

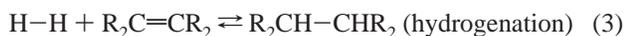
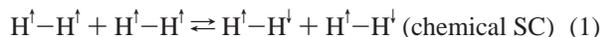
Bridging the Gap between Homogeneous and Heterogeneous Catalysis: Ortho/Para H₂ Conversion, Hydrogen Isotope Scrambling, and Hydrogenation of Olefins by Ir(CO)Cl(PPh₃)₂

Jochen Matthes,^{†,‡} Tal Pery,[†] Stephan Gründemann,[†] Gerd Buntkowsky,[†] Sylviane Sabo-Etienne,[‡] Bruno Chaudret,[‡] and Hans-Heinrich Limbach^{*,†}

Institute of Chemistry, Freie Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany, and Laboratoire de Chimie de Coordination du CNRS 205, Route de Narbonne, F-31077 Toulouse-Cedex 4, France

Received April 26, 2004; E-mail: limbach@chemie.fu-berlin.de

The application of concepts of homogeneous catalysis to heterogeneous catalysis and vice versa constitutes an area of current interest. Using the example of Vaska's catalyst Ir(CO)Cl(PPh₃)₂ (**1**),¹ we show that compounds that catalyze the chemical ortho-para nuclear spin conversion (SC) of dihydrogen (eq 1),² the associated isotope scrambling (IS) reaction of dihydrogen isotopologs (eq 2),³ and the hydrogenation of unsaturated compounds in organic solvents⁴ (eq 3) can do so also in the solid state. Our findings shed new light on the mechanisms of these reactions.



Initially, we wanted to study the magnetic SC (eq 4) of single dihydrogen pairs induced by binding to a transition metal. This binding increases the H-H distance and reduces the energy difference ΔE between the ortho and para states.^{5,6} Eventually, we expected magnetic SC to take place in the absence of an external magnetic field, induced by dipolar or scalar nuclear magnetic interactions.⁷ However, magnetic SC in dihydrogen complexes seems to be masked by chemical SC and IS. For example, polycrystalline W(CO)₃(P'Pr₃)₂(H₂) catalyzes IS,^{5b} and the solid HD complex disproportionates into a statistical mixture of the H₂, HD, and D₂ isotopologs. Therefore, our attention turned to transition metal complexes that are able to form dihydride complexes containing two inequivalent scalar coupled hydrogen sites, where ΔE is very small. The ¹H NMR signals of these sites exhibit just after the incorporation of *p*-H₂ a *para*-hydrogen-induced polarization (PHIP), a phenomenon that has been described by Eisenberg et al.⁸ and Bowers et al.⁹ PHIP has been used for the elucidation of the mechanisms of hydrogenation reactions catalyzed by transition metal catalysts in liquid solution.¹⁰ In fact, PHIP is the result of a magnetic SC, where the nuclear interaction involved is the frequency shift difference $\Delta\nu$ between the two hydrogen sites, induced by an external magnetic field. As has been shown by some of us,¹¹ $\Delta\nu$ has to be on the order of ΔE or smaller for magnetic SC to take place.

On the other hand, in the experiments performed by Eisenberg et al.,⁸ which led to the discovery of PHIP, *p*-H₂ had been formed in the absence of a magnetic field in frozen solutions of transition metal dihydride precursors in contact with dihydrogen at 77 K. After warming up to room temperature, the *p*-H₂ was detected via the PHIP phenomenon. As the mechanism of the low-temperature SC was unexplored to date, we performed the following experiments

in which both SC and IS could be detected at the same time. In experiment I, a saturated solution of **1** in C₆D₆ was frozen and kept at 77 K in the dark, in order to prevent photochemical reactions, for 5 days in an NMR tube equipped with a Teflon needle valve under a gaseous 1:1 mixture of H₂ and D₂ (each 400 mbar, 298 K). The addition of dihydrogen to **1** was then followed by ¹H NMR at 298 K for about 1 h. For comparison, experiment II was performed in a similar way but without solvent, i.e., with polycrystalline **1**. After 31 days at 77 K, the resulting gas mixture was transferred by vacuum methods into an NMR tube containing in the lower part a degassed, frozen solution of **1** in C₆D₆. The analysis was then done as in experiment I.

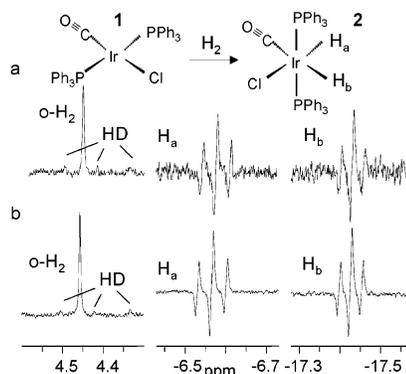


Figure 1. 500 MHz ¹H NMR spectra at 298 K of **1** dissolved in C₆D₆ in the presence of dihydrogen mixtures. (a) Experiment I: 400 mbar H₂ and 400 mbar D₂ were stored over a frozen solution of **1** in C₆D₆ for 5 days at 77 K prior to the NMR experiment. (b) Experiment II: 400 mbar H₂ and 400 mbar D₂ were stored over polycrystalline **1** for 31 days at 77 K and transferred into an NMR tube containing a frozen solution of **1** in C₆D₆. The spectra were taken after thawing.

The oxidative addition of H₂ to **1** leading to IrH₂(CO)Cl(PPh₃)₂ (**2**) does not occur at 77 K but starts at room temperature and is complete after about 1 h. The partial room-temperature ¹H NMR spectra of the samples 2 min after thawing are depicted in Figure 1. The two hydride sites of **2** give rise to triplets of doublets ($J_{\text{HP}} = 12$ Hz; $J_{\text{HH}} = 4.5$ Hz) at -6.6 and -17.35 ppm; moreover, they exhibit the well-known PHIP pattern with alternating enhanced positive and negative signal components as was described for this system by Duckett et al.¹² Around 4.45 ppm, we observe not only *o*-H₂ but also a signal for HD giving rise to the well-known triplet ($J_{\text{HD}} = 43$ Hz). These observations show that in the frozen solution and in the polycrystalline material, not only *p*-H₂ but also HD is formed. Control experiments performed without the catalyst showed no *p*-H₂ enrichment and no formation of HD. Although a quantitative determination of the relative rates of both processes was beyond the scope of this study, we can now conclude that a substantial part of *p*-H₂ is generated in the solid state by chemical SC, rather

[†] Freie Universität Berlin.

[‡] Laboratoire de Chimie de Coordination.

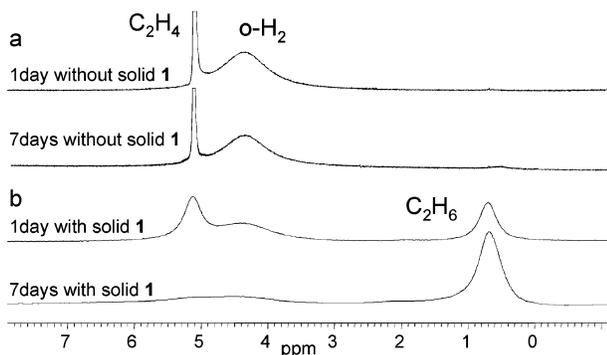
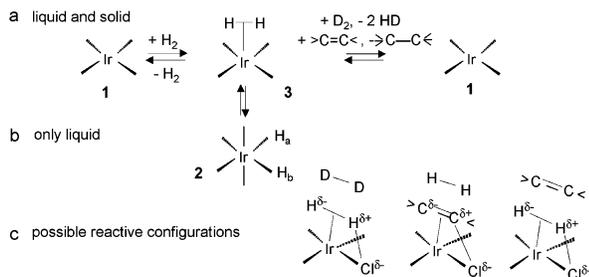


Figure 2. 500 MHz gas-phase ^1H NMR spectrum of H_2 and ethylene in an NMR tube that was (a) empty and (b) filled with $\text{Ir}(\text{Cl})\text{CO}(\text{PPh}_3)_2$ crystalline powder. Measurements were taken at 298 K after storage for x days at 298 K in the dark.

Chart 1



than by magnetic SC. The latter dominates, however, in the liquid state in the presence of a magnetic field.

This result was surprising for us because magnetic SC requires a strong interaction of only one dihydrogen molecule with a transition metal catalyst, whereas for chemical SC, at least two dihydrogen molecules are required. By contrast, in the case of Kubas dihydrogen complex^{5b} only one additional dihydrogen molecule is required for IS to occur. It was also surprising that dihydrogen could penetrate easily the frozen solid solutions and access the catalyst. This problem incited us to study the nature of the frozen solutions of **1** in benzene by optical microscopy at 258 K. We observed a microscopic phase separation into irregular formed particles of **1** and solid benzene and pores with typical in the 20 μm range. Thus, it is conceivable that dihydrogen can penetrate the frozen mixture via the pores and interact with small particles of **1**, in a similar way as with the polycrystalline samples. In the latter case, however, the particles are larger and the surface area is smaller; hence, the conversion efficiency is smaller.

Encouraged by these results, we checked whether the crystallites of **1** are also active catalysts for the hydrogenation of larger molecules such as alkenes (eq 3). For this purpose we stored a 1:2 mixture of ethene and H_2 (300 mbar C_2H_4 and 600 mbar H_2 , 298 K) in (a) an empty NMR tube and (b) in an NMR tube filled with polycrystalline **1**. The resulting gas mixtures were analyzed by gas-phase ^1H NMR (Figure 2). Without catalyst, the gas mixture did not react within 7 days; only a sharp peak of ethene is detected at 5.15 ppm and a broad one for $o\text{-H}_2$ at 4.45 ppm. However, when the mixture is stored over polycrystalline **1**, a sharp ethane peak appears at 0.83 ppm. The ethene peak is gone after 7 days.

All results are summarized in Chart 1. In the liquid phase, **1** reacts with dihydrogen to **2**, presumably via a (stretched)⁵ dihydrogen complex **3**, which also probably catalyzes the reactions of eq 1–3. In the solid state, the reaction of **1** to **2** is inhibited because it would require a major ligand reorientation. On the other hand, the formation of **3** may not require a ligand orientation and may,

therefore, take place either in the bulk solid or only in the crystal surfaces. It is unlikely that a purely magnetic spin conversion can take place in **3**.⁷

The details of the reaction pathways are not known, but they could involve species similar to those shown in Chart 1c. It is, however, natural to assume that **3** is also the active species of the hydrogenation of ethene. Evidence for a similar mechanism that excludes a direct binding of the substrate to the metal center was provided by Noyori et al.^{13a} and by Morris et al.^{13b} for the case of hydrogenation of ketones by Ru complexes. Currently, we are exploring the various mechanisms in more detail, both theoretically and experimentally.

We conclude that exploring both the liquid- and solid-state activity of a catalyst may help to bridge the gap between the homogeneous and heterogeneous catalysis and to provide additional information about the reaction mechanisms.

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Supporting Information Available: Experimental details and additional NMR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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