On the Accessibility of *cis*-Bisphosphine Intermediates in Homogeneous Hydrogenation catalysed by Wilkinson's Complex, $ClRh(PPh_3)_3$

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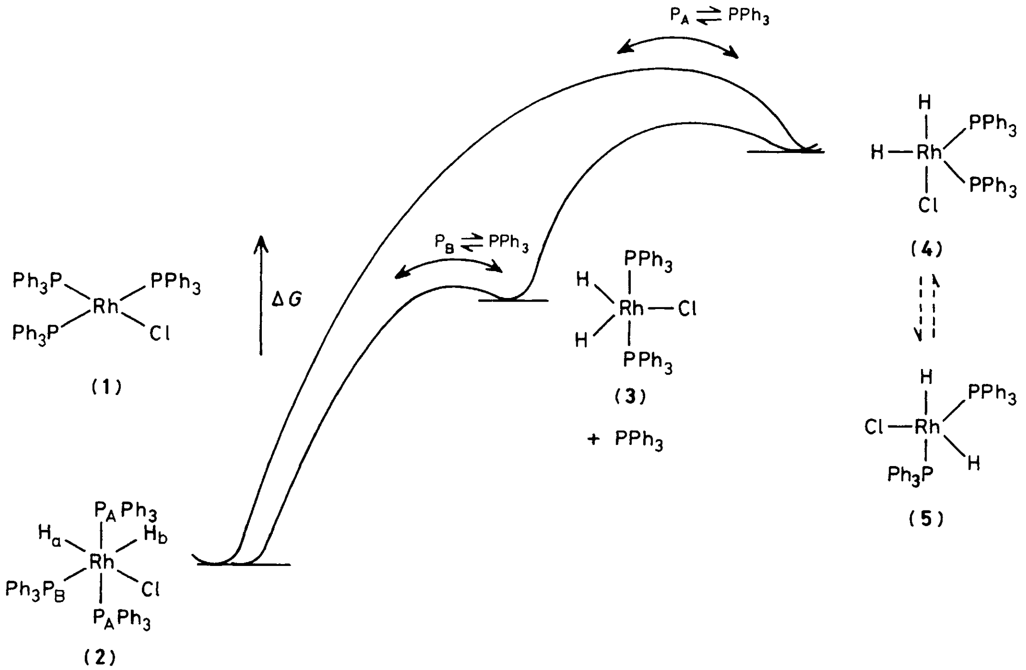
New information on the stereochemistry of intermediates in the catalytic cycle of hydrogenation by $ClRh(PPh_3)_3$ is revealed by magnetisation transfer experiments in ^1H and ^{31}P n.m.r. spectroscopy.

In mechanistic studies[1] of homogeneous hydrogenation catalysed by $ClRh(PPh_3)_3$ (**1**) emphasis has been placed on reaction kinetics and the structure of observable intermediates. Less information is available concerning the stereochemistry of transient species but it has generally been assumed[1] that two PPh_3 ligands are maintained in a mutually *trans*-configuration throughout the catalytic cycle, and the third is not involved other than in side-equilibria. We report experiments employing the DANTE pulse sequence[2,3] for spin-polarisation transfer in ^{31}P n.m.r. which reveal the possibility of a *cis*-$(PPh_3)_2Rh$ arrangement at key stages in the catalytic cycle.

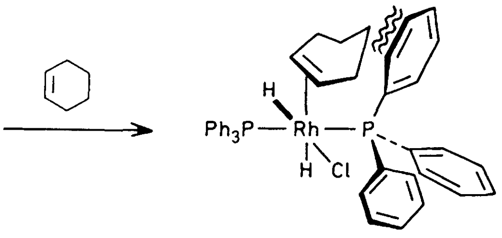
When the dihydride complex (**2**) (0.036 M, 40 : 60 CD_2Cl_2–[$^2H_8$]toluene, 273 K) is examined by ^1H n.m.r. spectroscopy, two sharp hydride signals [δ −16.5 (H_a) and −9.3 (H_b)] are observed. Inversion of H_a through the R.F. decoupler demonstrated an exchange process with $k_{ab} = 6.8\ s^{-1}$. The ^{31}P n.m.r. spectrum *of the same sample* at 273 K exhibited a double triplet at 21.1 p.p.m. (P_B) and a double doublet at 40.4 p.p.m. (P_A). Inversion of the lower-field component of the double triplet and monitoring the intensity of the higher-field component as a function of the delay between the inversion pulse train and the observation pulse demonstrates an exchange between the two sites with $k_{+-} = 7.1\ s^{-1}$. This reflects that rate at which P_B–Rh coupling is lost. These observations accord with a mechanism where P_B dissociates (a process known[1] to be rapid at room temperature) and H_a, H_b are equivalent in the 5-co-ordinate intermediate (**3**) leading to rate-constants for the two exchange processes which are identical within experimental error. In a control experiment conducted at 243 K it was shown that no magnetisation was transferred to P_A on excitation of P_B and thus complications due to scalar coupling[4] are minimal.

In the presence of a twelve-fold excess of PPh_3 [0.38 M *vs.* 0.032 M (**2**) in 40 : 60 CH_2Cl_2–toluene, 303 K] the ^{31}P n.m.r. spectrum of (**2**) reduces to a broadened doublet at 38.1 p.p.m. (P_A) and a singlet at −5.7 p.p.m. ($P_B \rightleftharpoons PPh_3$, $w_{\frac{1}{2}} = 13$ Hz). Inversion of the latter resonance leads to transfer of magnetisation to P_A with $k_{dis.} = 0.31\ s^{-1}$. The exchange process demands PPh_3 return to a five-co-ordinate intermediate of alternative stereochemistry [(**4**), or less likely (**5**)]. Under the conditions of the experiment, interconversion of the five-co-ordinate dihydridobisphosphinerhodium complexes ought to be fast[5] relative to PPh_3 trapping.

Insofar as the catalytic cycle of hydrogenation is concerned, interception of intermediate (**3**) by an alkene (say cyclohexene) leads to complex (**6**) and the stereoisomer (**7**) arises by interception of the alternative, (**4**). The relative concentrations of these two alkene complexes will reflect their thermodynamic stabilities and not the kinetics of alkene association since the latter step is reversible. Indeed, the reaction of *trans*-$(C_2H_4)(PPh_3)_2RhCl$ with H_2 and PPh_3 leads to rapid alkene displacement rather than hydrogenation.[6] There are several reasons why complex (**7**) is more likely to be the true catalytic intermediate. In the addition of a metal-hydrido ligand to an alkene, the best overlap ensues when the M–H and C–C bonds are coplanar in a 4-centre transition-state. The premise is supported by recent experimental studies on reversible insertion reactions[7] and by *ab initio* calculations on alkene hydroboration.[8]

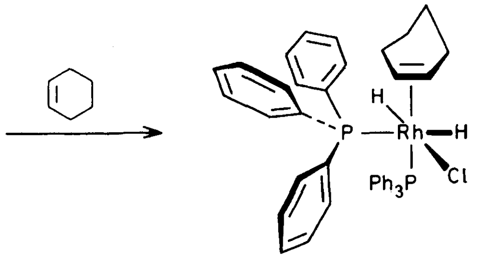


(3)



(6)

(4)



(7)

Molecular models indicate that the reactive conformation of complex (**6**) is sterically compressed relative to that of complex (**7**) and the difference is accentuated in an alkyl-like transition state. Furthermore, only the latter complex has a rhodium-hydrido ligand labilised towards alkene addition by a *trans*-phosphine. If *cis*-phosphine geometry is enforced by chelation, hydrogen transfer to co-ordinated alkene is very rapid.[9] In a thorough study[10] of the mechanism of alkene insertion in *cis–trans* fluxional $(C_2H_4)(PPr^i_3)_2RhH$, a *cis*-bisphosphine arrangement was inferred to be the reactive one. When rigidly *trans*-complexing ligands are employed[11] in homogeneous hydrogenation the reactivity is low.

The application of DANTE techniques to $ClRh(PPh_3)_3$[†] (**1**) (0.02 M, CH_2Cl_2; 0.25 M in PPh_3, 303 K) permitted direct observation of the dissociative phosphine exchange[1,12] with $k_{dis.} = 0.54\ s^{-1}$. In separate experiments it was shown that *cis–trans* isomerisation[13] in complex (**1**) which interchanges the two phosphine environments *via* a tetrahedral intermediate[13] is much faster, with $k_{isom.} = 22\ s^{-1}$. Thus the exchange experiment does not provide information on the preferred stereochemistry of the 14-electron intermediate[14] $ClRh(PPh_3)_2$.

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[†] It proved necessary to prepare complex (**1**) from $(cyclo\text{-}C_8H_{14}RhCl)_2$ to avoid relaxation by trace paramagnetic impurities formed in conventional syntheses. The method of synthesis did not affect catalytic activity in the hydrogenation of 3,3-dimethylbut-1-ene.

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