Stereochemistry of Intermediates in Homogeneous Hydrogenation catalysed by Tristriphenylphosphinerhodium Chloride, employing Nuclear Magnetic Resonance Magnetisation Transfer

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The DANTE technique has been employed to observe intra- and inter-molecular exchange equilibria in Wilkinson's catalyst, $ClRh(PPh_3)_3$ and its dihydride. The parent compound undergoes automerisation much faster than dissociative exchange with free PPh_3. The rate of the latter process, 0.31 s^{-1}, is in accord with that value deduced from the kinetics of H_2 addition and by other techniques. For $ClH_2Rh(PPh_3)_3$ the rapid exchange of PPh_3 *trans* to hydride occurs through an intermediate with effective C_{2v} symmetry in which the two hydrides are equivalent. A slower, previously unobserved exchange of the mutually *trans*-phosphines with free PPh_3 occurs, which is sufficiently rapid that the intermediate so generated can participate in the catalytic cycle of homogeneous hydrogenation. These results provide a basis for suggesting that the key intermediates in homogeneous hydrogenation have two mutually *cis*-biphosphine ligands bound to rhodium. Further justification arises from molecular modelling of transient olefin-bound intermediates based on authentic crystal structures. For several common olefins, the bound state involving *trans*-disposed triphenylphosphines is severely destabilised by unavoidable van der Waals repulsions, whereas the corresponding intermediate with *cis* phosphines is stable in catalytically realistic geometry.

Since its discovery and application in the mid-1960s,[1] the mechanism of action of Wilkinson's catalyst $ClRh(PPh_3)_3$ has been studied in considerable detail. The overall pathway has been delineated by kinetic studies, notably from Halpern's laboratory,[2] and the reactivity of intermediates studied by n.m.r.,[3] fast reaction kinetics,[4] and flash photolysis.[5] There is a considerable consensus about the broad outline of mechanism in that the major channel involves biphosphinerhodium species which sequentially co-ordinate H_2 and the olefinic substrate; *cis*-ligand migration of hydride then occurs in the rate-controlling step.[6] In the hydrogenation of styrene, a competitive pathway involves monophosphine complexes with two co-ordinated olefins, but this is not important in the reduction of cyclohexene.[2]

Despite this intense activity, the formal characterisation of intermediates on and associated with the catalytic pathway is lacking. This relates in part to the high reactivity of 14ε and 16ε intermediates, and the intrinsically low energy barriers of addition, migration, or elimination steps in the sequence. It means that the stereochemistry of the co-ordination sphere during the catalytic cycle is known only by inference from that of more stable species, with bulky or non-dissociating ligands, or in isostructural iridium complexes. The difficulty of experiment has encouraged numerous theoretical analyses pertaining both to the pathway for individual steps[7] and the overall catalytic cycle.[8]

The turnover rate for catalysis of olefin hydrogenation is typically 0.05—0.25 s.[2] Single stages may occur very much more rapidly, so that dynamic n.m.r., which provides useful information on processes with rate constants in the range 10^{-1}—10^5 s^{-1}, can be valuable.[9] In this paper we report a series of n.m.r. studies on different steps of the cycle in which the DANTE experiment devised by Morris and Freeman[10] is utilised.

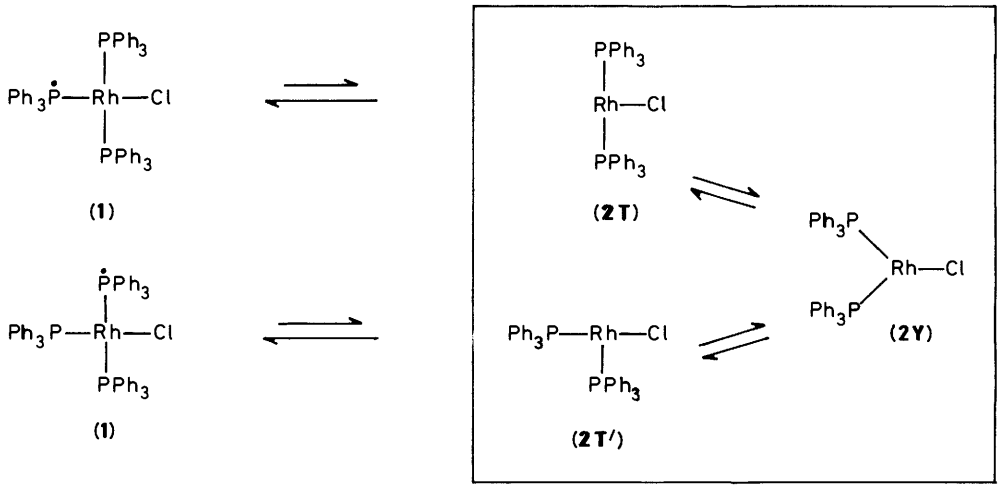


Figure 1. T and Y geometries of the 14-electron complex $ClRh(PPh_3)_2$ and the interconversion with $ClRh(PPh_3)_3$

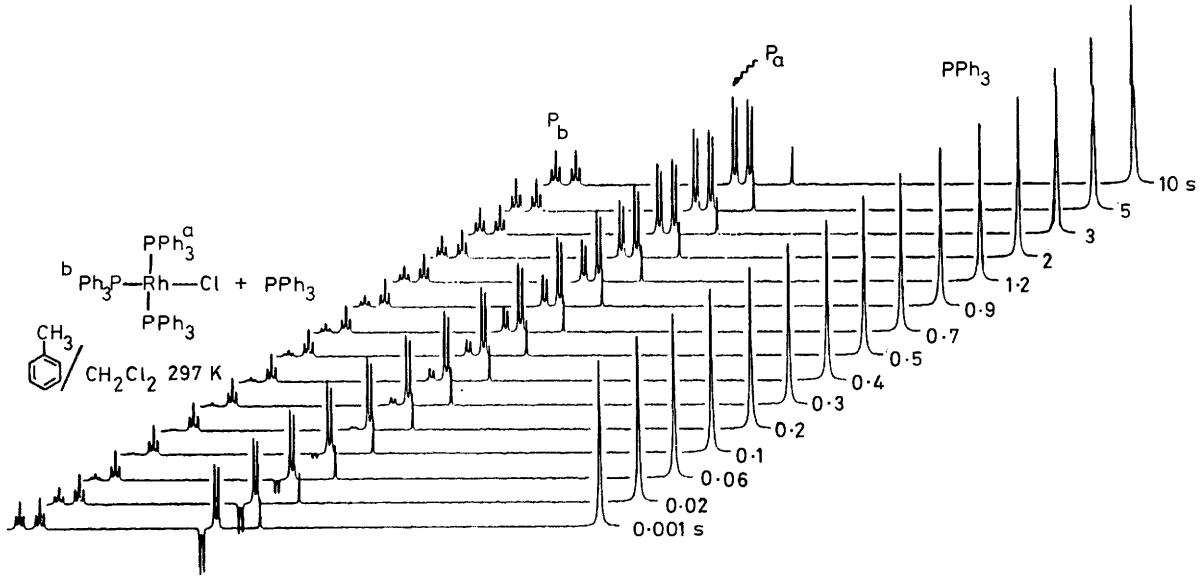


Figure 2. Intramolecular magnetisation transfer in $ClRh(PPh_3)_3$, irradiating the low-field doublet of P_a in the presence of excess of PPh_3 at 297 K in C_7H_8–CH_2Cl_2. The low-field position of the P_a signal has been irradiated by a DANTE sequence, and the major pathway for spin equilibration occurs *via* the low-field triplet of P_b with k_{obs} 22 s^{-1}. Exchange with external PPh_3 is *ca.* 50 times slower and can be ignored in the analytical treatment

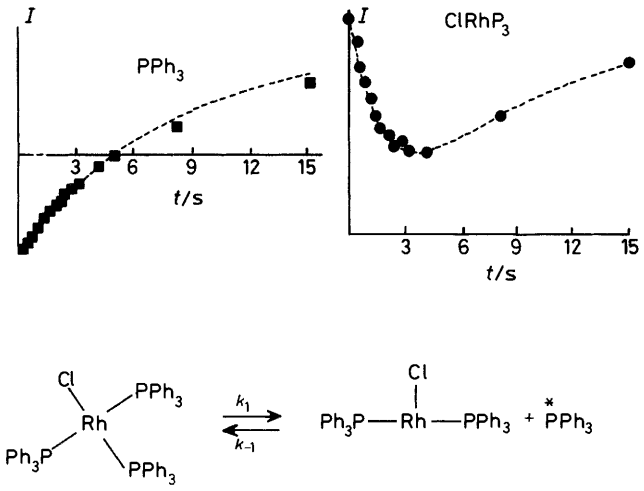


Figure 3. Variation in signal integrals with time following spin-excitation of PPh_3 by a DANTE sequence in the presence of $ClRh(PPh_3)_3$, summing the integral area of P_a and P_b in the latter. In CH_2Cl_2 at 303 K, a dissociation rate constant of 0.31 s^{-1} was derived employing relaxation times of 11 s for PPh_3 and 3.7 s for co-ordinated phosphine

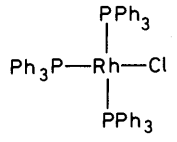
The Catalyst Precursor $ClRh(PPh_3)_3$.—One of the earliest questions settled by mechanistic studies was the route by which H_2 is added to the catalyst to form $ClH_2Rh(PPh_3)_3$.[2,3] It was conclusively proved that this required prior phosphine dissociation to give the co-ordinatively unsaturated 14ε complex $ClRh(PPh_3)_2$. The stereochemistry of this was unknown although it was well recognised that three possible geometrical isomers can exist (Figure 1). The 14ε cation $Rh^+(PPh_3)_3$ is T-rather than Y-shaped[11] and compounds of general type $XRhP_2$[12] are T-shaped with the phosphines disposed *trans*, although this may be due to steric constraints because all known examples possess bulky ligands.

$ClRh(PPh_3)_3$ has a distorted square-planar structure,[13] and the ^{31}P n.m.r. spectrum shows two inequivalent rhodium-coupled nuclei P_a and P_b in ratio 2:1. In an attempt to determine which phosphine dissociates more rapidly, a DANTE spin saturation transfer experiment was performed. The low-field doublet of P_a was excited in a sample containing free PPh_3, and it was observed that magnetisation was transferred rapidly to the low-field triplet of P_b, and much more slowly to external PPh_3 (Figure 2). This experiment requires that an isomerisation which makes the phosphine sites equivalent without dissociation of ligand is occurring, and analysis of the data shows that k_1 is 22 s^{-1} at 297 K. A similar process had been inferred in the case of the tri-*p*-tolyl analogue[14] by study of the ^{31}P n.m.r. spectrum at higher temperatures, and other $(PPh_3)_3RhX$ complexes behave similarly.[15] It implies that a higher energy state with C_{3v} symmetry is readily accessible, and precludes stereochemical analysis of the dissociation process.

In a separate experiment at 303 K, the resonance of free PPh_3 was excited and excitation transfer to the rhodium-bound phosphines (which occurred at identical rates) observed. On the basis of results obtained here, the dissociation rate constant for loss of phosphine from $ClRh(PPh_3)_3$ is 0.31 s^{-1} (Figure 3). This is roughly comparable with values obtained on analysis of the kinetics of H_2 addition, varying $[PPh_3]$,[2] or from the *ortho–para* H_2 interconversion catalysed by $ClRh(PPh_3)_3$ in dynamic equilibrium with $ClH_2Rh(PPh_3)_3$.[16]

The Stable Dihydride $ClH_2Rh(PPh_3)_3$ (**3**).—According to the accepted mechanism for homogeneous hydrogenation by Wilkinson's catalyst, the cycle involves only bis(phosphine) complexes, and the observed dihydride $ClH_2Rh(PPh_3)_3$ must therefore lose PPh_3 in order to participate. Under the normal reaction conditions it is the most stable species present, and therefore an important resting state.[2] Study of the phosphine dissociation step provides information on the co-ordinatively unsaturated species $ClH_2Rh(PPh_3)_2$ (**4**) which traps olefin on the catalytic pathway.

From the previous studies, it is well established that the phosphine *trans* to H_a dissociates very readily, k_{diss} being *ca.* 400 s^{-1} at ambient temperature.[3] The five-co-ordinated intermediate (**4**) is of unknown stereochemistry, but this fast exchange process does not result in equivalencing of P_a and P_b so that the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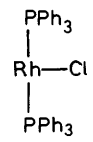
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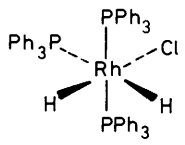
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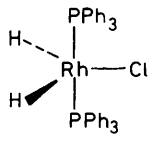
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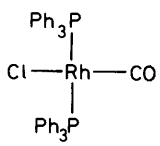
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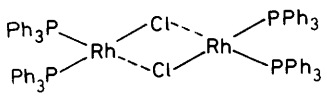
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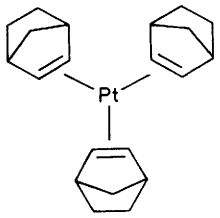
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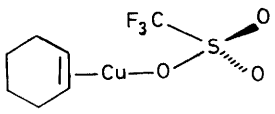
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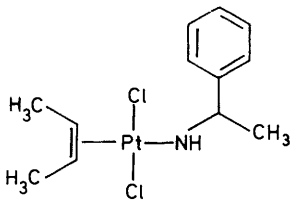
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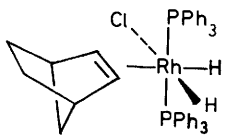
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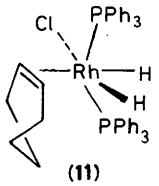
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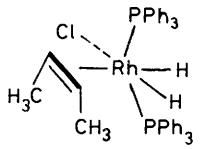
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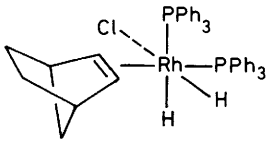
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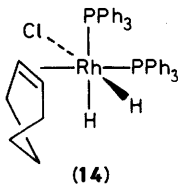
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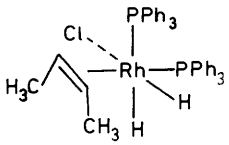
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reverse reaction (**4**) $\rightleftharpoons$ (**3**) is stereospecific with phosphine return *trans* to hydride. In the case of the stable iridium analogue $H_2ClIr(PMe_3)_3$ which is isotructural with compound (**3**), the slow exchange with added $P(CD_3)_3$ occurs only with the ligand *trans* to hydride.[17]

Two intermediate conformations are compatible with this observation, so that complex (**4**) may either be a trigonal bipyramid (C_{2v}) or a square-based pyramid (C_s). In the former case each exchange will result in equivalencing of H_a and H_b whilst in the latter H_a and H_b remain distinct (Figure 4). They were distinguished by a pair of experiments carried out on the same sample at a probe temperature of 273 K. The ^1H n.m.r. spectrum (C_7D_8; 233 K) consists in the hydride region of a Rh-coupled doublet at δ −9.2 ($J_{Rh\text{-}P}$ 155 Hz) with further fine structure due to Rh, P, and H couplings, and a multiplet at δ −16.5. The low-field signal is due to H *trans* to phosphine and the latter due to H *trans* to chloride. At higher temperatures broadening occurs,[3] and we observe coalescence at *ca.* 335 K. With the sample held at 273 K, the high-field signal was inverted by a DANTE pulse sequence and transfer of magnetisation to the low-field doublet monitored, varying delay time *T*. A rate constant for the process of k_H 3.65 s^{-1} was derived.

The ^{31}P n.m.r. spectrum of complex (**3**) consists of a Rh-coupled doublet at δ 41.4 p.p.m. (J_{PP} 21, J_{PRh} 113 Hz) and Rh-coupled triplet at δ 21.0 p.p.m. (J_{PRh} 88 Hz) at 233 K. As the temperature is increased, P–P coupling is lost from the low-field signal which otherwise remains sharp, whilst the high-field signal becomes very broad and eventually disappears; at 373 K it is still reasonably sharp. It proved possible to invert the lower half of the P_b double triplet using a DANTE pulse sequence and to monitor the transfer of magnetism to the upper half. This occurred with a rate constant k_P 4.5 s^{-1}, identical with k_H within experimental error. The first determination monitors the rate of equivalencing of H_a and H_b whereas the second measures the rate at which P_bRh coupling is lost. Since they are equal it means that dissociation and recombination of PPh_3 in complex (**3**) occurs through an intermediate which is effectively of C_{2v} symmetry (Figure 4).

This rapid phosphine dissociation process had led to the belief that the co-ordinatively unsaturated intermediate (**4**), which traps olefin in the catalytic cycle of hydrogenation, must have *trans*-biphosphines. This is not required by the experimental evidence and we present modelling work later which casts doubt on the viability of this step, when the geometry is as assumed. Since compound (**4**) is five-co-ordinate, it is presumably fluxional.[18] This leads to diverse dissociation–recombination pathways which are illustrated in Figure 5. By the conventional release of PPh_3 *trans* to hydride from the starting complex (**3**), intermediates **A** or **B** may be formed and these interconvert by pseudorotation. If P_a rather than P_b is involved in the dissociation process then either **B** or **C** may be formed. Two further five-co-ordinate intermediates **D** and **E** need to be considered. The relative energies of these isomers is unknown, but a tri-isopropylphosphine analogue is isostructural with **A**.[19] In principle, phosphine return can occur by a number of pathways, some of which result in the formation of the unobserved meridonal isomer of (**3**), and are therefore discounted. Those leading to the well established P_b exchange pathway are denoted by * whereas P_a exchanges, previously not identified, are denoted by ‡.

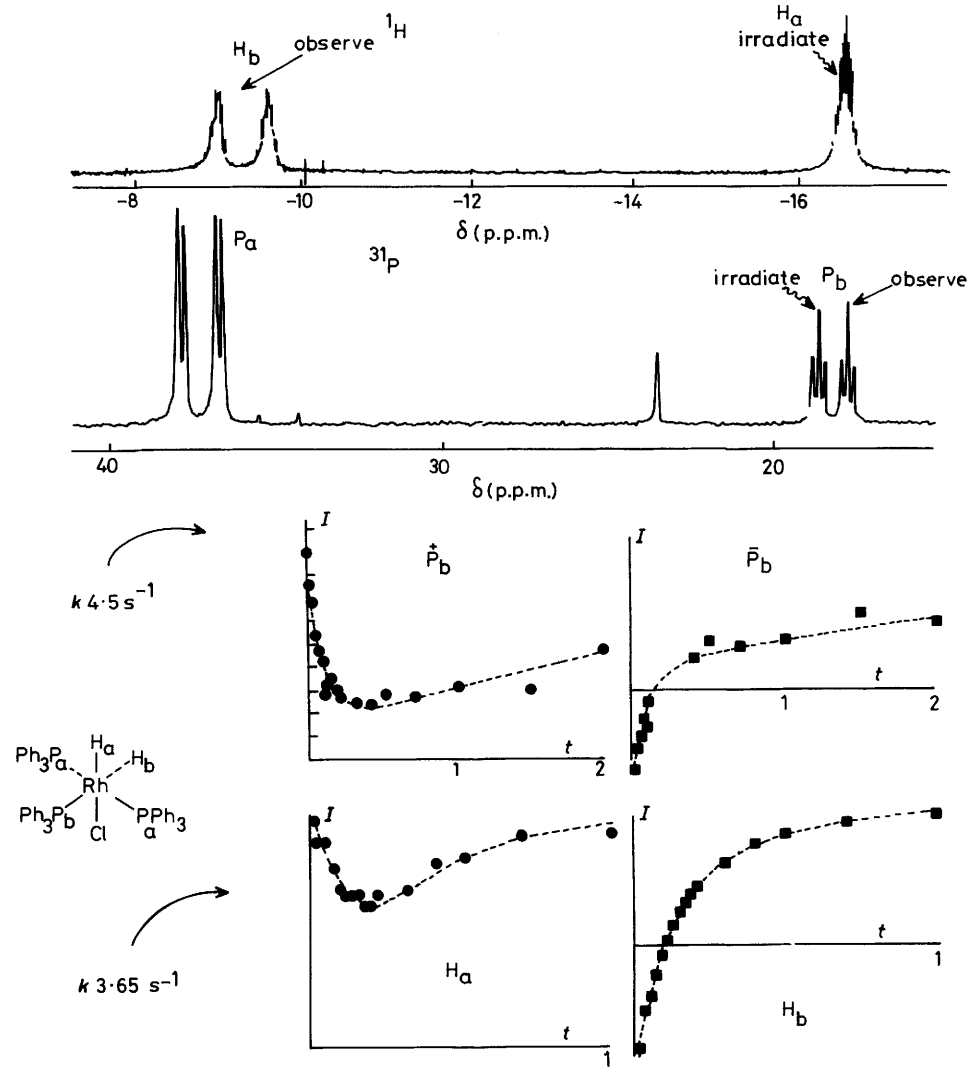

Figure 4. Comparison of the rates of H_a and H_b interconversion and PPh_3 dissociation in $ClH_2Rh(PPh_3)_3$, at 273 K. The data for proton site equilibration were obtained by inversion of the high-field signal and following magnetisation transfer to the low-field signal, with k_H 3.65 s^{-1} and relaxation times of 0.32 s^{-1} for both sites. Relaxation times for metal hydrides in the range 0.21—2.03 s have been reported (R. H. Crabtree, B. E. Segmuller, and R. J. Uriarte, *Inorg. Chem.*, 1985, **24**, 1949).The data for phosphine site equilibration were obtained by DANTE excitation of the lower-field part of the P_b signal, following excitation transfer to the higher-field part with k_P 4.5 s^{-1} and T_1 4.5 s. In a separate control experiment, no excitation transfer was observed in P_b at 233 K under otherwise identical conditions so that it occurs *via* phosphine dissociation rather than through the spin manifold (*cf.* S. Macura, Y. Huang, D. Suter, and R. R. Ernst, *J. Magn. Reson.*, 1981, **43**, 259)

The experimental test for P_a exchange was relatively straightforward. At 303 K, the ^{31}P n.m.r. spectrum of complex (**3**) in the presence of excess of PPh_3 consists of two signals, a sharp doublet at the resonance frequency of P_a and a broadened singlet (ω 12 Hz) representing P_b and PPh_3 approaching the fast-exchange limit. A DANTE pulse sequence was employed, irradiating the P_b–PPh_3 resonance. The results recorded in Figure 6 make it abundantly clear that site interchange is occurring. Assuming that P_a is involved in dissociative exchange, rather than loss of stereochemical rigidity in a six-co-ordinate dihydride,[20,21] then the rate constant for this process is 0.2 s^{-1} at 303 K. Since ligand return to the P_a site (‡, Figure 5) is permissible in this case it may occur more generally, so that olefin trapping by the five-co-ordinate dihydride can give rise to an intermediate with *cis*-biphosphine geometry. Furthermore, this is accessible on the time-scale of turnover in catalytic hydrogenation.

Molecular Modelling of Olefin-bound Intermediates.—Magnetisation transfer experiments of the type described can provide useful information on catalytic intermediates which are unsaturated and related to observable states by ligand dissociation. They point to a possible role for *cis*-biphosphine-rhodium complexes (rather than the conventionally drawn *trans*-biphosphinerhodium moiety) and these appear attractive for several reasons. First there is less steric crowding in the *cis* intermediate, based on inspection of molecular models. Secondly, it is to be expected that intermediates with hydride or alkyl *trans* to phosphine will be intrinsically more reactive than intermediates with *trans*-biphosphines.[22] Where there is a rigid *trans*-linked geometry, then the catalytic properties of the complex are weak.[23]

Since the olefin and hydridoalkyl[24] complexes in catalytic hydrogenation are transient, models of the various geometrical isomers were studied by computer simulation. The co-ordinates

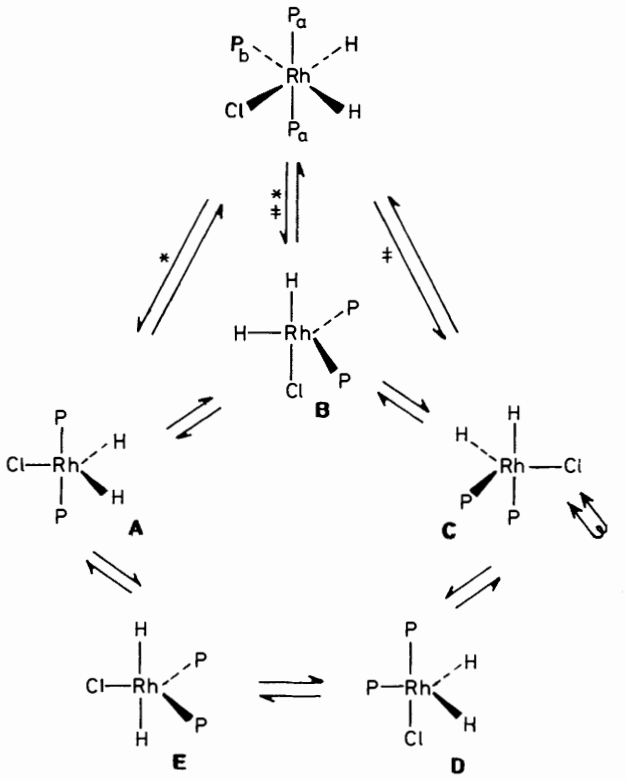

Figure 5. The stereochemistry of the five-co-ordinate complex (**4**) and its permutational isomerism in relation to PPh_3 recombination pathways

Consider first the bicyclo[2.2.1]heptene case. The olefin is known to hydrogenate with exclusive delivery of H_2 (D_2) to the *exo*-face,[30] and hence models corresponding to *exo*-co-ordinated olefin dihydride with *cis*- and *trans*-$(PPh_3)_2Rh$ entities were simulated (Figure 7). Attempts were made to minimise the energy of the *trans*-isomer with the olefinic double-bond held coplanar with Rh–H, necessary for the *cis*-ligand migration step.[31] The procedure involves a minimisation routine in which bond lengths and angles are fixed, whilst free rotation about Rh–P and P–Ph bonds is permitted, assuming the strain energy to be expressed entirely in van der Waals repulsion. The parameters used accord with established practice.[32] This approach is clearly a gross approximation, necessitated by the lack of appropriate force-constant data for co-ordinated ligands and justified by the fact that very large energy differences ensue when closely similar complexes are compared.

In fact the *trans*-complex, (**10**), is impossibly strained, with severe van der Waals interactions between the olefinic bridges and one co-ordinated PPh_3. Since *trans*-$(PPh_3)_2Rh$ complexes are known with up to 20° distortion in $P\widehat{RhP}$, notably the $(PPh_3)_3Rh$ cation,[11] this angle was reduced to 160°, distorting away from the co-ordinated olefin. The resulting structure, after minimisation as described earlier, had much less severe interatomic repulsions. There remained a close contact between the methylene bridge and atoms in the vicinity of P_a. Since much of the significant mechanistic work has been carried out with cyclohexene [2–4, 33] requiring a biphosphinerhodium entity at the bound olefin stage, a related molecular structure (**11**) was created which was energy-minimised in the previously described manner for $P\widehat{RhP}$ 160°. The most severe non-bonded interactions then arose from clashes between homoallylic CH_2 groups and *ortho*-aryl protons of P_a (Table). Replacement of

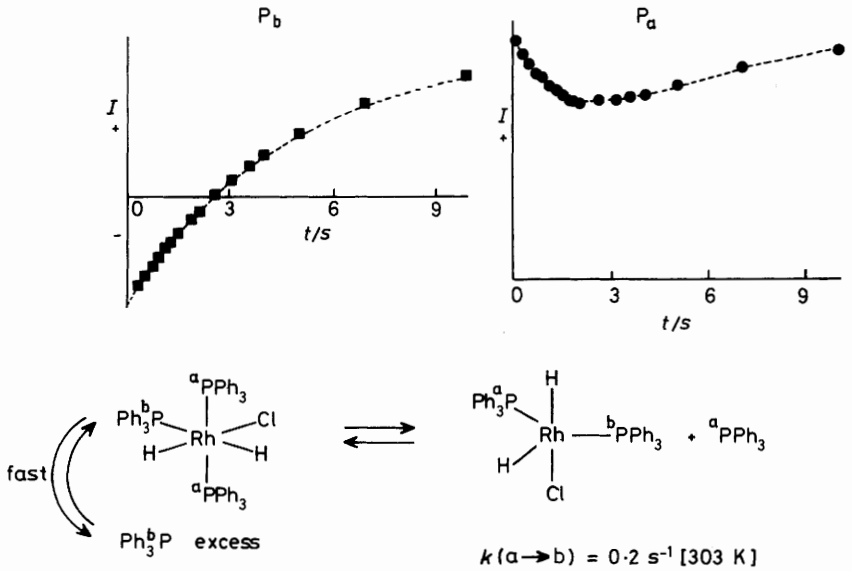

Figure 6. The slow PPh_3 dissociation process in $ClH_2Rh(PPh_3)_3$ (**3**) followed by spin excitation transfer from excess of PPh_3 (in rapid exchange with P_b) at 303 K in CH_2Cl_2, inverting the magnestisation by a DANTE pulse sequence. In two separate experiments with different concentrations of free PPh_3, k 0.174 s^{-1} and T_1 (P_a) 2.4 s, T_1 ('P_b') 5.5 s (illustrated); k 0.196 s^{-1} and T_1 (P_a) 2.8 s, T_1 ('P_b') 4.2 s

for *trans*-$(PPh_3)_2Rh$ were derived from the *X*-ray structure of compound (**5**),[25] and those for *cis*-$(PPh_3)_2Rh$ from the *X*-ray structure of compound (**6**).[26] For co-ordinated olefins, crystal structures of (**7**),[27] (**8**),[28] and (**9**)[29] were utilised. The appropriate fragments were assembled by application of molecular modelling programs MODEL and COSMIC,* and the latter employed to minimise the energy of the structure.

cyclohexene by *cis*-but-2-ene led to a structure (**12**) with much lower van der Waals energy. Only in this last case is the *trans*-biphosphine olefin complex a viable intermediate.

* MODEL Is a molecular modelling program available from Chemical Design Ltd.; COSMIC was written by Dr. J. G. Vinter, Smith Kline and French.

Table. Van der Waals energy of olefin dihydride complexes

Olefin	Configuration	Torsion angle (°)[a]	van der Waals energy[b]	Main van der Waals repulsions
Bicyclo[2.2.1]heptene	*trans*[c]	0	+48.8	CH_2/P; CH_2/C_{aryl}
	cis	0	−19.1	Rh–H/CH_2
				C_{ortho}/H_{vinyl}
	cis	270	+2.95	Rh–H/CH_2
				C_{aryl}/H_{vinyl}
Cyclohexene	*trans*[c]	0	+75.8	C_{ortho}/α-CH_2
				C_{aryl}/α-CH_2
	cis	0	−20.4	Cl/α-CH_2
cis-But-2-ene	*trans*[c]	0	−15.3	C_{ortho}/CH_3
				C_{aryl}/CH_3
	cis	0	−22.6	C_{ortho}/H_{vinyl}
				C_{aryl}/H_{vinyl}
	cis	90	+59.1	C_{ortho}/H_{vinyl}
				H_{ortho}/CH_3
	cis	270	+32.4	C_{aryl}/H_{vinyl}
				C_{aryl}/CH_3

[a] Between C=C and Rh–H. [b] In kcal mol^{-1}; high-energy species (> 100 kcal mol^{-1}) include all 180° *cis*-rotamers and are clearly unrealistic. [c] With $P\widehat{RhP}$ symmetrically distorted to 160° away from the Rh-olefin bond.

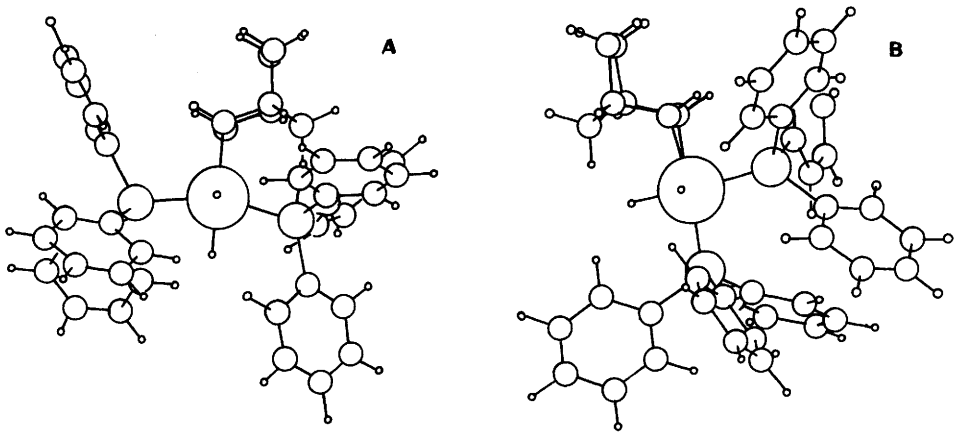

Figure 7. Minimised structures for bicyclo[2.2.1]heptene with $P\widehat{RhP}$ 160° (*trans*, **A**) and 96° (*cis*, **B**). The van der Waals interaction energies are respectively 48.8 and −19.1 kcal mol^{-1}

Since the present work indicates that *cis*-biphosphine intermediates are kinetically accessible at the dihydride stage, attention was then turned to the simulation of appropriate olefin complexes. The olefin was aligned with its π-bond parallel to Rh–H, which permits four complexes interconverted by rotation about the Rh–olefin centroid. When bicyclo-[2.1.1]heptene was employed, then one of the four, structure (**13**), was far lower in energy than the rest, which were impossibly strained (Table). This has the olefin aligned along the H–Rh–Cl axis with its ring framework remote from the *cis*-phosphine. Entirely related observations were made for the cyclohexene complex (**14**) and the *cis*-but-2-ene complex (**15**). For the cyclohexene case, the van der Waals energy was calculated as the olefin was permitted to rotate about its C=C centroid, minimising by C–P and P–Rh rotation at each point (Figure 8). It can be seen that serious non-bonded interactions occur outside a fairly restricted range of geometries.

Although the approach is simplistic in that angle bending and bond stretching are ignored in the minimisation procedure, these observations indicate that the cyclohexenerhodium dihydride must be a *cis*-biphosphine complex in order to avert steric clashes between olefin and ligand. These do not appear particularly dependent on the parameters chosen and we have been unable to construct an unencumbered *trans*-biphosphine complex. Even with the sterically less demanding reactant *cis*-but-2-ene it is necessary to distort the interligand angle to 160° to create a stable olefin complex in the *trans*-series and this must have an energetic cost.

It might be argued that the most relevant state is not that of co-ordinated olefin but the transition-state for hydride migration, which is rate-limiting in catalysis.[2] The best available approximation to this is an agostic complex, which may be regarded as a 'snapshot' of hydrogen delivery to the olefin.[34] In two examples,[35] the crystal structure of an agostic metal ethyl reveals the position of all the C–H atoms, and the latter was used, with appropriate modification, to model the transition state for hydride transfer to co-ordinated *cis*-but-2-ene. The *cis* and *trans* (160°) biphosphine complexes are shown in Figure 9, with the *cis*-form still energetically preferred. When cyclohexene is the olefinic ligand, the preference for *cis*-biphosphine geometry is much more marked.

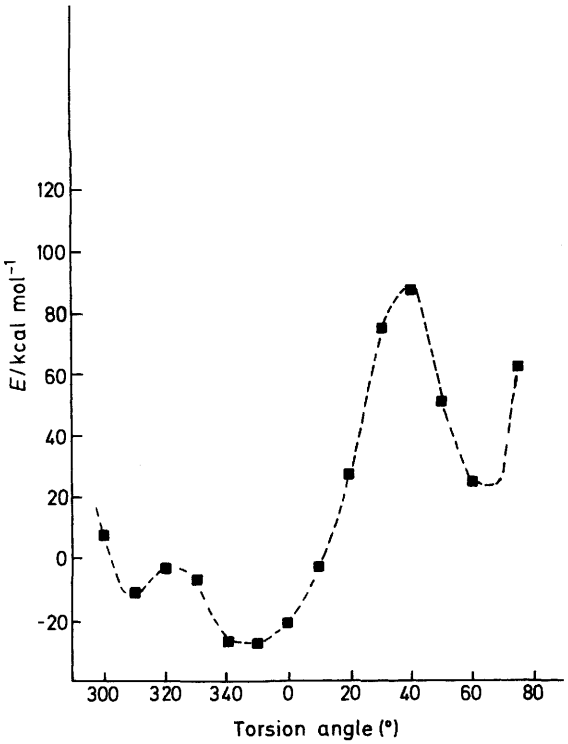

Figure 8. The van der Waals energy of complex (**14**) as a function of the torsional angle between C=C and Rh–H

Conclusions

The DANTE magnetisation transfer experiments provide new information on the stereochemistry of intermediates in homogeneous hydrogenation catalysed by $ClRh(PPh_3)_3$. In particular, they raise the possibility that *cis*-biphosphine-rhodium intermediates may be involved in the later stages of the catalytic cycle, contrary to the conventional view. The postulate is further refined by molecular modelling procedures which indicate that one possible *cis*-biphosphine olefin complex is strongly preferred on steric grounds. A modified mechanism incorporating these suggestions is delineated in Figure 10.

Experimental

$ClRh(PPh_3)_3$ was prepared[36] by the reaction of triphenylphosphine with $[(C_8H_{14})_2RhCl]_2$ a procedure which avoids the formation of trace paramagnetic Rh^{II} impurities.

All samples for ^1H and ^{31}P n.m.r. study were prepared on a vacuum line and stored at −80 °C prior to examination on a Bruker AM 250 equipped with multinuclear probe and operation at 250 (^1H) and 101.2 MHz (^{31}P). The normal technique involved sealing the sample in a 8.4 mm tube which was then contained in a 10 mm tube, with the concentric space containing CD_3OD when the solvent was protiated. Magnetisation transfer experiments were carried out using microprograms entered *via* the teletype terminal* and the data were processed on a HP85 microcomputer by simulation of the observed peak integrals; the programs are available from the authors.

Molecular modelling was carried out by means of structural fragments retrieved from the Cambridge Crystallographic Data File transferred to orthogonal co-ordinates by means of CRYSTALS (Chemical Crystallography Laboratory, Oxford) and CHEMX (Molecular Design, Ltd). The metal atom was placed on the origin and the co-ordinating ligands and groups placed in position, with simple trigonometric manipulation where necessary. The resulting atomic co-ordinate file was then transferred to the COSMIC software, and the energy of the structure minimised using the subroutine TORMIN, iterating until sequential calculations differed by <0.01 kcal mol^{-1}. The van der Waals energy was noted and its components realised *via* the ACIDBASE subroutine.

The validity of this approach was checked using the known[37] atomic co-ordinates for the two solid-state conformers of $ClRh(PPh_3)_3$. The crystallographic structures were minimised, involving very slight torsional changes, and van der Waals energies noted. Torsional angles of P_a–Ph and P'_a–Ph rings were then randomly rotated to give high-energy structures and minimisation applied as before. The final energies thus obtained were within 0.5 kcal mol^{-1} of the crystallographically defined structures in both cases.

* Using microprograms written according to the Bruker Aspect 2000 software manual.

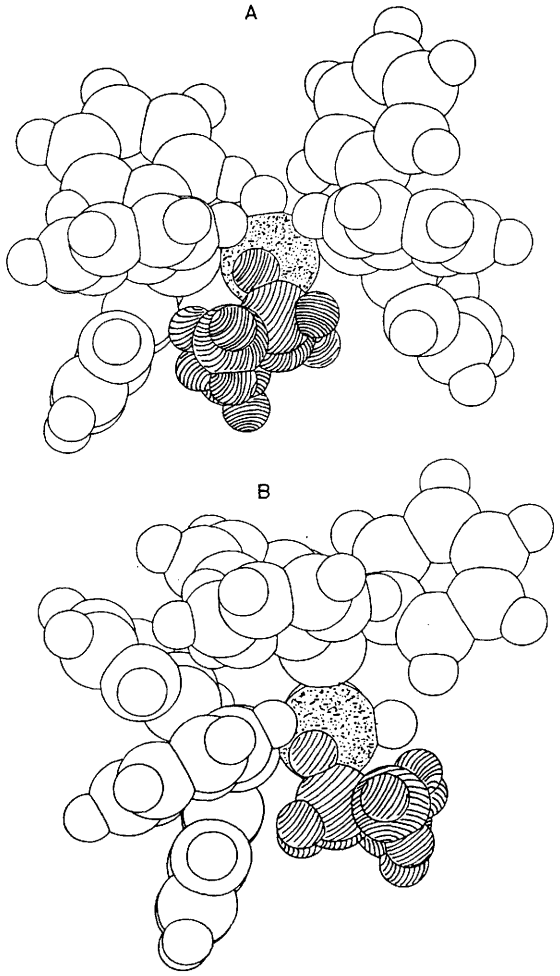

Figure 9. Agostic hydrogen complexes derived from incomplete hydrogen delivery to co-ordinated *cis*-but-2-ene. The interphosphine angle is 160° in A (van der Waals energy −23.4) and 96° in B (van der Waals energy −28.8 kcal mol^{-1})

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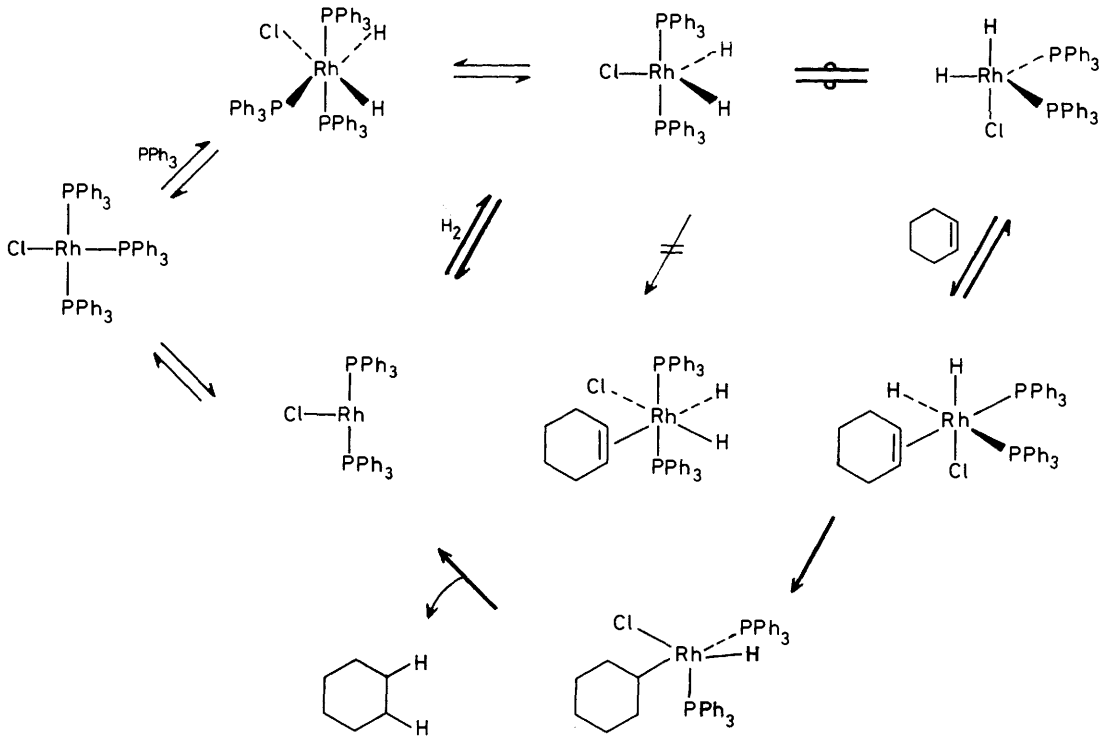

Figure 10. The mechanism of homogeneous hydrogenation by $ClRh(PPh_3)_3$ utilising the stereochemical information provided in prior discussion

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