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REACTION OF $(PPh_3)_2ReH_7$ WITH DIENES: PREPARATION AND SOME PROPERTIES OF TRIHYDRIDO η^4-DIENE COMPLEXES OF RHENIUM

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Summary

L_2ReH_7 ($L = PPh_3$) reacts smoothly with acyclic and cyclic dienes to give crystalline, air-stable, trihydrido-η^4-dienerhenium complexes $L_2(\eta^4\text{-diene})ReH_3$. The majority of these complexes are fluxional at room temperature; their NMR spectra suggest that at low temperature (—50°C) they are pentagonal bipyramidal, with the two phosphine ligands apical and the remaining ligands equatorial. Except for $L_2(\eta^4\text{-cyclopentadiene})ReH_3$, which readily loses dihydrogen to give $L_2(\eta^5\text{-}C_5H_5)ReH_2$, these diene trihydrides are thermally remarkably stable; $L_2(\eta^4\text{-cyclohexa-1,3-diene})ReH_3$ loses dihydrogen at >100°C to afford $L_2(\eta^5\text{-cyclohexadienyl})ReH_2$ and then $L_2(\eta^6\text{-}C_6H_6)ReH$, and $L_2(\eta^4\text{-butadiene})ReH_3$ and $L_2(\eta^4\text{-cycloocta-1,5-diene})ReH_3$ are stable in air up to 115 and 130°C, respectively. Protonation of the trihydrido-η^4-diene complexes affords the corresponding saturated hydrocarbons and/or olefins. Hydrogenation of $L_2(\eta^4\text{-2,3-dimethylbutadiene})ReH_3$ regenerates the heptahydride L_2ReH_7.

Introduction

Although di- (or poly-)hydrido mono- and di-olefin complexes of transition metals have been widely postulated as intermediates in the homogeneous catalytic hydrogenation of unsaturated hydrocarbons, very few such species have actually been isolated or, indeed, even observed [1], since in many cases they appear to be thermodynamically and kinetically unstable with respect to the other intermediates in the catalytic cycle [2].

Bis(triphenylphosphine)rhenium heptahydride (I) has been reported [3,4] to react readily under relatively mild conditions with various ligands L′ (phosphines, arsines, amines) to afford the pentahydrides (II) (Scheme 1); these react further under much more vigorous conditions to give the trihydrides (III). We were interested to see whether similar reactions could be carried out with olefins (L′ = monoene) and dienes (L'_2 = diene), and whether the corresponding

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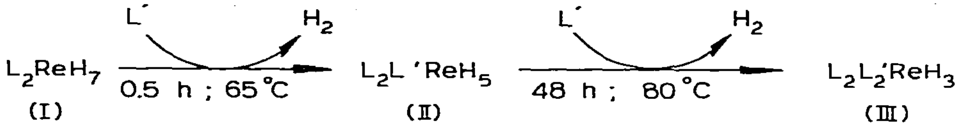
SCHEME 1. L = PPh_3; L′ = tertiary phosphine etc.



polyhydrido mono- and di-olefin complexes II and III would be stable enough to be isolated, or would lead directly to the hydrogenated hydrocarbons.

We have found that the reaction of the heptahydride I with a number of dienes leads, under mild conditions, to trihydridodienerhenium complexes (III, L'_2 = diene), and we present here a detailed account of our work [5] on the preparation and properties of these compounds.

Results and discussion

The bis(phosphine)heptahydride (I)

The heptahydride I was prepared in 65% yield by $LiAlH_4$ reduction of $(PPh_3)_2ReOCl_3$ [6], using a modification (see experimental) of the procedure of Chatt and Coffey [3]. These authors always obtained I contaminated with a red "dimer" (presumably [7] $[(PPh_3)_2ReH_4]_2$), which is a decomposition product of I [3]. No red dimer was formed in our preparation, and in fact reduction of $(PPh_3)_2ReOCl_3$ with excess $LiAlH_4$, using the procedure described by Chatt and Coffey [3] for $LiAlD_4$, also affords a ca. 60% yield of I uncontaminated with dimer [8].

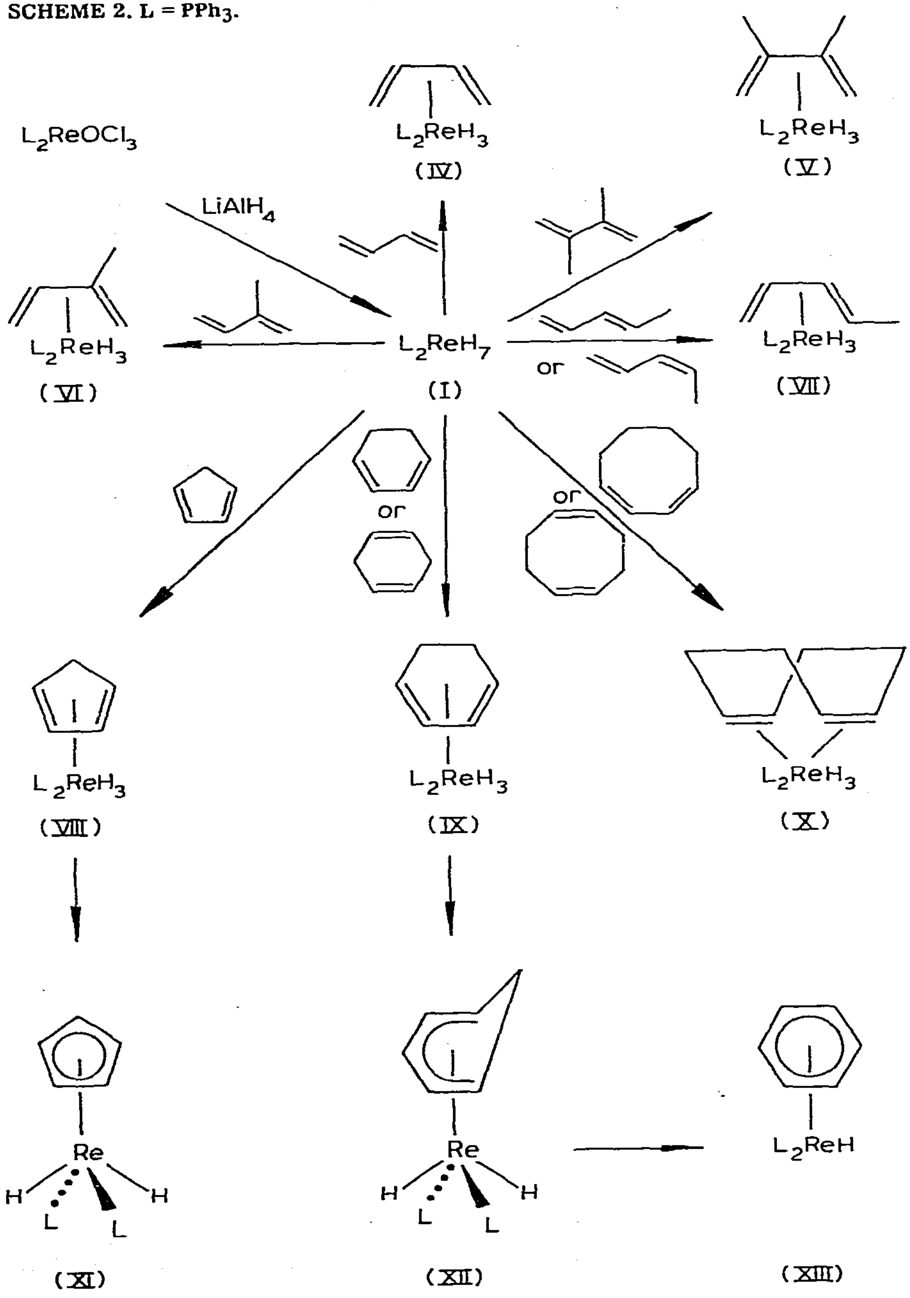
Previous authors [3,9] have noted that the accurate determination of the number of hydride protons in I by ^1H NMR is difficult because of slow decomposition in solution at room temperature, and we confirm this. Following a suggestion of Green and Green [10], we have taken the ^{31}P NMR spectrum of I with the phenyl protons decoupled, and this unequivocally shows the octet pattern expected for two equivalent phosphorus atoms coupled with seven equivalent hydrogens.

Reactions of I with acyclic conjugated dienes

The reactions of I with dienes are summarised in Scheme 2. The heptahydride I reacts under mild conditions (reflux for 5—15 min in tetrahydrofuran, THF) with a tenfold excess of the acyclic conjugated diene, 2,3-dimethylbuta-1,3-diene, isoprene, and *cis-* or *trans*-penta-1,3-diene, to give the trihydrodiene complexes V, VI and VII. Compound IV is obtained when buta-1,3-diene is bubbled through a refluxing solution of I in THF. These crystalline, pale yellow, complexes are remarkably stable, even in air. Thus, on a microscope hot-stage, compounds IV and V only start to decompose at 115 and 150°C, respectively.

Protonation of the trihydrido complexes IV and V with CF_3CO_2H in dichloromethane leads to the production of the saturated hydrocarbons, n-butane and 2,3-dimethylbutane, respectively (Scheme 3). This hydrogenation of the diene ligands in complexes IV and V, by treatment with acid, presumably occurs via a π-allyl intermediate, as formulated in Scheme 3. When the complexes are treated with an excess of HCl, $(PPh_3)_2ReCl_4$ [11] is formed.

SCHEME 2. L = PPh$_3$.



Hydrogenation of the trihydrodiene complex V (50°C, 50 atm H_2) leads to a mixture of 2,3-dimethylbutane and 2,3-dimethylbut-1-ene, and regenerates the heptahydride I.

Reactions of I with cyclic dienes

Treatment of the heptahydride I with cyclopentadiene in THF gives the colourless, air-stable, dihydridocyclopentadienyl complex XI, presumably in its preferred [12] diagonal configuration shown in Scheme 2. An intermediate in this reaction, the trihydridocyclopentadiene complex VIII, could sometimes be observed in the reaction mixture; it was characterised by means of its low temperature NMR spectrum and by the IR stretching vibration of the *exo*-C—H bond in the cyclopentadiene ligand (2780 cm^{-1}) [13]. It is not clear why the diene complex VIII is sometimes still present after 15 min in refluxing THF, whereas it is quantitatively transformed into XI after 20 min in dichloromethane at room temperature. Possibly, adventitious traces of acid in the dichloromethane catalyse the dehydrogenation of VIII to XI.

The cyclopentadienyl compound XI is protonated to $[(PPh_3)_2(\eta^5\text{-}C_5H_5)ReH_3]^+$ by CF_3CO_2H in dichloromethane.

The reaction of I with cycloocta-1,3-diene or cycloocta-1,5-diene (COD) gives, in 50% yield, the trihydrido(cycloocta-1,5-diene) complex X. The ^{13}C NMR spectrum of this complex exhibits only two resonances for the COD ligand (a 1,3-COD ligand would have four). It is noteworthy that the cyclooctadiene ligand in complex X has the 1,5-COD structure, as it does in iridium complexes [14a], in contrast to iron compounds in which the 1,3-COD ligand seems to be more stable [14b]. This is a further example of a heavier element preferring the 1,5-COD structure.

The cyclooctadiene complex X is stable in air up to 130°C (microscope hot-stage).

Cyclohexa-1,3-diene and cyclohexa-1,4-diene react with the heptahydride I in boiling THF to give, in 70% yield, a colourless, air-stable, compound which we incorrectly formulated in our preliminary communication [5] as dihydridobis(triphenylphosphine)(η^5-cyclohexadienyl)rhenium (XII) since its room-temperature ^1H NMR spectrum in deuteriopyridine showed a broad triplet at δ —5.8 ppm which integrated for ca. 2 H, and broad signals at δ 0.7, 1.6 and 3.4 ppm (ca. 7 H) which we attributed to the cyclohexadienyl ligand. We have now taken ^{13}C and low-temperature ^1H NMR spectra of this compound, and these show conclusively that it is in fact the trihydrido(η^4-cyclohexa-1,3-diene) complex IX. The ^{13}C NMR spectrum exhibits three signals for the cyclohexa-1,3-diene ligand (cyclohexadienyl would have four, and cyclohexa-1,4-diene two), and the ^1H NMR spectrum in CD_2Cl_2 (see below) shows a broad, high-field triplet at δ —6.55 ppm at room temperature which integrates for ca. 3 H, and which is split at —50°C into two triplets (relative intensities 2 and 1) *.

Dehydrogenation of IX, by heating it in vacuo or in refluxing toluene, gives the yellow, air-sensitive, benzene derivative XIII in 20—50% yield. The dienyl dihydride XII has been prepared from I and benzene, and has also been shown to afford compound XIII upon pyrolysis [15]; it is formed as an intermediate in the pyrolysis of IX, since its presence can be observed (NMR) when IX is heated in deuteriotoluene.

Protonation of the cyclic diene complex IX with CF_3CO_2H in dichloromethane gives cyclohexene, and that of X gives a mixture (80/20) of cyclooctane and cyclooctene. These cycloolefins, and especially cyclohexene, are presumably very labile as ligands, as has been observed in the case of iron

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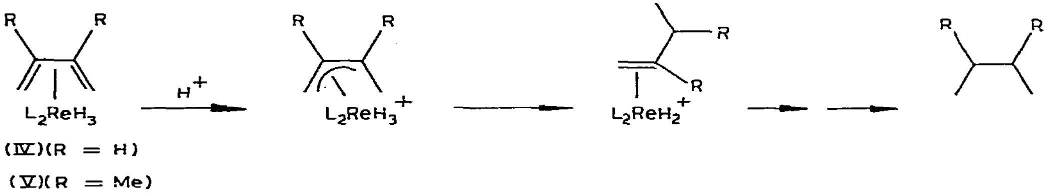
* When recently the ^1H NMR spectrum of IX was taken again in deuteriopyridine, the high-field triplet integrated as ca. four protons; we can offer no explanation for this disparity.

complexes [16], and are lost from the rhenium atom before they are completely hydrogenated. In the case of compound X, the hydrogenation by treatment with acid cannot occur directly via a π-allyl intermediate (see Scheme 3).

SCHEME 3. L = PPh_3.

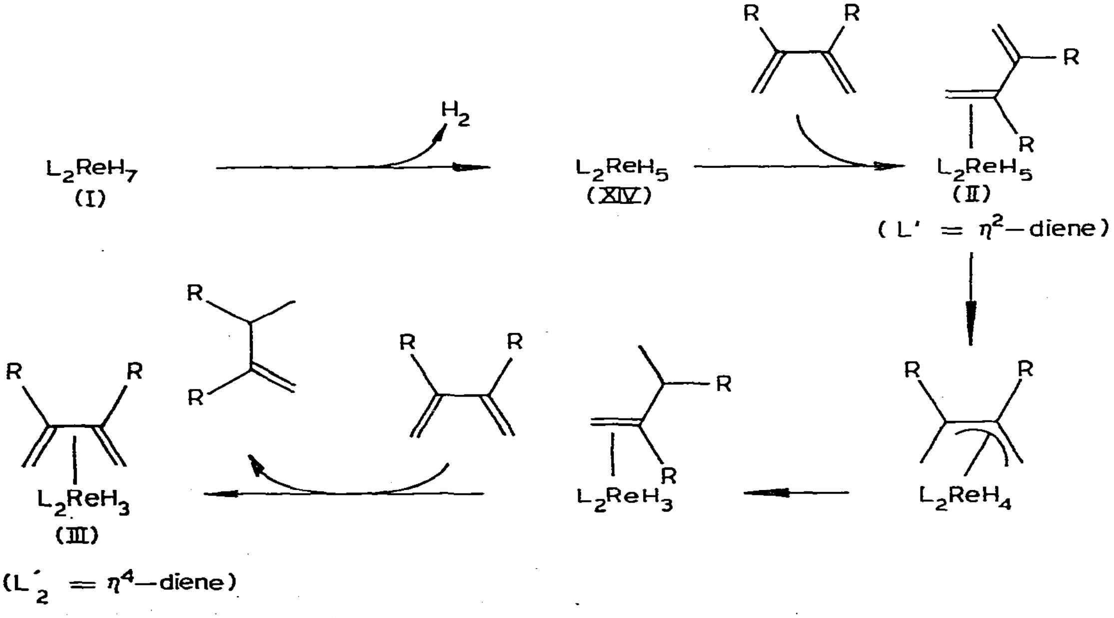


Mechanism of formation of the trihydridodiene complexes

The conditions required to form the trihydrido η^4-diene complexes IV—X, (i.e. III, $L'_2 = \eta^4$-diene), with the loss of four hydrogens, are relatively mild, and analogous to those used [3,4] to prepare the pentahydrido tris-ligand complexes II (L′ = non-hydrocarbon ligand; see Scheme 1), with the loss of only two hydrogens. Far more vigorous conditions [3,4] are necessary to replace two further hydrogens in these pentahydrido complexes (II) by a second non-hydrocarbon ligand to form the trihydridotetrakis-ligand complexes (III).

The thermal stability of the heptahydride I in solution is very low (see above). Its decomposition presumably involves the reductive elimination of one mol of dihydrogen leading to the bis-phosphine pentahydride XIV as a first intermediate, which can then react with ligands L′ to form the pentahydrido complexes II. When L′ is a non-hydrocarbon ligand, these complexes are thermally much more stable than the heptahydride I, and more vigorous conditions are required to convert them into the trihydrides III. In the reaction with dienes, however, the olefin ligands in the intermediates II ($L' = \eta^2$-diene) can assist the reaction by acting as hydrogen acceptors (Scheme 4). That this

SCHEME 4. L = PPh_3.

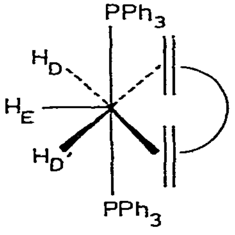


kind of assistance is indeed occurring is consistent with the fact that in the reaction between I and an excess of 2,3-dimethylbuta-1,3-diene, leading to the trihydridodiene complex V, only one mol of dihydrogen is evolved, and the two other hydrogens end up in 2,3-dimethylbut-1-ene (70%) and 2,3-dimethylbutane (15%) *. It also explains why the intermediates II (L′ = η^2-diene) are much less stable than the pentahydridotris-ligand complexes (II) (L′ = non-hydrocarbon ligand), and have therefore not been isolated.

NMR spectra and structure of the (η^4-diene)rhenium trihydrides

Most of the NMR signals for the hydride and olefinic protons of the complexes shown in Scheme 2 are broad; the line widths for the high field hydride signals, at 34°C, range from 7 Hz in compounds XI and XIII to about 25 Hz in IV and IX. Line broadening has been observed with other rhenium phosphite and phosphine complexes [17] and has been attributed to (a) coupling between ligand protons, phosphorus atoms and rhenium hydrides, (b) large rhenium quadrupolar relaxation effects, and (c) the presence of interconverting isomers in solution.

Because of the very small bonding-stretching modes required to effect interconversion of the various possible seven-coordinate structures, stereochemically non-rigid structures are expected to be especially common in seven-coordination [18], and their NMR spectra show that, except for X, the trihydrido-η^4-diene complexes are indeed fluxional at room temperature. At lower temperatures, they all appear to possess the pentagonal bipyramid structure [18] shown in XV, with two apical phosphine ligands, and the remaining ligands equatorial.



(XV)

The ^{1}H NMR spectra of the trihydridodiene complexes are described in Table 1. The pattern of the acyclic diene ligand spectra, although broad, is basically similar to that of other known diene complexes [19]. Double resonance experiments permitted the assignment of the signal of each proton in the diene ligand of VII (see Table 1). The cyclic diene ligands exhibit two (X) or three broad signals (VIII, IX). As already mentioned, the ^{13}C NMR spectra were consistent with the 1,3-cyclohexadiene and 1,5-cyclooctadiene structures of the ligands in IX and X, respectively.

At 34°C, the cyclooctadiene trihydride X shows two high-field signals (broad triplets) of relative intensities 2 and 1, corresponding to protons $H_DH_{D'}$ and H_E in XV. At the same temperature, all the other diene trihydrides show only one

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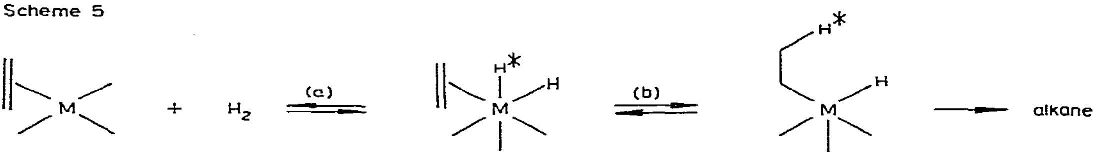
* These hydrocarbons could not have been formed by hydrogenation of the trihydridodiene complex (V) itself, since far more vigorous conditions (50°C, 50 atm H_2) are required to effect this reaction.

broad high-field signal (relative intensity 3), generally a triplet, but this is split upon cooling into two signals of relative intensities 2/1. The lower field signal (H_E, relative intensity 1) is in all cases a broad triplet; the higher field signal ($H_DH_{D'}$, relative intensity 2) is also a broad triplet in the case of the compounds with symmetrical diene ligands (except for compound V, for which the signal is so broad that the triplet structure cannot be distinguished) and a broad multiplet in the case of compounds VI and VII with unsymmetrical dienes, in which H_D and $H_{D'}$ are inequivalent.

The room-temperature $^{31}P\{^1H\}$ spectra of the diene trihydrides V, IX and X all exhibit a singlet signal; at −70°C, this is split into two doublets, corresponding to two phosphorus atoms coupled to each other, in the case of compounds V and IX, the pentagonal bipyramid structure XV of which comprises two inequivalent phosphorus atoms, but it remains a singlet in the case of the cyclooctadiene trihydride X, in which the two phosphorus atoms are equivalent. It is perhaps significant that, in the case of the cyclohexadiene trihydride IX, coalescence of the hydride (H_DH_E) and ^{31}P signals appears to occur at approximately the same temperature (−25°C), indicating that the two processes may be linked.

The pentagonal bipyramid structure XV is consistent not only with the low-temperature ^1H and ^{31}P spectra of the diene trihydrides, but also with their remarkable thermal stability (see above). Polyhydridoolefin complexes normally decompose easily either (a) by concerted reductive elimination of dihydrogen, or (b) by insertion of the olefin into one of the M—H bonds (Scheme 5), a key step in the catalytic hydrogenation of olefins, where it is followed by reductive elimination of alkane [20]. Reductive elimination of dihydrogen (path a) is clearly not an easy process in the thermally very stable [2] tetrakis-ligand-rhenium trihydrides (III), and it is not expected to be easier in the η^4-diene-bis-ligand trihydrides (XV) (≡ III, $L'_2 = \eta^4$-diene). The unavailability of the second possible decomposition pathway, insertion of olefin into an M—H bond (path b), is, we think, due to the stereochemistry of the trihydrido-η^4-diene complexes XV. This process has been shown to occur readily only when the carbon—carbon double bond and a metal—hydride bond are parallel (as are the double bond and M—H* in Scheme 5) [1a]; in structure XV, none of the Re—H bonds are parallel to the double bonds. Conversely, pentahydrido-(η^2-monoene) (II, L′ = olefin) and trihydridobis(η^2-monoene) (III, L′ = olefin) complexes, in which there is nothing to prevent the double bonds adopting a conformation such that they lie parallel to the Re—H_D and Re—$H_{D'}$ bonds, have proved impossible to isolate from the reaction between the heptahydride I and monoolefins under conditions under which I and dienes afford the stable trihydrido-η^4-diene complexes XV; the pentahydrido-η^2-diene complexes II, L′ = η^2-diene), which are presumably formed as intermediates in the latter reaction, are also too unstable to isolate (see above).

Scheme 5



Conclusion

Bis(triphenylphosphine)rhenium heptahydride (I) reacts under mild conditions with dienes to give the first examples of trihydridodiene-transition metal complexes (IV—X). These compounds, which are thermally stable, undergo some interesting reactions and provide a new entry into organorhenium chemistry.

Experimental

Microanalyses were carried out by the Service Central d'Analyses du C.N.R.S. The infrared spectra were recorded (in Nujol mulls) on a Perkin—Elmer Infracord 137 instrument, the mass spectra on an AEI MS 50 instrument, and the NMR spectra on Perkin—Elmer R12B (60 MHz), Bruker WP 80 (low temperature), Bruker HX 90 (^{13}C) and Bruker WH 90 (^{31}P) instruments.

TMS was the internal reference for the ^{13}C NMR spectra and for the ^{1}H NMR spectrum of XIII in C_6D_6. Otherwise, the ^{1}H NMR chemical shifts from TMS were calculated using $CHDCl_2$ (δ 5.25 ppm from TMS) as internal reference. The ^{31}P NMR spectra were recorded in CD_2Cl_2; chemical shifts are given in ppm downfield from H_3PO_4 as external reference.

All manipulations were carried out under nitrogen, the evaporations under reduced pressure. THF was dried over sodium benzophenone ketyl and diethyl ether over sodium. Commercial dienes (Fluka) were used without further purification. Alumina (Merck) was grade II-III. $(PPh_3)_2ReOCl_3$ was prepared as in [6].

^{1}H NMR spectra and analytical data are given in Tables 1 and 2.

Heptahydridobis(triphenylphosphine)rhenium (I)

$LiAlH_4$ (250 mg) * was added to a magnetically stirred suspension of $(PPh_3)_2ReOCl_3$ (800 mg) in dry diethyl ether (50 ml). After 30 min, the yellow colour had disappeared, and the grey suspension was filtered and the filtrate evaporated to dryness. Wet CH_2Cl_2 was added, and when the hydrolysis was complete the mixture was dried over Na_2SO_4, filtered, and evaporated to give a pale tan solid. After washing with ether (25 ml) the heptahydride I so obtained (470 mg, 65%) was used without further purification.

Integration of the ^{1}H NMR spectrum of a freshly prepared solution of I in CD_2Cl_2 showed 6.5 hydridic protons (δ —5.05 ppm, t, J 19 Hz) for 30 phenyl protons. After 20 min at 34°C, this number was about 5 and it decreased progressively with time [3,9]. The ^{31}P NMR spectrum of I with the phenyl protons decoupled, showed an octet at δ 29.5 ppm. The experimental and simulated ^{31}P NMR spectra were identical.

Trihydrido(buta-1,3-diene)bis(triphenylphosphine)rhenium (IV)

A stream of buta-1,3-diene was passed for 15 min through a boiling solution of I (300 mg) in THF (50 ml). The yellow solution was evaporated and acetone

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* Contrary to the footnote in our preliminary communication [5], best results are obtained using ca. 7 mmol of $LiAlH_4$ per mmol of $(PPh_3)_2ReOCl_3$, rather than 3 mmol.

(10 ml) was added. The solution rapidly deposited pale yellow crystals which were collected, washed with acetone and dried in vacuo (230 mg, 71%). An analytical sample was prepared by recrystallisation from THF/acetone (^{13}C NMR $\delta(CD_2Cl_2)$: 41 (CH_2), 73 (CH) ppm).

Trihydrido(2,3-dimethylbuta-1,3-diene)bis(triphenylphosphine)rhenium (V)

A solution of I (720 mg) and 2,3-dimethylbuta-1,3-diene (0.8 ml) in THF (50 ml) was refluxed for 15 min. Evaporation of the yellow solution gave the crude product. Acetone (10 ml) was added and the solution rapidly deposited pale yellow crystals, which were collected, washed with acetone and dried in vacuo (520 mg, 65%). The compound was further recrystallised from THF/acetone ($^{31}P\{^1H\}$ NMR $\delta(CD_2Cl_2)$ at 30°C, 35(s); at −70°C, 43.5 (d, J 62 Hz) and 28.5 ppm (d, J 62 Hz).

The same reaction of I (200 mg) and 2,3-dimethylbuta-1,3-diene (150 μl) in THF (10 ml) was carried out in an evacuated Schlenk tube in the presence of cyclohexane (15 μl) as internal standard for GLC analysis. Dihydrogen (1.0 eq. measured in the vacuum line) was evolved, and 2,3-dimethyl-but-1-ene (0.7 eq) and 2,3-dimethylbutane (0.15 eq) were formed during the reaction.

Trihydrido(2-methylbuta-1,3-diene)bis(triphenylphosphine)rhenium (VI)

A solution of I (400 mg) and isoprene (0.4 ml) in THF (50 ml) was refluxed for 5 min. After evaporation of the THF, the oily brown residue was dissolved in ether (10 ml), and this solution was evaporated to dryness to lead to a solid foam. Addition of ether (10 ml) gave a grey solid, which was washed with acetone until it was colourless (214 mg, 50%). The product was recrystallized from CH_2Cl_2/acetone.

Trihydrido(penta-1,3-diene)bis(triphenylphosphine)rhenium (VII)

The same procedure as for VI with either *cis*- or *trans*-penta-1,3-diene gave colourless crystals of VII. Yield 30%.

Dihydrido(cyclopentadienyl)bis(triphenylphosphine)rhenium (XI)

A solution of I (300 mg) and cyclopentadiene (0.5 ml) in THF (50 ml) was refluxed for 15 min. The yellow solution was evaporated to dryness. Acetone (10 ml) was added, and the solution rapidly deposited colourless crystals which were collected, washed with acetone and dried in vacuo (200 mg, 61%).

In some cases, these crystals were found to be a mixture of XI and trihydrido(cyclopentadiene)bis(triphenylphosphine)rhenium (VIII), characterised by its ^1H NMR spectra (see Table 1) and by its IR spectrum (2780 cm^{-1} (cyclopentadiene *exo*-CH) and 1940, 1920 cm^{-1} (ν(ReH)).

At 34°C, compound VIII in CH_2Cl_2 was completely converted into XI in 20 min. Compound XI was recrystallised from THF/acetone. (^1H NMR δ (CD_2Cl_2): 7.2 (m, 30 H, Ph), 4.2 (s, 5 H, η^5-C_5H_5), −10.5 ppm (t, J 40 Hz, 2 H, ReH_2)) *.

(continued on p. 374)

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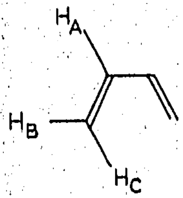
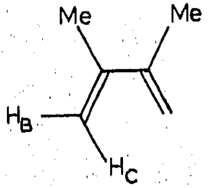
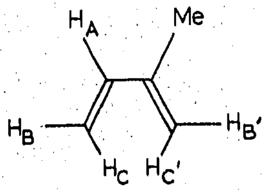
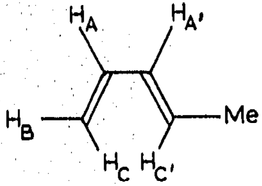
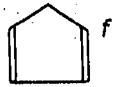
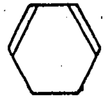
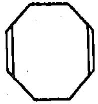
* The hydride resonance at −10.5 ppm was erroneously reported at −15.5 ppm in our preliminary communication [5].

TABLE 1

^{1}H NMR SPECTRAL DATA [a, b] FOR THE TRIHYDRIDO(DIENE) COMPLEXES $(PPh_3)_2(DIENE)ReH_3$

Compound	Ligand	Ligand protons at 34°C [c] δ (ppm)	δ(ReH) [d]	
			at 34°C	at −50°C
IV		3.5(br), 2 H (H_A) 1.9(br), 2 H (H_B) −1.5(br), 2 H (H_C)	−6.1t (25), 3 H	−3.1t (34), 1 H (H_E) −7.9t (18), 2 H (H_D)
V		1.7(br), 2 H (H_B) −1.6(br), 2 H (H_C) 1.55 s, 6 H (Me)	−6.6t (29), 3 H	−4.4 [e] t (35), 1 H (H_E) −8.0 [e] (br) 2 H (H_D)
VI		3.45(br), 1 H (H_A) 1.8(br), 2 H (H_BH_B') −1.8(br), 2 H (H_CH_C') 1.9s, 3 H (Me)	−6.2t (27), 3 H	−3.6t (38), 1 H (H_E) −7.5m, 2 H (H_DH_D')

VII		3.5(br), 1 H (H_A); 3.1(br), 1 H ($H_{A'}$) 1.8(br), 1 H (H_B) −1.5(br), 1 H (H_C); −0.9, br, 1 H ($H_{C'}$) 1.3d (6), 3 H (Me)	−6.2(br), 3 H	−3.1t (35), 1 H (H_E) −8.2, m, 2 H ($H_DH_{D'}$)
VIII	 [f]	3.5, 2.9 and 2.3	−6.15t (28)	−2.95t (39) −7.85t (18)
IX		3.2(br), 4 H 1.3(br), 2 H 0.4(br), 2 H	−6.55t (28), 3 H	−3.15, t (38), 1 H (H_E) −8.05t (19), 2 H (H_D)
X		3.15m, 4 H 1.60m, 8 H	−4.9t (40), 1 H −7.3t (20), 2 H	−5.05t (40), 1 H (H_E) −7.65t (20), 2 H (H_D)

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[a] In CD_2Cl_2;reported as δ in ppm from TMS, multiplicity (J in Hz), intensity (assignment). [b] All the compounds showed a multiplet (30 H, Ph) at about δ 7.3—7.7 ppm. [c] 60 MHz. [d] 80 MHz. [e] At −70°C. [f] The spectrum of this compound could not be integrated because of decomposition to XI (see text).

TABLE 2

ELEMENTAL ANALYSES, MASS SPECTRA AND IR (ν(Re—H)) FREQUENCIES FOR SOME RHENIUM HYDRIDE COMPLEXES

Compound	Analyses (Found (calcd.) (%))			Mass spectrum [a]	ν(Re—H) [b] (cm^{-1})
IV	62.18	5.25	8.41	764 [$M-4$]	1960, 1925
	(62.48)	(5.07)	(8.07)		
V	63.24	5.23	7.80	792 [$M-4$]	1950, 1900
	(63.32)	(5.40)	(7.78)		
VI	63.00	5.33	7.98	778 [$M-4$]	1980, 1940
	(62.91)	(5.24)	(7.92)		
VII	62.49	5.25	8.21	778 [$M-4$]	1960, 1930
	(62.91)	(5.24)	(7.92)		
IX	63.58	5.19	7.73	790 [$M-4$]	1925, 1900
	(63.47)	(5.16)	(7.80)		
X	63.85	5.53	7.70	818 [$M-4$]	1960, 1920
	(64.23)	(5.47)	(7.54)		
XI	62.96	4.99	8.21	776 [$M-2$]	1980
	(63.24)	(4.75)	(7.96)		
XIII	63.40	5.30	7.80	790 [M]	1950
	(63.79)	(4.68)	(7.84)		

[a] Highest peak corresponding to the ^{187}Re isotope. [b] Nujol mull.

Trihydrido(cycloocta-1,5-diene)bis(triphenylphosphine)rhenium (X)

A solution of I (400 mg) and either 1,3- or 1,5-cyclooctadiene (0.4 ml) in THF (50 ml) was refluxed for 5 min. The dark solution was evaporated to dryness. Traces of cyclooctadiene in the oily residue were eliminated by two successive dissolutions in ether and evaporations. The oil solidified by addition of pentane (10 ml). After filtration the grey solid was washed with ether (10 ml) and acetone (10 ml) until it was colourless (205 mg, 45%). The compound was recrystallised from THF/acetone (^{13}C NMR δ(CD$_2$Cl$_2$), 33 and 61. ^{31}P{^{1}H} NMR δ(CD$_2$Cl$_2$) at 30°C, 25 (s); at —70°C, 23 (s)).

Trihydrido(cyclohexa-1,3-diene)bis(triphenylphosphine)rhenium (IX)

A solution in THF (50 ml) of I (860 mg) and either 1,3- or 1,4-cyclohexadiene (0.8 ml) was refluxed for 15 min. Evaporation of the yellow solution gave the crude product, which was dissolved in acetone (10 ml). This solution rapidly deposited colourless crystals which were collected, washed with acetone and dried in vacuo (700 mg, 74%). The compound was recrystallised from THF/acetone. (^{13}C NMR δ(CD$_2$Cl$_2$), 25, 55 and 71 ppm (C_6H_8). ^{31}P{^{1}H} NMR δ(CD$_2$Cl$_2$) at 3C°C, 31 (s); at —70°C, 35 (d, J 74 Hz) and 27.5 (d, J 74 Hz)).

Hydrido(benzene)bis(triphenylphosphine)rhenium (XIII)

Compound IX (200 mg) was heated in a Schlenk tube at 150°C (oil bath) in vacuo (0.3 mmHg) for 1 min. The dark residue was dissolved in benzene (1 ml) and chromatographed on alumina. The yellow compound XIII was eluted with an 80/20 mixture of pentane and acetone, and was recrystallised from pentane. Yields: 20—50%. (^{1}H NMR δ(C_6D_6): 7.5—6.9 (m, 30 H, Ph), 4.1 (s, 6 H, C_6H_6), —7.2 (t, J 36 Hz, 1 H, ReH).

Compound XIII can also be prepared by pyrolysis of IX in refluxing toluene (reaction time: 30 min) followed by chromatography as above. When IX was heated at 100°C in deuteriotoluene in an NMR tube for 30 min, signals attributable to XII [15] were observed.

Protonation of $(PPh_3)_2(\eta^5\text{-}C_5H_5)ReH_2$ (XI)

CF_3CO_2H (10 μl) was added to a solution of XI (100 mg) in CD_2Cl_2 (0.4 ml) in an NMR tube. The quantitative protonation of XI into $[(PPh_3)_2(\eta^5\text{-}C_5H_5)\text{-}ReH_3]^+$ was observed: the signals of XI at δ 4.2 and —10.5 ppm were replaced by signals at δ 4.6 (s, 5 H, η^5-C_5H_5) and —6.0 ppm ((br) t, J = 30 Hz, 3 H, ReH_3). Addition in the NMR tube of 1,4-diazabicyclo[2.2.2]octane (20 mg) gave back XI.

Protonation of compounds IV, V, IX and X

CF_3CO_2H (20 μl) was added to a solution of V (100 mg) in CD_2Cl_2 (1 ml). 2,3-Dimethylbutane was formed and identified by its NMR spectrum and retention time (GLC). The yield of the reaction (93%) was determined by integration of the NMR methyl signal of V and the doublet methyl signal of 2,3-dimethylbutane.

Similarly, protonation of IV gave n-butane, identified by its NMR spectrum, and protonation of IX and X, respectively, gave cyclohexene and a mixture (80/20) of cyclooctane and cyclooctene, identified by their retention times (GLC).

Reaction of compounds IV and V in CH_2Cl_2 with an excess of a saturated solution of HCl in ether led to the formation of a red compound, the IR spectrum of which was identical with the IR spectrum of $(PPh_3)_2ReCl_4$, prepared as described in ref. 11.

Hydrogenation of compound V

A solution of compound V (200 mg) in benzene (10 ml) was treated at 50°C during 3 h with dihydrogen (50 atm) in an autoclave. A mixture (80/20) of 2,3-dimethylbutane and 2,3-dimethylbut-1-ene was formed (GLC analysis) and the heptahydride (I) was regenerated (NMR analysis).

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