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

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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), † we show that compounds that catalyze the chemical ortho-para nuclear spin conversion (SC) of dihydrogen (eq 1), ‡ the associated isotope scrambling (IS) reaction of dihydrogen isotopologs (eq 2), ‡ and the hydrogenation of unsaturated compounds in organic solvents ‡ (eq 3) can do so also in the solid state. Our findings shed new light on the mechanisms of these reactions.

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\begin{align*}
\text{H}^1-\text{H}^1 + \text{H}^1-\text{H}^1 &\rightleftharpoons \text{H}^1-\text{H}^1 + \text{H}^1-\text{H}^1 \quad \text{(chemical SC)} \quad (1) \\
\text{H}_2 + \text{D}_2 &\rightleftharpoons 2\text{HD} \quad \text{(IS)} \quad (2) \\
\text{H}^1-\text{H}^1 + \text{R}_2\text{C} \rightleftharpoons \text{R}_2\text{CH} + \text{CHR}_2 \quad \text{(hydrogenation)} \quad (3) \\
\text{H}^1-\text{H}^1 &\rightleftharpoons \text{H}^1-\text{H}^1 \quad \text{(magnetic SC)} \quad (4)
\end{align*}
\]

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 \(\Delta E\) between the ortho and para states. §, ‡ Eventually, we expected magnetic SC to take place in the absence of an external magnetic field, induced by dipolar or scalar nuclear magnetic interactions. § However, magnetic SC in dihydrogen complexes seems to be masked by chemical SC and IS. For example, polycrystalline W(CO)₅(PPh₃)₂(H₂) catalyzes IS, ‡ and the solid HD complex disproportionates into a statistical mixture of the H₃, 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 \(\Delta E\) is very small. The \(^1\text{H}\) 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. § and Bowers et al. § PHIP has been used for the elucidation of the mechanisms of hydrogenation reactions catalyzed by transition metal catalysts in liquid solution. ‡ 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, † † \(\Delta \nu\) has to be on the order of \(\Delta E\) or smaller for magnetic SC to take place.

On the other hand, in the experiments performed by Eisenberg et al. ‡ 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 \(^1\text{H}\) 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.

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 \(^1\text{H}\) 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 (\(J_{\text{HH}} = 12\) Hz; \(J_{\text{HP}} = 4.5\) 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 Dukett et al. ‡ 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 than by magnetic SC.

Figure 1. 500 MHz \(^1\text{H}\) 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.

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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 transition metal catalyst, whereas for chemical SC, at least two states in the presence of a magnetic field.

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

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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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1998, 120, 709. 7. Preliminary model calculations show that a dipolar magnetic SC is operative in the solid state and a scalar magnetic SC in the liquid state when δE is reduced to the order of the magnetic interactions involved. For that purpose, the H–H distances need to be increased to more than about 1.5 Å.

