NOE (Nuclear Overhauser Effect) Transfers from *para*-H_2 Enhanced Magnetizations in Alkene Moieties at Rh(I) Centers

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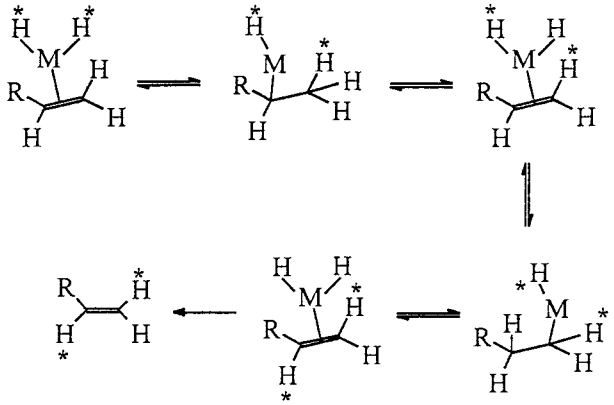
The hydrogenation of symmetric dienes with *para*-H_2 catalyzed by Rhodium complexes leads to remarkable effects in the ^{1}H NMR spectra of the corresponding alkene derivatives, namely, an emission peak (negative peak) in the aliphatic region ascribed to protons of the hydrogenated double bond and one or more enhanced absorption peaks. The strongest absorption peak is invariantly assigned to the two equivalent olefinic protons in the free alkene. The possibility that the observed behavior could be associated with a reversible exchange between *para*-H_2 and the olefinic hydrogens has been ruled out on the basis of the lack of deuterium incorporation when the experiments are carried out with D_2. Variable magnetic field experiments have indicated that the positive peaks arise from relaxation processes, i.e., from cross-relaxation transfers (generally denoted as NOE transfers; NOE = nuclear Overhauser effect) originating from the enhanced magnetization at the hydrogenation sites in the product or, more likely, at the hydride ligands in intermediate species.

Introduction

Since its discovery in 1986, *para*-H_2 effects in the NMR spectra have been widely exploited in several applications, mostly dealing with the characterization of solution structures of species present in very low concentration and the elucidation of reaction mechanisms.[1−10] The remarkable enhancement of absorption and emission signals in the hydrogenated substrate molecule is the result of the transfer from the nuclear spin-order (in *para*-H_2 molecule) to the magnetization order (in the product). The detection of *para*-H_2 effects in NMR spectra has been associated with the occurrence of two basic requisites, i.e., the addition of both hydrogen atoms has to take place at the same substrate molecule and it has to occur at two chemically unequivalent positions.[2] Later it was shown that *para*-H_2 effects can be detected also in products containing equivalent hydrogen sites.[6,11−13] This finding was accounted for in terms of the relaxation processes occurring in an intermediate species containing two structurally different hydride ligands, which leaves a memory in the NMR spectrum of the product.[11,13]

An interesting case dealing with the reversible hydrogenation of an alkene substrate by $[Rh(diene)L_2]^+A^-$ (diene = cyclooctadiene; L = phosphine, phosphite or arsine, $A^- = ClO_4^-$, BF_4^-, PF_6^-) catalysts [14−19] has been recently reported by Bargon et al.[20,21] They showed that the ^{1}H NMR spectra of diene and alkene molecules in the presence of the Rh catalyst and *para*-H_2 displayed the typical *para*-H_2 effects, without being hydrogenated. The observed behavior was explained in terms of the reversible addition−elimination of hydrogen, leading to the incorporation of *para*-H_2 atoms in the alkene molecule (Scheme 1).

SCHEME 1: Reversible Hydrogenation of a Double Bond with *para*-H_2 Which Leads to Incorporation of Polarized Hydrogens in the Alkene Molecule



In principle, one may envisage routes able to induce *para*-H_2 effects on substrate resonances without proceeding to its hydrogenation. For instance, this objective could be pursued through the intermediacy of an adduct formed by *para*-hydrogenated metal hydride complex and the substrate of interest, provided that suitable magnetic interactions between the hydrides and the hydrogens on the substrate take place in order to allow a magnetization transfer between the two moieties. The elucidation of mechanisms promoting the enhancement of substrate's resonances not implying its hydrogenation may be relevant to envisage novel applications of PHIP (*para*-hydrogen induced polarization) effects, for example in the MRI field.

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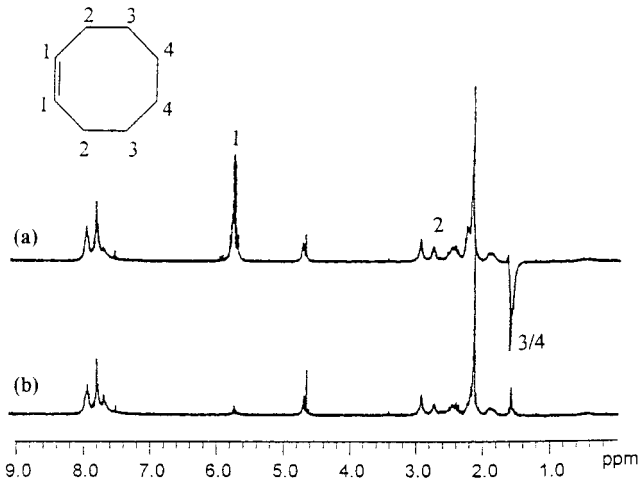


Figure 1. ^{1}H NMR spectra of the mixture [Rh(COD)(dppb)]$^+$/*para*-H_2 recorded (a) 20 s after agitation of the sample and (b) after complete relaxation of the *para*-H_2 polarization (270 MHz, acetone-d_6, RT).

In this paper we report about the observation of a polarization transfer, achieved through spin relaxation phenomena, from *para*-H_2 to monoalkenes (e.g., cyclooctene, norbornene, etc.), which are formed during the first stage of the hydrogenation of dienes in the presence of [Rh(diene)(dppb)]$^+BF_4^-$ (dppb = bis-(diphenylphopsphino)butane).

Results and Discussion

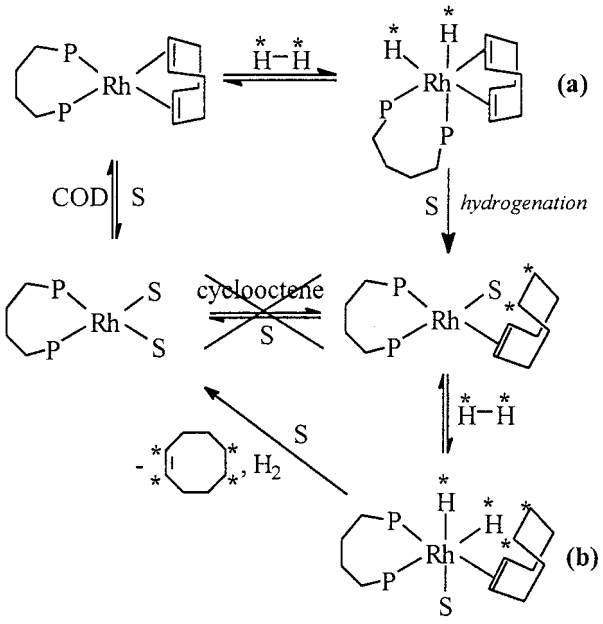
1. [Rh(COD)(dppb)]$^+$ (COD = Cyclooctadiene). An ALTADENA[22] experiment carried out on the [Rh(COD)(dppb)]$^+$/*para*-H_2 system showed two enhanced signals in the ^{1}H NMR spectrum (270 MHz, acetone-d_6, RT) (Figure 1a). The strong absorption peak at 5.80 ppm is assigned to the olefinic hydrogen atoms of free cyclooctene, and the emission one at 1.58 ppm corresponds to the overlap of aliphatic protons from both free cyclooctene and cycloctane (which results from the complete hydrogenation of COD). The *para*-H_2 enhancement is lost within few seconds. From the ^{1}H NMR spectrum reported in Figure 1b, one may note that the peak at 5.80 ppm has almost disappeared at the end of the PHIP effect, reflecting the very low concentration of free cyclooctene generated in the first stage of the COD hydrogenation.

As previously observed,[11,13] the negative signal of cyclooctene aliphatic protons (Figure 1a) is the result of the transfer of polarized hydrogens, necessarily at two equivalent positions, from non equivalent positions in an intermediate hydrido metal complex which thereafter eliminates cyclooctene (see Schemes 2 and 3 for possible mechanisms).

However, the observation of a strong enhancement (about 20 times) for the olefinic protons of free cyclooctene (5.80 ppm) is of great interest. This peak may be due (i) to the exchange of the *para*-H_2 hydrogen atoms with the olefinic protons of cyclooctene, as proposed by Bargon et al. in systems containing the same Rh catalyst with alkenic substrates (for example styrene, Scheme 1),[20,21] (ii) to magnetization transfer originating from the enhanced magnetization of the two aliphatic protons in the resulting cyclooctene molecule, or (iii) to magnetization transfer between the *para*-hydrogen hydrides and the olefinic protons of coordinated substrate in intermediate species such as those sketched in Chart 1.

To assess whether route (i) is that responsible for the observed behavior, [Rh(COD)(dppb)]$^+$ was reacted with deuterium gas under the same experimental conditions. In the resulting ^{2}H NMR spectra no signal was detected at 5.80 ppm, even after 30 min of accumulation and vigorous mixing of the sample, while the resonance at 1.58 ppm due to the aliphatic deuterons

SCHEME 2: Proposed 2-stages Mechanism for the Polarization Transfer from *para*-H_2 to Cyclooctene on the [Rh(COD)(dppb)]$^+$ Complex (Path 1))



SCHEME 3: Proposed Concerted Single-stage Mechanism for the Polarization Transfer from *para*-H_2 to Cyclooctene on the [Rh(COD)(dppb)]$^+$ Complex (path 2))

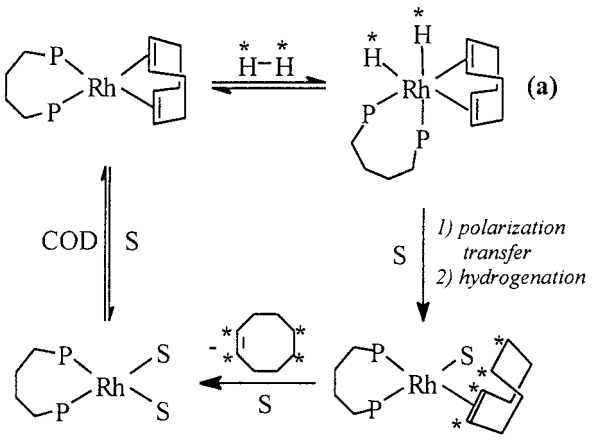
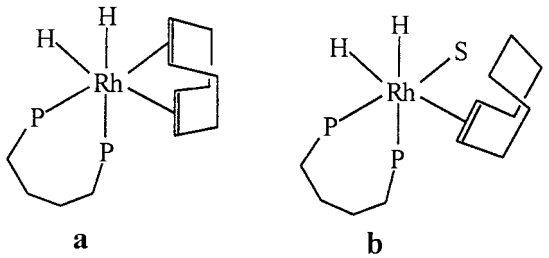


CHART 1: Possible Structures of the Intermediate Dihydride Species Responsible for the Polarization Transfer to Cyclooctene[a]



[a] Two possibilities may be envisaged: structure **a** represents the step which preceeds the hydrogenation of one of the two olefinic bonds in the coordinated cyclooctadiene whereas structure **b** represents a later stage, which is formed upon addition of a second *para*-H_2 molecule to the Rh(I) center once one of the olefinic moieties has been hydrogenated. S stands for solvent.

was clearly detected in the spectrum already after few runs. This result allows us to rule out the possibility that *para*-H_2 hydrogen atoms could have been exchanged into the olefinic positions of the cyclooctene molecule.

Thus, the enhancement of the olefinic resonance has to be associated with magnetization transfer. First, one may wonder about the possibility of polarization transfers by J coupling which, in an ALTADENA experiment, would occur at the initial stage, that is outside the magnet. As all nuclei become undistinguishable relative to their chemical shift, the Hamiltonian reduces to the *J* coupling terms, namely $H = \sum_{i<j} J_{ij}(I_x^i I_x^j + I_y^i I_y^j + I_z^i I_z^j)$. Suppose now that the hydrogenation process concerns the two sites *A* and *B* so that the state of the corresponding two spin system is described by $K(I_x^A I_x^B + I_y^A I_y^B + I_z^A I_z^B)$ where *K* is a factor standing for the enhanced polarization originating from *p*-H_2 (the same spin order is achieved along the three equivalent directions). In a general way, the evolution of a given quantity *G* is governed by $dG/dt = \sum_k a_k G_k$ where the G_k represent all quantities necessary to the description of the spin system; the coefficient a_k as well as the nature of G_k arise from the calculation of the commutator $[H,G]$. Let us assume that a spin *B* is *J*-coupled to *A* and let us look for a possible polarization transfer from *A* to *B* under the action of the Hamiltonian *H*; obviously, only the term $J_{AB}(I_x^A I_x^B + I_y^A I_y^B + I_z^A I_z^B)$ could be responsible for such a transfer. For instance, with $G \equiv I_z^B$, the relevant commutator yields $(I_x^A I_y^B - I_y^A I_x^B)$; because none of these quantities is present in the expression describing the spin system after *para*-H_2 hydrogenation, the possibility of any transfer toward *B* magnetization components is ruled out. Concerning a quantity such $I_z^A I_z^B$ (which could as well be a possible candidate for polarization transfer), the relevant commutator is simply zero. Therefore, we can definitely forget about transfers outside the magnet and thus under the sole *J*-coupling Hamiltonian.

Likewise, in the second part of the experiment, i.e., in the presence of a static magnetic field (even much weaker than that at the center of the magnet), since no special spin excitation is performed (one is just dealing here with a simple read pulse) and since magnetization is purely longitudinal prior to observation, transfers mediated by *J* couplings can be disregarded. In both cases they would anyway lead to an enhancement much greater than the one experimentally observed.

We are thus left with relaxation processes and more specifically cross- relaxation between aliphatic (H_4) and olefinic (H_1) protons in cyclooctene, or between the hydrides and the olefinic protons (H_1) in the intermediate complex, these processes being conceivable owing to the proximity of the two groups of protons (Chart 1). It has to be outlined that such a process is effective as far as specific longitudinal relaxation rates are not too large, otherwise they would kill cross-relaxation at its onset. To get more insight into the magnetization transfer mechanism, let us consider the Solomon equations for two spins *A* and *B* ($I_z^{A,B}$ being the longitudinal components of their magnetization, I_{eq} the magnetization at thermal equilibrium and $R_1^{A,B}$ their longitudinal relaxation rates). They are supposed to interact by dipolar coupling (of course modulated by molecular motions) leading to a cross-relaxation rate σ, actually proportional to r_{AB}^{-6} (r_{AB} being the internuclear distance). One has[23]

$$\frac{d}{dt} I_z^A = -R_1^A(I_z^A - I_{eq}) - \sigma(I_z^B - I_{eq})$$

$$\frac{d}{dt} I_z^B = -\sigma(I_z^A - I_{eq}) - R_1^B(I_z^B - I_{eq}) \qquad (1)$$

The matrix

$$\begin{pmatrix} -R_1^A & -\sigma \\ -\sigma & -R_1^B \end{pmatrix}$$

is called the relaxation matrix. Solomon equations can be generalized to larger spin systems implying relaxation matrices whose dimension is equal to the number of spins in the considered system.

Now, we shall perform an expansion up to second order in *t*, assuming that only spin *A* benefited from the *para*-H_2 polarization enhancement. We thus can write $I_z^A(0) = -KI_{eq}$ (*K* standing for the enhancement factor), $I_z^B(0) = I_{eq}$, and

$$I_z^B(t) \approx I_z^B(0) + t\left(\frac{d}{dt} I_z^B\right)_{t=0} + \frac{t^2}{2}\left(\frac{d^2}{dt^2} I_z^B\right)_{t=0}$$

as far as the evolution of the *B* longitudinal magnetization is concerned. Using the expressions given by eq 1, this yields

$$I_z^B(t) \approx \sigma(K+1) I_{eq}\left(t - \frac{R_1^A + R_1^B}{2} t^2\right) \qquad (2)$$

Although this expansion is of course valid only at short times, it tells us that a transfer (such a transfer is usually referred as nuclear Overhauser enhancement, NOE) leading to a *positive signal* can occur provided that the cross-relaxation rate σ (always positive in the case of small molecules in non viscous media) is not negligible and that the second term in t^2 (affected by a minus sign) does not compete with the first one (*t*). These conclusions are consistent with experimental observations (enhanced positive peak for olefinic protons) and with the intuitive predictions proposed above. Of course, at longer times (Figure 1b), cyclooctene appears with line intensities corresponding to thermal equilibrium.

Additional ALTADENA experiments under the same conditions were carried out at 90 and 400 MHz: the obtained spectra are reported in Figure 2. By comparing the intensity ratios between the signal at 5.8 ppm and the signal of the aromatic protons of the phosphine ligand, it is evident that there is a large inverse dependence of the intensity of the cyclooctene olefinic protons signal on the magnetic field strength.

How can route (ii) or route (iii) account for the observed behavior?

At a first glance the magnetization transfer in cyclooctene trough route (ii) would appear unlikely as relaxation rates of small molecules in a nonviscous medium are usually frequency independent. This is indeed confirmed by longitudinal relaxation measurements performed on cyclooctene (in solvent and temperature conditions as close as possible to those which prevailed in the ALTADENA experiments: $T_1(H_1) = 29.2$ s at 90 MHz and 28.0 s at 400 MHz; $T_1(H_{2,3,4}) = 11.5$ s at 90 MHz and 10.6 s at 400 MHz), these results indicate that a possible CSA (chemical shift anisotropy) contribution in the organic molecule is negligible (otherwise a variation proportional to the square of the measurement frequency would be observed). Therefore, if route (ii) is contributing to the observed enhancement in the olefinic resonance, we should look for another property which is field dependent. The only one which is left is chemical shift itself. At 90 and 270 MHz, resonances of protons 3 and 4 are degenerate and, as a consequence, it is impossible to distinguish these two spins, as far as polarization enhancements (arising from *para*-H_2) are concerned. In other words, any cross-relaxation effect from 4 to 3 cannot be detected. Conversely, at

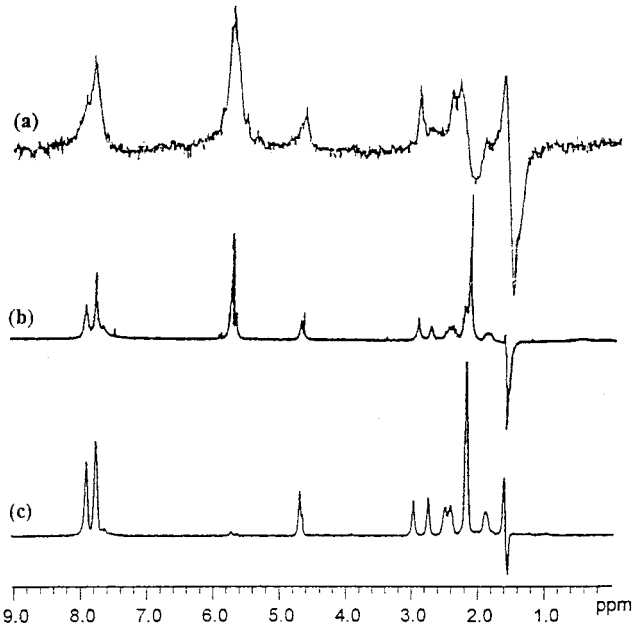


Figure 2. ^{1}H NMR spectra of the mixture [Rh(COD)(dppb)]$^+$/*para*-H_2 recorded 20 s after agitation of the sample (a) at 90 MHz, (b) at 270 MHz, and (c) at 400 MHz (acetone-d_6, RT).

400 MHz, resonances corresponding to protons 3 and 4 become distinct and cross-relaxation (nOe) from 4 to 3 can take place. It can be noticed that the H_4-H_3 distance (ca. 2.6 Å) is shorter than the H_4-H_1 distance (ca. 2.9 Å) thus making cross-relaxation transfers easier (it has to be reminded that the cross-relaxation rate σ_{ij} depends on $r_{H_iH_j}^{-6}$). It is evident that if the major part of H_4 magnetization has flowed, it is no longer available for H_1. Thus, the lack of a strong signal at 5.80 ppm in the 400 MHz spectrum could be explained by the fact that degeneracy of H_3 and H_4 resonances has been lifted. In fact, the above analysis is somewhat intuitive; more reliable conclusions would require the consideration of the full relaxation matrix.

The fact that polarization is transferred solely at the olefinic protons H_1 and not to the adjacent protons H_2, which would be closer to the propagation center according to this mechanism, seems to be better explained by a magnetization transfer occurring through route (iii), where the propagation center would be represented by the hydride ligands at the intermediate species. In fact, the changes observed upon varying the applied magnetic field strength could be explained on the basis of the CSA contribution to relaxation of the hydride ligands in the intermediate species (it has been shown for similar metal complexes that this contribution is not negligible[24]). At higher magnetic field strength this contribution would be greater and thus it would increase the value of R_1^A in eq 2, therefore causing a decrease in the longitudinal component of the olefinic protons magnetization I_z^B.

The polarization transfer from *para*-H_2 to cyclooctene olefinic protons through route (iii) is then dependent upon the lifetime of the intermediate hydride species and it may be envisaged to occur through one of the two alternative pathways depicted in Schemes 2 and 3. (1) After the addition of one *para*-H_2 molecule to form the coordinated cyclooctene moiety, there is the coordination of a second *para*-H_2 molecule at the coordinative vacancy of the Rh center: it is at this stage that magnetization transfer from hydrides to olefinic protons could take place (Scheme 2); (2) a "concerted" mechanism, in which both the magnetization transfer and the hydrogenation of the COD ligand

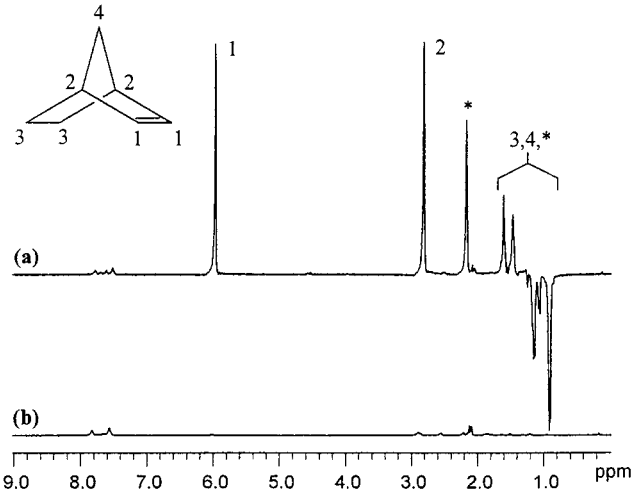


Figure 3. ^{1}H NMR spectra of the mixture [Rh(NBD)(dppb)]$^+$/*para*-H_2 recorded (a) 20 s after agitation of the sample and (b) after complete relaxation of the *para*-H_2 polarization (400 MHz, acetone-d_6, RT). The peaks marked with "*" are attributed to norbornane.

occur simultaneously, then involving only one *para*-H_2 and one COD molecule (Scheme 3). After the complete transformation of COD into cyclooctene no effect is detected on the cyclooctene olephinic signal, even after vigorously shaking the sample and the replacement of the *para*-H_2 atmosphere. Analogously, experiments carried out in the presence of free cyclooctene and other alkenes did not yield any enhancement in the olefinic signals of these molecules. On the basis of these observations one can rule out the occurrence of a reversible coordination of the mono-ene substrate at the bis hydridic Rh center.

Now, the differences in the field dependence of the aliphatic and olefinic resonances (it can be observed from Figure 2 that the intensity ratio between the two classes of protons is not maintained on going from low to high magnetic field) could be accounted for on the basis of the evolution of the longitudinal component of aliphatic proton magnetization, which, in accord with the notations of eqs 1 and 2, can be denoted by I_z^A (where A = hydride ligands) because these protons derive from the direct transfer of the hydride ligands on the organic substrate:

$$I_z^A(t) \approx I_{eq}\left[-K + R_1^A(K+1)t - \frac{(R_1^A)^2 + \sigma^2}{2}(K+1)t^2\right] \quad (3)$$

Since the dependence of I_z^A (eq 3) and I_z^B (eq 2) upon R_1^A and σ is quite different, it is not surprising that a different *para*-H_2 effect is detected on the two types of protons, even if the intermediate species involved in the magnetization transfer and in the hydrogenation reaction is the same.

2. [Rh(NBD)(dppb)]$^+$ (NBD = Norbornadiene). By reacting [Rh(NBD)(dppb)]$^+$ with *para*-H_2 under the same conditions as above, analogous results to those reported for the COD complex have been obtained. The ^{1}H NMR spectrum recorded at 270 MHz is reported in Figure 3. The signal at 5.93 ppm attributed to the double bond of free norbornene (derived from the monohydrogenation of NBD) is clearly highly polarized. Furthermore, polarization is observed also on the signals corresponding to H_2 (positive signal) and H_3 (negative signal), H_4 (positive signal) (see assignments in Figure 3).

Deuterium studies have shown that also in this case there is not direct hydrogen transfer in the double bond protons (H_1) of free norbornene, thus suggesting that magnetization transfer to these protons occurs as in the previous case.

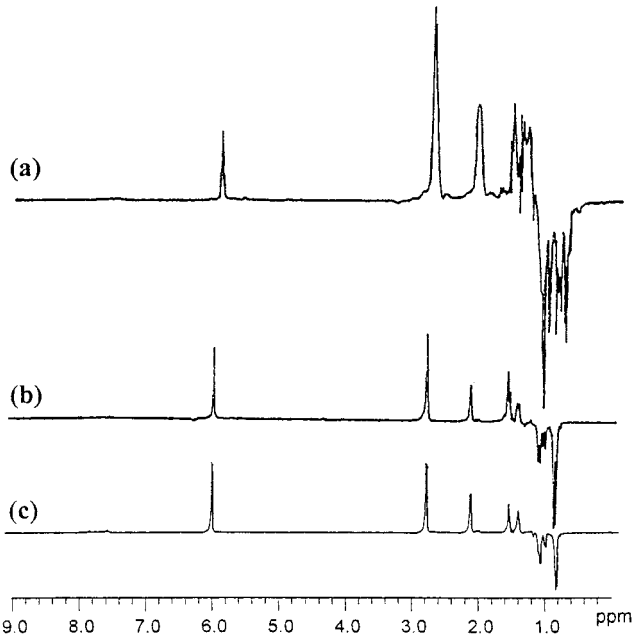


Figure 4. ^{1}H NMR spectra of the mixture [Rh(NBD)(dppb)]$^+$/*para*-H_2 recorded 20 s after agitation of the sample (a) at 90 MHz, (b) at 270 MHz, and (c) at 400 MHz (acetone-d_6, RT).

The main difference with respect to the COD case lies in the observation that also the resonance due to protons adjacent to the olefinic linkage is strongly enhanced. Experiments performed at different magnetic field strength (Figure 4) have shown that only the intensities of the signals attributed to H_2, H_3 and H_4 in the norbornene molecule are field-dependent. Furthermore, the H_2/H_3 ratio results unchanged in all the spectra, indicating that the most likely pathway which brings polarization on H_2 is the transfer from H_3 (derived from hydrogenation). On the other hand, the olefinic protons peak displays the same intensity on going from higher to lower magnetic field strength.

All these observations are indeed quite consistent with the interpretation based on nOe transfers from the hydride ligands to the olefinic protons of norbornene in the intermediate species, as in the COD case. The maintenance of the same intensity of the H_1 signals (while H_2, H_3, and H_4 vary with the applied field strength) can be taken as an evidence that the magnetization transfer from H_3 is not likely to occur, since if this was the case the same field dependence should be observed for all the norbornene protons signals intensities, even for the olefinic ones.

The nondependence of the norbornene olefinic protons resonance on the magnetic field strength could be due to different efficiency of the NOE between the hydridic and the olefinic protons of the bound alkene molecule with respect to the cyclooctene case. It may be possible that the norbornene molecule, which is less sterically demanding than cyclooctene, may be allowed to get closer to the hydride ligands. In this case the dipolar interaction between the hydrides and the olefinic protons would then be greater. Consequently, the CSA containing contributions would become less important with respect to the cyclooctene case and the field dependence of the signals intensities would become smaller, as observed. In other words, σ in eq 2 would be greater for the norbornene intermediate than for the cyclooctene one, rendering the CSA containing term $(R_1^A + R_1^B)$ still less competitive.

3. [Rh(diene)(dppb)]$^+$ (diene = COD, NBD) in the Presence of Free Dienes. As it has been noted above, the affinity of the [Rh(diene)(dppb)]$^+$ complexes toward monoalkenes is rather low as compared with the affinity toward dienes and this fact explains why no polarization can be transferred to monoalkenes in the reaction mixture.[14] However, the great tendency of dienes to bind to the Rh atom can be exploited to polarize the proton resonances of free dienes, in an analogous way to that depicted above (Scheme 2) for bound COD and NBD. This would be very useful for further applications, since it would be the way to transfer polarization in a continuous way to target molecules.

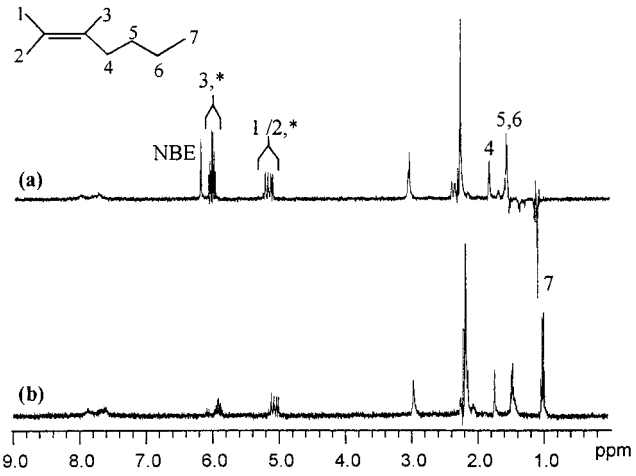


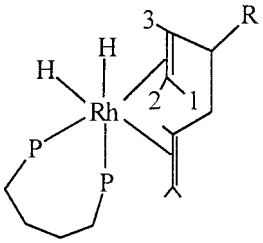
Figure 5. ^{1}H NMR spectra of the mixture [Rh(NBD)(dppb)]$^+$/1,5-hexadiene/*para*-H_2 recorded (a) 20 s after agitation of the sample and (b) after complete relaxation of the *para*-H_2 polarization (400 MHz, acetone-d_6, room temperature). NBE = free norbornene, "*" = unreacted 1,5-hexadiene, the signal at ca. 3 ppm is due to water.

A series of experiments using both the [Rh(COD)(dppb)]$^+$ and [Rh(NBD)(dppb)]$^+$ complexes in the presence of free dienes (COD, NBD, 1,5-hexadien-3-ol, 1,5-hexadiene) and *para*-H_2 were then carried out. In all cases polarization was observed on the double bonds in the corresponding monoalkenes even after several seconds (about 180 s). By successive shakings of the samples (in order to dissolve "novel" *para*-H_2 in solution) the effects on the olefinic protons of the free monoalkenes can be observed until all the *para*-H_2 has been consumed. This indicates that the continuous interaction of the dienes with the metallic center induces magnetization transfers, even after the complete conversion of the originally bound COD or NBD molecule.

In the cases of 1,5 hexadiene and 1,5-hexadien-3-ol (in Figure 5 the spectra of the former molecule are reported as an example), negative polarization is observed on the methyl group deriving from the hydrogenation of one of the two double bonds, while, as in the COD and NBD cases, positive enhancement is observed on the olefinic region of the spectra. No effect is detected on the resonances attributed to the intermediate CH_2 protons (H_4 and H_5/H_6 for 1,5-hexadiene). This allows one to state that also in this case a magnetization transfer via nOe occurring from the hydride ligands in the intermediate complex is more likely than that from the aliphatic protons in the hydrogenated product.

Furthermore, double bond polarization is observed only on the olefinic proton H_3, and not on H_1/H_2. The observed "selective magnetization transfer" on H_3 can be explained on the basis of the geometry of the coordinated diene in the intermediate species: it is reasonable to suppose that the less crowded part of the double bonds (i.e., the moiety containing H_1 and H_2) can more easily be turned toward the phosphinic ligand, while the most crowded moiety, i.e., that containing H_3, can be turned toward the hydride ligands, as depicted in Chart 2. The latter protons would then be closer to the polarized

CHART 2: Proposed Structure of the Dihydride Intermediate Species Involved in the Polarization Transfer to 1,5-Hexadiene and 1,5-Hexadien-3-ol



R = H, OH

hydrides, and as a consequence could more easily be polarized themselves by nOe.

Conclusions

Through the present work, we have demonstrated that the observed enhanced absorption signals in the NMR spectra of alkenes derived from hydrogenation of dienes on a Rh catalyst can be explained on the basis of NOE transfers which are possible both within a *para*-H_2 hydrogenated substrate and within metal-hydrido complexes. A similar effect has been suggested by Eisenberg et al. as responsible for ^{31}P signals enhancements in Ir complexes.[25] Further quantitative studies would imply the determination of the relaxation matrix (for instance by classical NOESY measurements [23] performed on the considered alkene in conditions similar to those of the ALTADENA experiments) and the analysis of build-up curves (obtained by recording spectra at different times after the introduction of the sample in the NMR probe).

The NOE transfer in metal complexes can be taken as a starting point for the development of magnetization transfer systems based on the reversible interaction of a target molecule to be polarized (for further applications, such as MRI) and *para*-H_2 on a metal center.

Experimental Section

Cyclooctadiene, norbornadiene, 1,5-hexadien-3-ol, 1,5-hexadiene, and $[Rh(diene)(dppb)]^+BF_4^-$ (dppb = bis(diphenylphosphino)butane; diene = cyclooctadiene (COD); norbornadiene (NBD)) were purchased from Aldrich Chemicals and used withouth further purification. *para*-H_2 (50% enriched in the *para* form) was prepared according to the published method.[12,11]

In a typical ALTADENA [22] experiment, 3 mg of catalyst were dissolved in 0.6 mL of acetone-d_6 in a 5 mm resealable NMR tube having a total volume of 3 mL. For the experiments carried out in the presence of free dienes, an excess of diene (about 5:1 with respect to the catalyst) was added in the solution. The solution was frozen, the air was pumped-off, and about 1 atm of *para*-H_2 was added. The sample was then warmed to room temperature, vigorously shaken, and introduced into the spectrometer. The first spectrum was recorded 20 s after shaking of the sample.

^1H NMR spectra were recorded on JEOL EX-400, JEOL GX-270, and JEOL EX-90 instruments, operating at 399.65, 270.05, and 90.0 MHz, respectively. One scan spectra (45° pulse) were acquired in each experiment.

^2H NMR spectra were recorded on the JEOL EX-400 spectrometer, operating at 61.64 MHz. 90° pulses and repetition times of 1.0 s were used for acquiring these spectra.

T_1 measurements were carried out by using the inversion recovery pulse sequence.

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