

THE STRUCTURE AND DYNAMIC BEHAVIOUR IN SOLUTION OF THE TRIHYDRIDODIENERHENIUM COMPLEXES $(\text{Ph}_3\text{P})_2(\eta\text{-1,3-DIENE})\text{ReH}_3$

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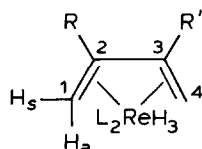
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Summary

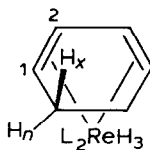
The structure and fluxionality of the trihydridodiene complexes $(\text{Ph}_3\text{P})_2(\eta\text{-1,3-diene})\text{ReH}_3$ have been studied by NMR spectroscopy ($\eta\text{-1,3-diene}$ = buta-1,3-diene, 2-methylbuta-1,3-diene, 2,3-dimethylbuta-1,3-diene, cyclohexa-1,3-diene, penta-1,3-diene, hexa-1,3-diene and hexa-2,4-diene). Several rearrangement processes have been observed; they are, in order of increasing temperature: (a) ligand interchange; (b) reversible migration of a hydride ligand on to the diene ligand, leading to $\eta\text{-allyl}$ species and, in the case of the cyclohexadiene trihydride, degenerate isomerisation of the cyclohexadiene moiety; and (c), in the case of the pentadiene and hexadiene derivatives, isomerisation of the diene ligand.

Introduction

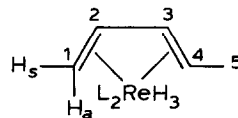
The first examples (I–V) of trihydrido- $\eta\text{-diene}$ transition metal complexes were recently obtained by the reaction of bis(triphenylphosphine)rhenium heptahydride $(\text{Ph}_3\text{P})_2\text{ReH}_7$ with cyclic and acyclic dienes [1]. Their 60 and 80 MHz ^1H NMR



- (I: $\text{R} = \text{R}' = \text{H}$;
 II $\text{R} = \text{R}' = \text{Me}$;
 III $\text{R} = \text{Me}$; $\text{R}' = \text{H}$)



(IV)



(V)

$\text{L} = \text{Ph}_3\text{P}$

spectra indicated that these remarkably stable complexes are fluxional in solution at room temperature; at -50°C , however, the slow limit spectra were observed, and were consistent with a pentagonal bipyramidal structure in which the apical posi-

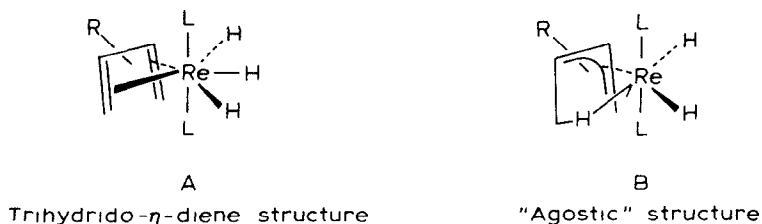


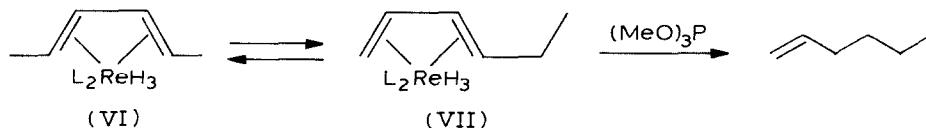
Fig. 1. Possible structures of the rhenium complexes I-V ($L = \text{Ph}_3\text{P}$)

tions are occupied by the phosphine ligands and the equatorial positions by the two double bonds of the diene and the three hydrides (Fig. 1A).

Brookhart and Green [2] have recently proposed that certain compounds described in the literature as hydrido- η^4 -1,3-diene complexes should, in fact, be formulated as η^3 -allyl complexes with a 3-centre 2-electron "agostic" C-H $\rightarrow$ M bond. This suggestion prompted us to investigate the possibility of such an "agostic" interaction in the $L_2(\eta$ -1,3-diene) ReH_3 complexes (Fig. 1B), since our previous data [1] are equally consistent with a rapidly equilibrating pair of "agostic" structures, as found recently in the case of a bis(ethylene)cobalt hydride cation [2b].

Our primary interest was, however, to analyse the various fluxional and rearrangement processes taking place in these complexes. We recently found that a 1:2 mixture of the isomeric η -hexadiene trihydrides VI and VII, prepared from $(\text{Ph}_3\text{P})_2\text{ReH}_7$ and either hexa-1,5-diene (see Experimental section), or *n*-hexane and 3,3-dimethylbutene as a hydrogen acceptor [3], is converted by trimethyl phosphite into 1-hexene [3]. The high yield (> 95%) of the latter reaction shows that VI must have rearranged to VII, since only the latter can lead to 1-hexene (Scheme 1). Similar

SCHEME 1



$L = \text{Ph}_3\text{P}$

rearrangements involving IV and V would, of course, be degenerate, but we felt that they might be detected by suitable NMR techniques. Furthermore, we felt that a study of these rearrangements might contribute to our understanding of the isomerisation of dienes catalysed by transition metal hydrides [4].

With these ideas in mind, we have carried out a detailed NMR study of the trihydrido- η -diene complexes I-VII. The results of this investigation are presented here; they lead to a qualitative description of the dynamic behaviour of these complexes in solution.

Results

We report, in increasing order of complexity, the results obtained with the butadiene, cyclohexadiene, pentadiene and hexadiene complexes.

TABLE 1
TEMPERATURE AND SPIN SATURATION TRANSFER EFFECTS ON THE ^1H NMR SPECTRA ^a OF THE BUTADIENE COMPLEXES I-III

Complex	<i>T</i> (°C)	R	R'	H ₃ (1), H ₄ (4)	H _a (1)	H _a (4)	ReH ₃
I	30	3.75 (20) 100%		2.25 (15) 50%	-1.05 (15) 55%		-5.5 (70)
	90	3.75 (15)			-1.75 (300)		
II	40	1.75 (4) 100%		2.1(br) <100% ^b	-1.05 (30) 25%		-6.05 ^c
	90	1.75(4)			-2.3 (350)		
III	30	2.14 (5) ^d	3.57 (15) 100%	2.1(br) <100% ^b	-1.12 (15) 20%	-1.38 (20) 20%	-5.62(80)

^a In toluene-*d*₈ (phenyl resonances omitted); I and II at 80 MHz, III at 250 MHz; reported as δ in ppm from TMS (peak width at half-height in Hz), and residual intensity, as percentage of original intensity, observed when the hydride signal ReH₃ was irradiated. ^b The decrease in the intensity of this signal could not be evaluated owing to overlap with the deutenotoluene methyl signal; irradiation at 2.1 ppm brought about a decrease in intensity of the H_a and ReH₃ signals to 20–30% of their original values. ^c Triplet, (*J* 30 Hz). ^d The effect on this signal appeared to be nil, as expected; it could not be measured owing to overlap with the H₁ signal.

The butadiene complexes I–III

The 60 and 80 MHz ^1H NMR spectra of these complexes were described in our previous paper [1]. Above -10°C , the three hydride ligands become equivalent and show a single broad triplet (in CD_2Cl_2).

Some new facts have emerged from NMR spectra recorded in deuteriotoluene above room temperature, and further information has been obtained by means of spin saturation transfer (SST) experiments [5] (Table 1).

At 30 – 40°C , SST was observed between the hydride (ReH_3), H_v and H_a atoms in the three complexes; the R and R' signals were not affected. In the 250 MHz spectrum of III, the two *anti* hydrogens ($\text{H}_\text{a}(1)$ and $\text{H}_\text{a}(4)$) are resolved; their intensity decreased by the same amount (80%) when the $\text{H}_\text{v}(1)$ or the hydride signal was irradiated. As the temperature was increased, the hydride signal and the H_a and H_v signals broadened; coalescence was observed around 90°C . The R and R' signals remained unchanged.

The cyclohexadiene complex IV

The 60 MHz ^1H NMR spectrum [1] being poorly resolved, the 250 MHz spectra were used to study the fluxionality of the cyclohexadiene compound IV; at this frequency, the olefinic hydrogens H(1) and H(2) are separated. At 30°C , the ring hydrogen signals are broadened, especially that of H(1), and when the hydride signal was irradiated the intensity of signal from the *endo* hydrogens (H_n) decreased by 65% (Table 2).

Since IV loses dihydrogen at high temperature [1], it was necessary to determine the coalescence temperatures from the 80 MHz spectra. At this frequency, coalescence of the H(1), H(2) and H_x signals (the “*exo* pool”) and coalescence of the H_n and hydride signals (the “*endo* pool”) both took place between 70 and 80°C . At 90°C , the spectrum (apart from the phenyl resonances) consisted of two signals of relative intensity 5/6 corresponding to the “*endo* pool” and the “*exo* pool” (Table 2).

The cyclohexadiene ligand of IV gives rise to three signals in the low temperature ^{13}C NMR spectrum, one triplet and two doublets, corresponding to the three different pairs of carbon atoms.

TABLE 2

TEMPERATURE AND SPIN SATURATION TRANSFER EFFECTS ON THE ^1H NMR SPECTRA ^a OF THE CYCLOHEXADIENE COMPLEX IV

T ($^\circ\text{C}$)	H(2)	H(1)	H_v	H_n	ReH_3
-10	3.60 (15) 100%	3.38 (15) 100%	1.70 (20 ^b) 100%	0.78 (20 ^b) 100%	-6.0 (300)
30	3.62 (30) 100%	3.32 (50) 100%	1.69 (30 ^c) 100%	0.82 (35) 35%	-5.8 (110)
90		2.83 (15)(“ <i>exo</i> pool”)		-3.2 (75)(“ <i>endo</i> pool”)	

^a In toluene- d_8 (phenyl resonances omitted); at 250 MHz when $T = -10$ and 30°C , at 80 MHz when $T = 90^\circ\text{C}$; reported as δ in ppm from TMS (peak width at half-height in Hz), and residual intensity, as percentage of original intensity, observed when the hydride signal ReH_3 was irradiated. ^b Doublet, (J 8 Hz). ^c Irradiation of this signal brought about a decrease in intensity of the H(2) and H(1) signal to 30% of their original values.

TABLE 3

TEMPERATURE AND SPIN SATURATION EFFECTS ON THE ^1H NMR SPECTRA ^a OF THE PENTADIENE COMPLEX V

<i>T</i> (°C)	H(5)	H(4)	H(3)	H(2)	H _s (1)	H _a (1)	ReH ₃
40	1.56 ^b 100%	−0.45 (20) 60%	3.40 (15) 100%	3.72 (15) 100%	2.1(br) < 100% ^c	−1.02 (20) 15%	−5.8 (110)
80	1.53(10) 60%	−0.44 (20) 5%	3.40 (15) 100%	3.70 (15) 50%	<i>d</i>	<i>d</i>	−5.7 (130)
110	1.53 (10)	−0.44 (60)	3.47 (15)	3.69 (20)		−3.3 (130)	

^a In toluene-*d*₈ (phenyl resonances omitted) at 80 MHz; reported as δ in ppm from TMS (peak width at half-height in Hz), and residual intensity as percentage of original intensity, observed when the hydride signal ReH₃ was irradiated. ^b Doublet (*J* 7 Hz). ^c The decrease in intensity of this signal could not be evaluated owing to overlap with the deuteriotoluene methyl signal; irradiation at 2.1 ppm brought about a decrease in intensity of the H_a(1) and ReH₃ signals to 20–40% of their original values. ^d Not visible.

The pentadiene and hexadiene complexes V–VII

The 80 MHz ^1H NMR spectrum of the pentadiene complex V was examined at various temperatures (Table 3). At 40°C, spin saturation transfer was observed between the three hydrogens on the metal, H_a(1), H_s(1) and H(4). At 80°C, the signals corresponding to the methylene hydrogens (H_a(1) and H_s(1)) were no longer visible in the spectrum and the methyl hydrogens H(5) appeared as a singlet. At this temperature, spin saturation transfer was observed between all the hydrogens except H(3). Coalescence of the hydrides and the methylene hydrogens H(1) occurred at about 100°C, and at 110°C the H(4) signal was significantly broadened and a new broad signal (relative intensity ca. 5H) was visible in the hydride region.

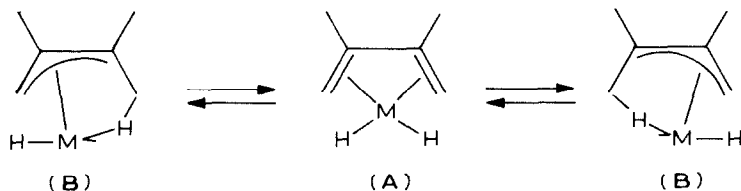
The complexity of the spectra of the mixture of hexadiene complexes VI and VII precluded a detailed analysis of the fluxionality of these molecules. Nevertheless, it was possible to distinguish all the hydrogens of both isomers in the 400 MHz ^1H NMR spectrum, and to observe that the isomers are present in the statistical ratio of 2 parts of VII to 1 part of VI. Moreover, when the methyl signal of VII was irradiated in the 250 MHz spectrum at 90°C, there was a significant diminution of the intensity of the methyl signal of VI.

The structure of the (Ph₃P)₂(η -1,3-diene)ReH₃ complexes

The spectroscopic data for the complexes I–V, presented in an earlier paper [1], are consistent with a pentagonal bipyramidal structure (Fig. 1A). However, they could also be explained by a rapidly equilibrating pair of “agostic” structures (Fig. 1B); Scheme 2 shows such a process in the case of II.

This process has, in fact, recently been observed in a closely related complex [(Ph₃P)₂(2,3-dimethylbutenyl)IrH]⁺ (VIII); in the NMR spectrum of VIII at −20°C, the more stable “agostic” structure VIIIB is frozen out [6]. Of the criteria put forward by Brookhart and Green [2] for recognition of “agostic” hydrogens, values of the ^{13}C – ^1H coupling constants appear to be particularly useful for the series of complexes I–VII. In an “agostic” structure, the carbon atom involved in a CH–H–M interaction gives rise to a doublet of doublets. This was not observed in

SCHEME 2



(II. $M = (\text{Ph}_3\text{P})_2\text{ReH}$, VIII. $M = (\text{Ph}_3\text{P})_2\text{Ir}^+$)

the ^{13}C NMR spectrum of IV. IR spectra were also found to be characteristic of "agostic" systems with absorption between 2350 and 2700 cm^{-1} . Such absorptions are not apparent in the IR spectra [1] of complexes I–V. We conclude, therefore, that the complexes I–VII possess the trihydrido- η -diene structure shown in Fig. 1A. The X-ray crystal structure of IV [7] is compatible with this conclusion. It shows, however, that the idealised pentagonal bipyramid depicted in Fig. 1A is, in fact, strongly deformed (the PReP angle is 142°), presumably because of steric compression between the diene ligand and the two phosphines. The details of the structure of IV, and the possible factors which lead the rhenium complexes I–VII to adopt the $18e$ trihydrido- η -diene structure, rather than the isomeric $16e$ dihydrido- η -allyl structure or an "agostic" structure (Fig. 1B), are discussed in the accompanying paper [7].

The rearrangement processes occurring in the $(\text{Ph}_3\text{P})_2(\eta\text{-}1,3\text{-diene})\text{ReH}_3$ complexes

Previous work [1] has shown that, at -50°C , the (deformed [7]) pentagonal bipyramidal structure (Fig. 1A) of the complexes I–V is frozen out; their NMR spectra show two inequivalent phosphorus atoms, and two (or three) inequivalent hydrides. Coalescence occurs at about -25°C , and above this temperature the diene trihydrides I–V are fluxional. Fluxionality is common in seven-coordination [8], and the tetrakis(phosphine)rhenium trihydrides behave similarly [9]. As the temperature is raised, other rearrangement processes occur, and these are discussed below.

The butadiene and cyclohexadiene complexes I–IV

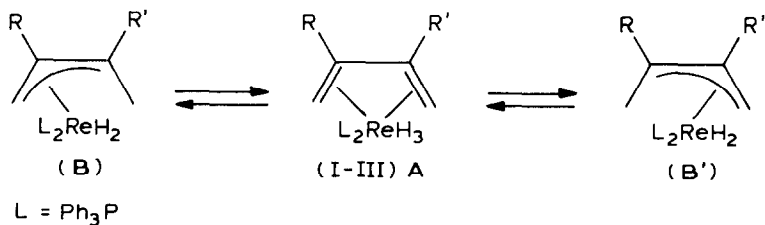
The NMR spectra of the trihydridobutadiene complexes (I–III) indicate that, at $30\text{--}40^\circ\text{C}$, these complexes are in equilibrium with the $16e$ dihydridobutenyl species **B** and **B'** shown in Scheme 3, by means of the reversible migration of a hydride ligand onto a terminal carbon of the diene ligand*. This leads to exchange between the hydride ligands and the methylene hydrogens; R and R' are not affected.

The same reversible migration occurs in the cyclohexadiene complex IV: the hydrides and the *endo* hydrogens exchange via the symmetrical η -cyclohexenyl intermediate IVB (Scheme 4).

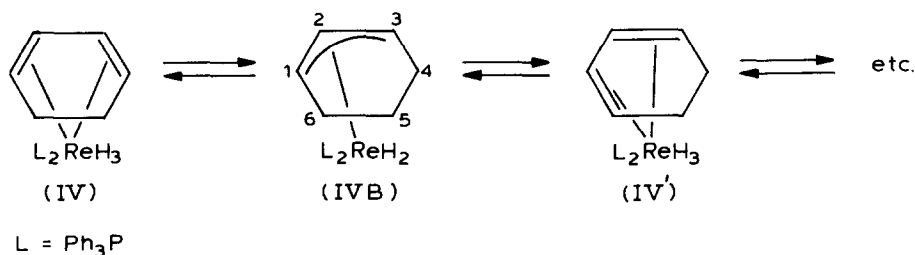
The intermediate IVB can give the two degenerate cyclohexadiene complexes IV and IV' by migration of the 4-*endo* or 6-*endo* hydrogen, respectively. By means of

* The dihydrido butenyl intermediates **B** and **B'**, which were not observed, could be either the $16e$ complexes shown in Scheme 3 or $18e$ "agostic" species.

SCHEME 3



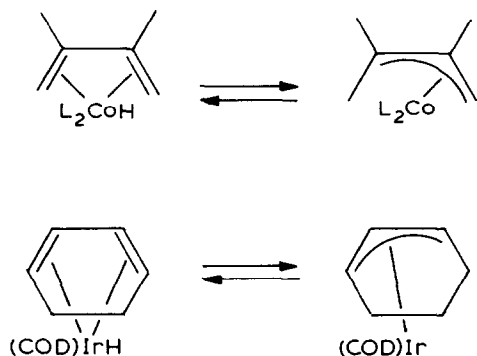
SCHEME 4



successive migrations, therefore, the olefinic and the *exo* hydrogens (the *exo* pool) exchange, as do the hydrides and the *endo* hydrogens (the *endo* pool); thus, in the fast limit spectrum of the complex IV, the five hydrogens of the *endo* pool are equivalent, as are the six hydrogens of the *exo* pool.

A number of closely related systems are known. Thus, Rinze [10] has reported the equilibria shown in Scheme 5, and the acid-catalysed H-D exchange of the

SCHEME 5

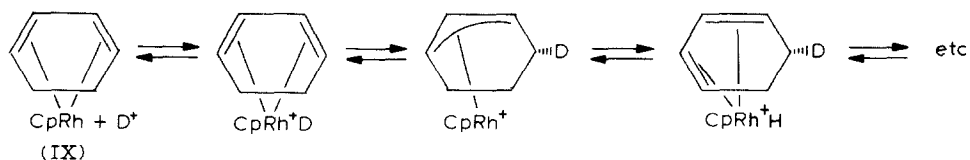


$\text{L} = \text{Ph}_3\text{P}$; COD = cycloocta-1,5-diene

cyclohexadiene *endo* hydrogens in the η -cyclohexadienerhodium complex IX (Scheme 6) takes place via the reversible deuteration of the metal followed by the reversible migration of the deuteride ligand on to the *endo* face of the cyclohexadiene ring to give an η -cyclohexenyl intermediate [11].

We originally suggested [1] that the remarkable thermal stability of the trihydrido- η -diene complexes I-V was due to their pentagonal bipyramidal structure

SCHEME 6



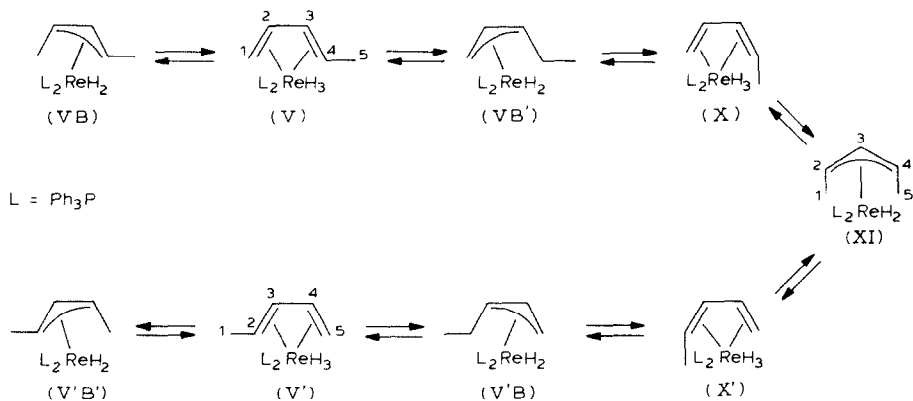
(Cp = $\eta\text{-C}_5\text{H}_5$)

(Fig. 1A) in which the C=C and M-H bonds are not parallel, this being thought to hinder the migration of H on to the diene ligand [12]. This suggestion is clearly invalidated by the results reported above, since the complexes are thermally stable up to at least 100°C [1], whereas the transfer of H from metal to carbon can be detected by SST at 30°C. Possibly the migration of a second hydride on to the η -allyl ligand, leading ultimately to decomposition, is disfavoured because it would involve formation of a 14e intermediate.

The pentadiene and hexadiene complexes V, VI and VII

As for the complexes discussed above, spin saturation transfer experiments revealed the reversible migration of a hydride ligand on to the 1 and 4 positions of the pentadiene ligand in the complex V. Thus, above 40°C, a fast equilibrium between V and the two η -allyl species VB and VB' occurs (Scheme 7).

SCHEME 7

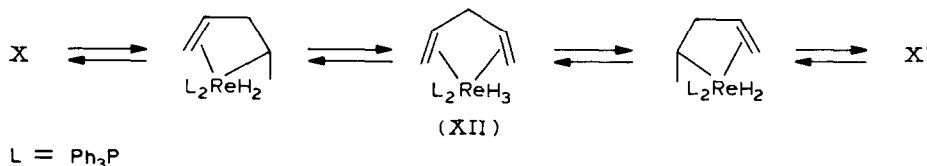


At 80°C, it is possible to observe the exchange between the hydride ligands and all the hydrogens of the pentadiene moiety, with the exception of the hydrogen in the 3 position, which remains unaffected. These observations are consistent with an interconversion between the two degenerate forms V and V'. This process, which involves the exchange between the 1 and 5 and between the 2 and 4 positions of the pentadiene ligand, is a relatively high energy process compared to the transfer of hydrogen, observed at 30°C, between the 1 and 4 positions in V via VB and VB'.

The equilibrium between the two degenerate forms V and V' must involve a symmetrical intermediate such as XI, which may be formed via X or X', the *cis*-pentadiene isomers of V and V', as shown in Scheme 7. The η -allyl intermediate

XI could also be formed from VB or V'B', but this route would involve a 14e σ -allyl intermediate and seems to us less probable (see above). Another possible symmetrical intermediate is the non-conjugated penta-1,4-dienerrhenium trihydride XII (Scheme 8). The interconversion of conjugated and non-conjugated species in these

SCHEME 8



rhenium systems is clearly an easy process, since the reaction between (Ph₃P)₂ReH₇ and isomeric (conjugated or non-conjugated) dienes leads in all cases to the same trihydrido- η -diene complex. Thus, both penta-1,3-diene (*cis* or *trans*) [1] and penta-1,4-diene (see Experimental) and both cyclohexa-1,3- and -1,4-diene [1], afford the conjugated trihydrido- η -1,3-diene complexes V and IV, respectively; conversely, both cycloocta-1,3- and -1,5-diene afford the non-conjugated trihydrido- η -cycloocta-1,5-diene complex [1]. We imagine that the penta-1,4-diene trihydride XII is an intermediate in the formation of V from (Ph₃P)₂ReH₇ and penta-1,4-diene, and that the reverse reaction (V $\rightarrow$ XII) is also possible.

The equilibration of the hexadiene complexes VI and VII (Scheme 1) may be presumed to occur by the same mechanism as the degenerate isomerisation of the pentadiene complex V. It is interesting that the ratio of the two isomers VI and VII at equilibrium corresponds to the statistical ratio of 1/2; VI and VII therefore have equal thermodynamic stabilities.

Experimental

Microanalyses were carried out by the Service Central d'Analyses du C.N.R.S.

The ¹H NMR spectra were recorded on a Bruker WP-80 (80 MHz), a Cameca 250 (250 MHz) or a Bruker WM-400 (400 MHz) instrument. TMS was the internal reference, otherwise the chemical shifts from TMS were calculated using CHDCl₂ (δ 5.25 ppm from TMS) or C₆D₅CHD₂ (δ 2.06 ppm from TMS) as internal reference. The ¹³C NMR spectrum was recorded on a Bruker WM-400 instrument at 100.6 MHz; the chemical shifts were calculated using the toluene-*d*₈ signal (δ 20.5 ppm from TMS) as internal reference.

All manipulations were carried out under nitrogen, the evaporations under reduced pressure. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Commercial dienes (Fluka) were used after filtration through a short alumina (grade II-III) column.

The butadiene complex I-III and the cyclohexadiene complex IV

These complexes were prepared as in [1]. Their variable temperature ¹H NMR spectra are summarized in Tables 1 and 2. The possibility of an "agostic" structure of IV was investigated; its ¹³C NMR spectrum does not show any sign of a C-H $\rightarrow$ Re interaction. (IV, ¹³C NMR, -60°C, δ (toluene-*d*₈): 70.5 (d, *J* 170 Hz), 54.4 (d, *J* 150 Hz), 25.2 (t, *J* 130 Hz)).

The pentadiene complex V

This compound was previously prepared from the reaction of $(\text{Ph}_3\text{P})_2\text{ReH}_7$ with either *cis* or *trans* penta-1,3-diene [1]. The following procedure using penta-1,4-diene gives significantly better yields.

A solution of $(\text{Ph}_3\text{P})_2\text{ReH}_7$ (1.0 g) and penta-1,4-diene (1 ml) in THF (40 ml) was refluxed for 5 min. The yellow solution was evaporated to dryness to give a solid foam. Acetone (10 ml) was added and the solution rapidly deposited pale yellow crystals which were collected, washed with acetone and dried in vacuo (850 mg, 77%). The product was recrystallized from CH_2Cl_2 acetone.

The variable temperature ^1H NMR spectra of V are summarized in Table 3.

The hexadiene complexes VI and VII

These complexes were formed in the reaction of $(\text{Ph}_3\text{P})_2\text{ReH}_7$ with n-hexane in the presence of 3,3-dimethylbutene [3] or by treatment of $(\text{Ph}_3\text{P})_2\text{ReH}_7$ with either *cis* hexa-1,4-diene or *trans-trans* hexa-2,4-diene. The following procedure using hexa-1,5-diene gives significantly better yields.

A solution of $(\text{Ph}_3\text{P})_2\text{ReH}_7$ (300 mg) and hexa-1,5-diene (0.3 ml) in THF (30 ml) was refluxed for 5 min. The yellow solution was evaporated to dryness to give a yellow foam, which was dissolved in CH_2Cl_2 and filtered through a short alumina (grade II-III) column. The pale yellow solid obtained after evaporation of CH_2Cl_2 was recrystallized from hexane at -20°C (250 mg, 75%). An analytical sample was prepared by recrystallisation from CH_2Cl_2 acetone at -20°C . Analysis: Found: C, 63.48; H, 5.36; P, 7.57. $\text{C}_{42}\text{H}_{43}\text{P}_2\text{Re}$ calcd.: C, 63.38; H, 5.43; P, 7.78%.

The 400 MHz ^1NMR spectrum in C_6D_6 at 25°C of the mixture VI + VII shows the phenyl resonances and two very broad signals for the hydrides (δ -3.1 and -8.0 ppm). Double resonance experiments allowed us to assign all the signals corresponding to the diene ligand hydrogens. Integration of these signals, in particular those of the methyl groups, indicates that the compounds VI and VII are in the ratio 1/2.

For the hexa-2,4-diene isomer VI: ($\delta(\text{C}_6\text{D}_6)$: 3.58 (m, H(3) and H(4)), 1.74 (d, J 6 Hz, CH_3), -0.30 (m, $\text{H}_a(1))$).

For the hexa-1,3-diene isomer VII: ($\delta(\text{C}_6\text{D}_6)$: 3.92 (br, H(2)), 3.45 (br, H(3)), 2.25 (br, $\text{H}_s(1))$, 1.99 and 1.56 (m, CH_2), 0.75 (t, J 7 Hz, CH_3), -0.40 (m, H(4)), -0.80 (m, $\text{H}_a(1))$).

The 250 MHz ^1H NMR spectrum at 90°C of the mixture VI + VII in toluene- d_8 shows a doublet at 1.61 ppm (CH_3 in VI) and a triplet at 0.72 ppm (CH_3 in VII). Irradiation of the methyl signal of VII brought about a decrease in intensity of the methyl signal of VI to 70% of its original value.

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