Rhodium- and palladium-catalysed proton exchange in styrene detected *in situ* by *para*-hydrogen induced polarization

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***In situ* NMR spectroscopy of *para*-hydrogen induced nuclear polarization shows a pairwise proton exchange mechanism in styrene during homogeneous hydrogenation with rhodium(I) and palladium(0) catalysts.**

Recently, we evaluated the pairwise proton exchange mechanism during the homogeneously catalysed hydrogenation of α- or β-unsaturated carbonyl compounds with a rhodium(I) bisphosphinite catalyst and *para*-hydrogen.[1] The coordination of α,β-unsaturated dimethyl itaconic acid to rhodium(I) bisphosphinite catalysts has previously been described to proceed preferentially *via* intramolecular major–minor isomerization.[2,3] Here, we investigate the generality of the proton exchange mechanism by variation of the substrate and the catalyst. The advantage of using *para*-hydrogen (p-H_2) for homogeneously catalysed hydrogenation is the sensitivity of this technique for pairwise hydrogen transfer. This means that both hydrogen atoms of the former *para*-hydrogen molecule have to be transferred to the product in order to give rise to characteristic emission/absorption signals during *in situ* NMR experiments.[4] The polarization signals are due to a selective population of product nuclear spin levels associated with some degree of singlet character, which causes a deviation from the usual Boltzmann distribution. As a consequence, polarization signals can be enhanced by some orders of magnitude; therefore, the method is extremely sensitive for the detection of intermediates[5] and reaction products in low concentrations. The method has been termed PHIP[6] and PASADENA.[4]

We propose the pairwise mechanism of proton exchange in the geminal positions of terminal alkenes to proceed *via* a reversible equilibrium between the dihydrido substrate complex and the monohydrido alkyl complex. To transfer both polarized hydrogen atoms by this key step, the sequence of equilibrium reactions has to be passed through at least twice. Therefore, the unsaturated substrate must remain in the coordination sphere of the catalyst after the first hydrogen exchange step as is depicted in Fig. 1.

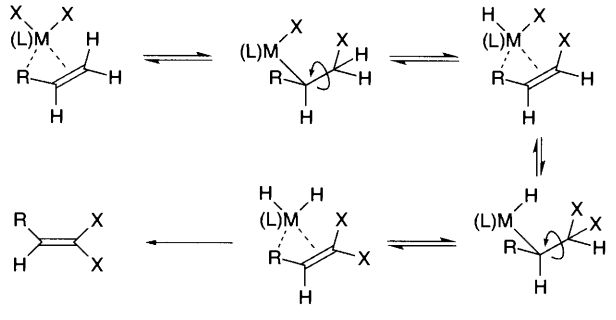

Fig. 1 Proposed pairwise exchange mechanism for the geminal positions of terminal alkenes [M = Rh, X = H (from p-H_2), D; R = carbonyl or phenyl; L = bidentate phosphinite or phosphine ligand; M = Pd; X = H (from p-H_2), D; R = phenyl; L = bidentate imine ligand]. Only relevant exchange steps leading to the geminally exchanged product are considered.

According to the theory of the PHIP method, a single H/D exchange by itself as demonstrated by Blagbrough and coworkers[7] should not lead to polarization signals in the substrate as observed here. A second coordination of the substrate to the metal centre, however, seems to favour the pairwise proton exchange. This is the case for α,β-unsaturated carbonyl compounds, where both the carbonyl and the alkenic group are coordinated to the catalyst.[8] Likewise, during the hydrogenation of styrene with the rhodium(I) complex [Rh(cod)(dppb)]BF_4 **1** [dppb = 1,4-bis(diphenylphosphino)butane], the second coordination is possibly due to the phenyl group of the substrate or of its hydrogenation product, respectively.

The spectrum in Fig. 2 confirms that the geminal proton exchange mechanism is indeed not limited to the hydrogenation of unsaturated carbonyl compounds with rhodium(I) bisphosphinite complexes.

Moreover, we studied the hydrogenation of phenylacetylene to styrene by the palladium(0) bisimino precatalyst [PdL(dmfu)][10] **2** [L = bis(*p*-tolylimino)acenaphthene, dmfu = dimethylfumaric acid]. A comparison of the experimental polarization spectrum detected after the hydrogenation of phenylacetylene with *para*-hydrogen with simulations that are performed by use of the computer program PHIP^{++}[11] reveals both a pairwise *cis* and a geminal hydrogenation leading to formation of styrene (Fig. 3).

In order to differentiate whether phenylacetylene is hydrogenated *cis* and geminal at the same time by **2** or whether phenylacetylene is first hydrogenated *cis* and in the formed styrene the protons are subsequently exchanged, deuteriation experiments were performed. The ^2H NMR spectra observed after the deuteriation of phenylacetylene and styrene prove that styrene is, in both cases, deuteriated in position D^3 (*i.e. cis* to the phenyl group). From the observed ^2H NMR spectrum, it is not evident whether the deuterium atom D^3 in Fig. 4(*a*) is transferred by *trans*- or geminal-deuteriation of phenylacetyl-

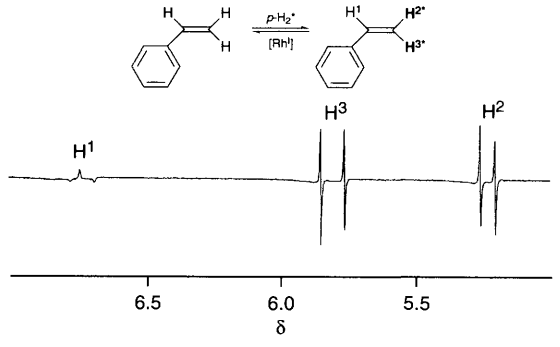

Fig. 2 Alkenic portion of the 200 MHz ^1H NMR polarization spectrum of the hydrogenation of styrene† by **1**. Usual (*i.e.* unpolarized) NMR signals are eliminated by accumulation of four single spectra that are recorded successively by −45 and 135° pulses.[9]

ene, but *trans*-deuteration can be excluded because of the detected polarization signals in Fig. 3(*a*).

Deuteration of the substrate styrene produces geminally deuteriated styrene, apparently by multiple H/D exchanges [Fig. 4(*b*), signals D^2, D^3] beside deuteriated ethylbenzene (signals D^4, D^5). By contrast, styrene which is preferentially

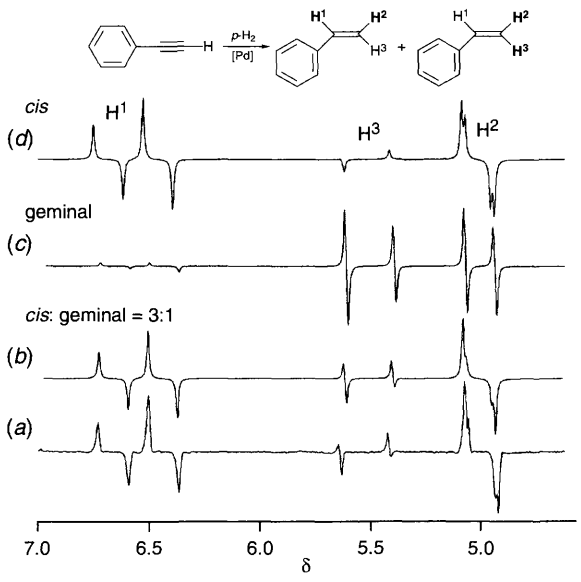

Fig. 3 Analysis of the 80 MHz ^{1}H NMR polarization spectrum detected during the hydrogenation of phenylacetylene‡ by **2**: (*a*) experimental spectrum, (*b*) simulation spectrum considering *cis*- and geminal-hydrogenation in a 3 : 1 ratio, (*c*) simulation spectrum of a geminal p-H_2 transfer into position H^2 and H^3; (*d*) simulation spectrum of a *cis* p-H_2 transfer into position H^1 and H^2

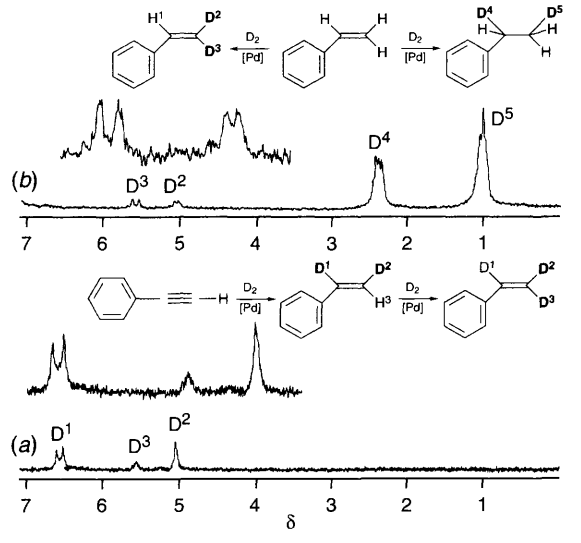

Fig. 4 37 MHz ^{2}H NMR spectra from: (*a*) deuteration of phenylacetylene, (*b*) deuteration of styrene. Signal D^3 in spectrum (*a*) proves a H/D exchange in [$^2H_2$]styrene that is previously generated by *cis*-deuteration from phenylacetylene. In the spectra (*a*) and (*b*) monodeuteriated products due to H/D exchange cannot be distinguished from bisdeuteriated products and are, therefore, not depicted in the reaction scheme.

formed by *cis*-deuteration of phenylacetylene (D^1, D^2) is not deuteriated to ethylbenzene while phenylacetylene is present in the reaction solution, indicating that free phenylacetylene displaces coordinated styrene, but it is deuteriated in the geminal position D^3 [Fig. 4(*a*)] by H/D exchange. The broad signal D^3 in Fig. 4(*a*) corresponds to threefold deuteriated [$^2H_3$]styrene but possibly covers a potential doublet that indicates geminally deuteriated styrene. Therefore, geminal deuteriation of phenylacetylene cannot be totally excluded. In comparison, the signal D^3 in Fig. 4(*b*) includes a $^3J_{DH}$ *trans*-coupling of 2.7 Hz demonstrating that there is still a proton in position H^1 of the H/D-exchanged product. In conclusion, signal D^3 in Fig. 4(*a*) indicates that phenylacetylene is at least preferentially deuteriated *cis* to yield styrene. The generated styrene is simultaneously deuteriated geminally *via* an H/D exchange process. By this route, perdeuteriated alkenes can be synthesized from monosubstituted alkynes by only one catalytic reaction.

The deuteriation experiments confirm that the polarization signal of the geminal p-H_2 transfer to phenylacetylene results from a pairwise proton exchange in the hydrogenation product styrene. Consequently, both the rhodium(I) and the palladium(0) catalyst effect a proton exchange in the geminal position of styrene. This catalytic exchange represents an unusual procedure to synthesize deuteriated alkynes.

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Footnotes

† NMR data for styrene (200 MHz ^{1}H NMR in [$^2H_6$]acetone): δ 5.23 [dd, $^2J(H^2H^3)$ 1.2, $^3J(H^2H^1)$ 10.8 Hz], 5.8 [dd, $^2J(H^3H^2)$ 1.2, $^3J(H^3H^1)$ 17.6 Hz].

‡ NMR data for styrene (80 MHz ^{1}H NMR in [$^2H_6$]benzene); δ 5.03 [dd, $^2J(H^2H^3)$ 1.2, $^3J(H^2H^1)$ 10.8 Hz], 5.54 [dd, $^2J(H^3H^2)$ 1.2, $^3J(H^3H^1)$ 17.6 Hz], 6.56 [dd, $^3J(H^1H^2)$ 10.8 Hz, $^3J(H^1H^3)$ 17.6 Hz]. Cross relaxation effects are considered as described in the literature.[12]

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