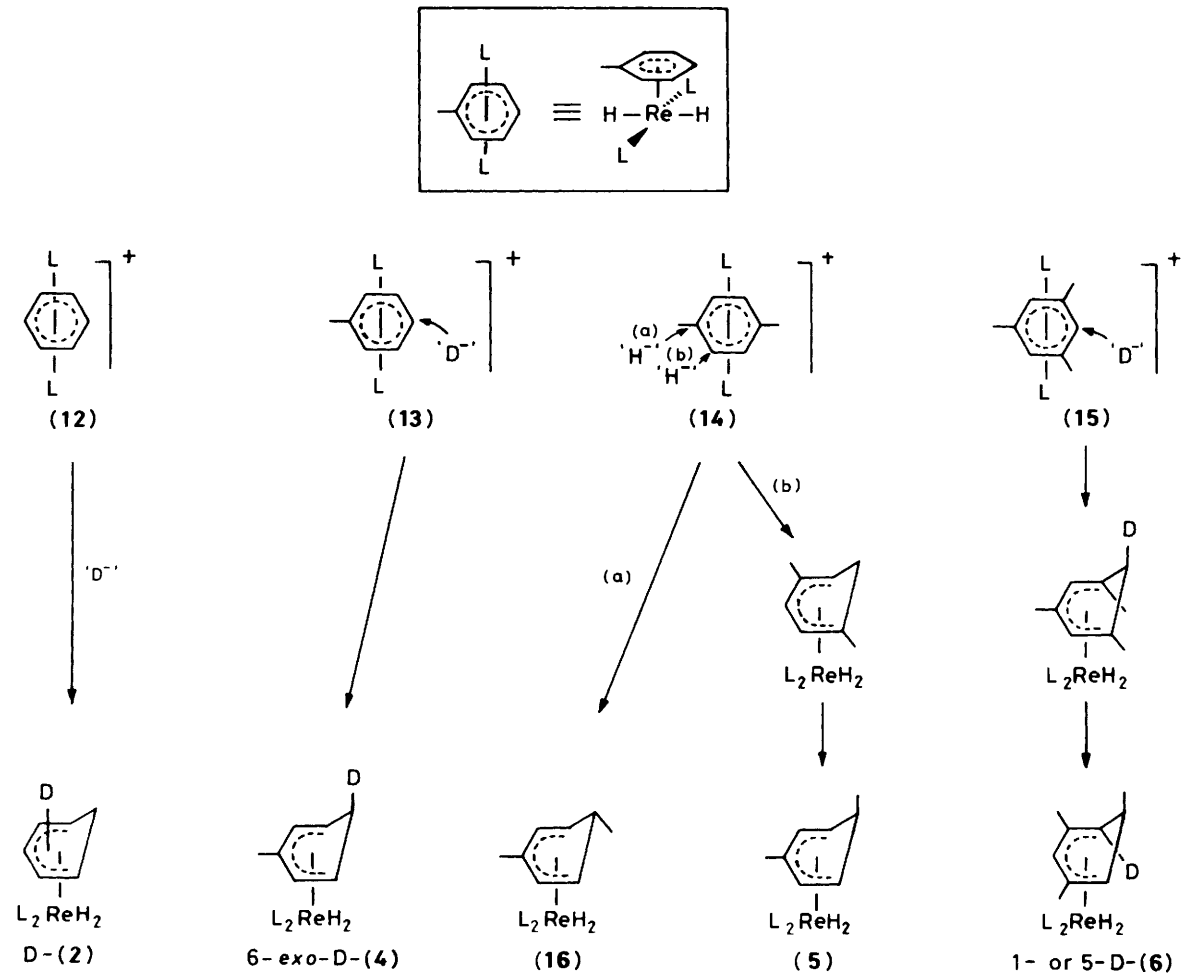
Complex (**12**) *from* (**2**) *and* MeI. To a solution of complex (**2**) (110 mg, 0.139 mmol) in CH_2Cl_2 (10 cm^3) was added MeI (13 μl, 0.209 mmol). After stirring for 16 h a yellow solution was obtained. The solvent was evaporated and the residue dissolved in CH_2Cl_2 (0.5 cm^3). The solution was decanted into diethyl ether (5 cm^3). The resulting suspension was filtered and the residue was dissolved in CH_2Cl_2 (10 cm^3). This solution was shaken with a 10% aqueous solution of NH_4BF_4 (10 cm^3). The organic layer was washed with water (2 × 10 cm^3), dried over Na_2SO_4, and filtered. The Na_2SO_4 was washed with CH_2Cl_2 (2 cm^3). The organic fractions were recombined and the solvent evaporated to *ca.* 0.5 cm^3. The solution obtained was decanted into ether (5 cm^3) and the resulting suspension was filtered. The residue was washed with ether (2 cm^3), dried, and recrystallised from CH_2Cl_2–methanol. The pale yellow crystals of complex (**12**) obtained were washed with methanol and dried under vacuum (27 mg, 27%). When the same experiment was conducted in an n.m.r. tube [(**2**) (63 mg, 0.080 mmol), MeI (6 μl, 0.098 mmol), and CH_2Cl_2 (*ca.* 0.7 cm^3)] a peak at 0.0 p.p.m. characteristic of methane was observed.

Complex (**12**) *from* $[Re(\eta\text{-}C_6H_7)H_3(PPh_3)_2]BF_4$ (**7**). To a pale buff solution of complex (**7**) (74 mg, 0.084 mmol) in CH_2Cl_2

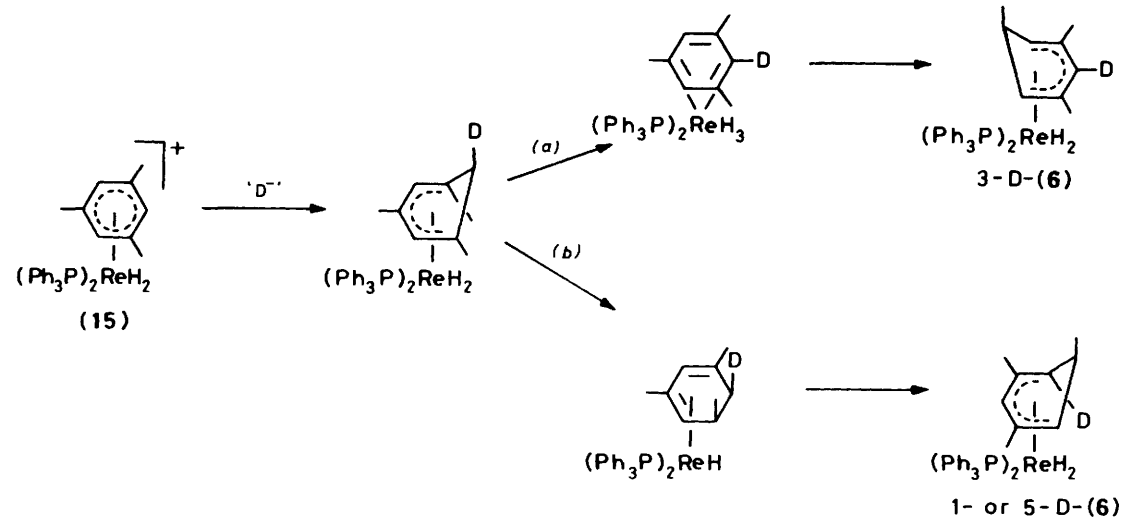
Table. Analytical and physical data for the η-arene cations (**12**)—(**15**) and the η-cyclohexadienyl complex (**16**)

Complex	^{1}H N.m.r.[a]	ν̃(Re–H)[b]/cm^{-1}	*m/z*	Analysis[c]/% C	H	P
(**12**)	7.40 (30 H, m, PPh_3), 5.62 (6 H, s, η-C_6H_6), −7.95 [2 H, t, *J*(PH) 37, Re–H]	2 030m	791	57.3 (57.5)	4.5 (4.1)	7.15 (7.1)
(**13**)	7.39 (30 H, m, PPh_3), 6.28 (1 H, t, *J* 5, 4-H), 5.17 (2 H, t, *J* 5, 3,5-H), 4.89 (2 H, d, *J* 5, 2,6-H), 2.36 (3 H, s, Me), −8.11 [2 H, t, *J*(PH) 38, Re–H]	2 000w	805	57.6 (57.9)	4.7 (4.5)	7.2 (6.95)
(**14**)	7.35 (30 H, m, PPh_3), 4.95 (4 H, s, 2,3,5,6-H), 2.46 (6 H, s, 1,4-Me), −8.17 [2 H, t, *J*(PH) 37, Re–H]	2 010m	819	57.8 (58.35)	4.8 (4.7)	6.9 (6.8)
(**15**)	7.30 (30 H, m, PPh_3), 5.13 (3 H, s, 2,4,6-H), 1.96 (9 H, s, 1,3,5-Me), −7.67 [2 H, t, *J*(PH) 38, Re–H]	Not visible	833	59.0 (58.8)	4.8 (4.8)	6.8 (6.7)
(**16**)[d]	7.8 (12 H, m, *o*-H of PPh_3), 7.0 (18 H, m, *m,p*-H of PPh_3), 4.04 (1 H, m, 6-*exo*-H), 3.74 (2 H, d, *J* 6, 2,4-H), 2.72 (3 H, s, 3-Me), 1.97 (2 H, d, *J* 6, 1,5-H), 1.55 (3 H, d, *J* 6, 6-*endo*-Me), −3.00 [1 H, dt, *J*(PH) 37 and *J*(HH) 10, Re–H], −11.56 [1H, dt, *J*(PH) 37 and *J*(HH) 10, Re–H]	1 930w	818 (*M* − 2)	64.4 (64.45)	5.3 (5.3)	7.6 (7.6)

[a] At 25 °C in [$^2H_6$]acetone, except for complex (**15**) in [$^2H_2$]dichloromethane and (**16**) in [$^2H_6$]benzene. Given as δ/p.p.m., intensity, multiplicity, coupling constant *J* in Hz, and assignment. [b] In Nujol. [c] Required values in parentheses. [d] Deduced from the n.m.r. spectrum of complexes (**5**) and (**16**) in the ratio 15:85.



Scheme 2. Cations (**12**)—(**15**): their most stable conformations, and their reactions with $LiAlH_4$ and $LiAlD_4$. L = PPh_3



Scheme 3. Possible products of the reaction between cation (**15**) and $LiAlD_4$, as predicted from two different mechanisms: (*a*) Brookhart 1,4 migration; (*b*) Werner 1,2 migration

(2 cm^3) was added methanol (10 cm^3). The colour immediately turned yellow. The solvent was evaporated. The n.m.r. spectrum of the crude product indicated the formation of complex (**12**) in *ca.* 85% yield. The residue was dried under vacuum and recrystallised from CH_2Cl_2–methanol. The pale yellow crystals of (**12**) obtained were washed with methanol and dried under vacuum (45 mg, 61%).

Cation $[Re(\eta\text{-}1,3,5\text{-}Me_3C_6H_3)H_2(PPh_3)_2]^+$ (**15**) *from* $[Re(\eta\text{-}2,4,6\text{-}exo\text{-}Me_3C_6H_4)H_3(PPh_3)_2]BF_4$ (**8**). The same method as above was employed except that it was necessary to reflux the CH_2Cl_2–methanol solution for 30 min. Yield: 18%.

Cation $[Re(\eta\text{-}C_6H_5Me)H_2(PPh_3)_2]^+$ (**13**) *by* (*reversible*) *protonation of* $[Re(\eta\text{-}C_6H_5Me)H(PPh_3)_2]$ (**10**). To a solution of complex (**10**) (140 mg, 0.174 mmol) in ether (20 cm^3) was added HBF_4–Et_2O (40 μl, 0.212 mmol). The resulting white suspension was filtered and the residue washed with ether. Crystallisation from CH_2Cl_2–methanol gave analytically pure pale yellow crystals of complex (**13**) which were washed with methanol and dried under vacuum (105 mg, 68%).

To a pale yellow solution of complex (**13**) (75 mg, 0.084 mmol) in CH_2Cl_2 (*ca.* 0.5 cm^3) was added a 0.83 mol dm^{-3} methanolic solution of KOH (120 μl, 0.996 mmol). The solution immediately turned bright yellow and a white precipitate was formed. The ^1H n.m.r. spectrum of this suspension showed only signals due to complex (**10**). The solvent was evaporated and the residue extracted with toluene (5 cm^3). The solvent of the filtrate was evaporated, and acetone (0.5 cm^3) was added. Bright yellow crystals of (**10**) were rapidly deposited and were washed with acetone and dried under vacuum (26 mg, 38%).

Reactions of (η-*Arene*)*dihydridorhenium Cations with* $LiAlH_4$ *and* $LiAlD_4$.—All reactions were carried out in the same general way: full details of the reaction of cation (**12**) with $LiAlH_4$ are presented as an example.

Complex (**12**) *with* $LiAlH_4$. To a suspension of complex (**12**) (79 mg, 0.090 mmol) in ether (5 cm^3) was added $LiAlH_4$ (35 mg, 0.921 mmol). The suspension was stirred at room temperature for 15 min. At the end of this period a pale yellow solution and a white precipitate were obtained. The mixture was hydrolysed with a few drops of water, dried over Na_2SO_4, and filtered; the residue was washed with CH_2Cl_2 (3 cm^3). The filtrates were recombined and the solvent evaporated. Acetone (1 cm^3) was added to the crude product. The resulting solution rapidly deposited pale yellow crystals of complex (**2**) which were washed with acetone and dried under vacuum (36 mg, 51%).

Complex (**12**) *with* $LiAlD_4$. The reaction was carried out at 0 °C. The mass spectrum of the product showed a peak m/z = 791 corresponding to (M − 2) for $C_{42}H_{38}DP_2Re^+$. The ^1H n.m.r. spectrum in $[^2H_2]$dichloromethane was similar to that of complex (**2**),[1] consistent with the ring signals (apart from 6-*endo*-H) being diminished in intensity by 17%. Yield 47%.

Complex (**13**) *with* $LiAlH_4$. The reaction was conducted at 0 °C. The ^1H n.m.r. spectrum of the crude reaction product indicated the exclusive formation of complex (**4**) [< 5% (**3**)]. Yield 30%.

Complex (**13**) *with* $LiAlD_4$. The reaction was conducted at 0 °C. The 80-MHz ^1H n.m.r. spectrum of the crude product indicated the exclusive formation of complex (**4**) [< 5% (**3**)]. The signal at 4.0 p.p.m. [6-*exo*-H of (**4**)] was absent. After crystallisation in acetone, the spectrum recorded at 400 MHz of a solution of the complex in $[^2H_6]$benzene was similar to that of the mixture of (**3**) and (**4**) prepared by the reaction of (**1**) with toluene. The complexes (**3**) and (**4**) were present in the ratio *ca.* 10:90. The intensities of the signals at 4.04 p.p.m. [6-*exo*-H of (**4**)] and at 6.32 p.p.m. [3-H of (**3**)] were reduced by 90 and 80% respectively. The signal at 3.61 p.p.m. [2,4-H of (**3**)] was a doublet (J 6 Hz). Yield 42%.

Complex (**14**) *with* $LiAlH_4$. Crystallisation from acetone afforded yellow crystals of a mixture of the complexes (**5**) and (**16**) in the ratio 15:85 (overall yield 59%). Recrystallisation from acetone did not alter this ratio.

Complex (**15**) *with* $LiAlH_4$. Yield of (**6**) 40%.

Complex (**15**) *with* $LiAlD_4$. The reaction was conducted at 0 °C. The n.m.r. spectrum of the product was analogous to that of complex (**6**) except that the intensity of the signal at 2.9 p.p.m. (1,5-H) was diminished by *ca.* 50%. The solution, still in the n.m.r. tube, was heated to 65 °C for 90 min. The n.m.r. spectrum was still analogous to that of (**6**) except that the peaks at 5.5 p.p.m. (3-H) and 2.9 (1,5-H) were diminished by *ca.* 33%.

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