Acceptorless, intramolecular, alkyl dehydrogenation in the solid-state in a rhodium phosphine complex; reversible uptake of three equivalents of H_2 per molecule

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Addition of H_2 to the phosphine alkene ligated complex [Rh(dppe)($PCyp_2Cyp'$)][BAr^F_4] **1** (Cyp = cyclo-C_5H_9; Cyp′ = cyclo-C_5H_7, Ar^F = 3,5-$(CF_3)_2C_6H_3$) in the solid state results in hydrogenation of the alkene and uptake of two further equivalents of H_2 to afford the dihydride–dihydrogen complex [Rh(dppe)($PCyp_3$)$(H)_2(\eta^2\text{-}H_2)$][BAr^F_4] **2**. Placing **2** under a vacuum or argon results in sequential loss of H_2 and dehydrogenation of one of the cyclopentyl rings to reform **1**. The hydrogenation–dehydrogenation cycle has been repeated 5 times without apparent degradation and has been followed by solid-state $^{31}P\{^1H\}$ NMR spectroscopy. Intermediates on this process have been trapped using acetonitrile to give stable complexes that have been characterised in solution. We have previously shown that this hydrogenation–dehydrogenation process also happens in the solution-state; and evidence is presented that shows that, apart from a subtle difference, the same overall transformation occurs in the solid-state.

Introduction

The selective activation of C–H bonds in hydrocarbons has been a long-standing topic of interest.[1,2] Transition metal catalyzed alkane dehydrogenation to afford the corresponding olefin is particularly interesting as it delivers valuable unsaturated functionality. Although many dehydrogenations require a sacrificial hydrogen acceptor,[3] "acceptorless" dehydrogenation using transition metal catalysts has been achieved.[4] As well as this synthetic utility, the dehydrogenation of alkanes,[5] or alkane analogs such as ammonia boranes,[6] also represents a possible vector for the storage and transportation of H_2, which is of current interest due to the potential use of hydrogen as an energy carrier.[7] Many of these elegant systems, however, are not as yet truly reversible, or require forcing conditions (heat) and only work in solution. Of interest, then, would be a system that performed this transformation reversibly at ambient, or near ambient, conditions in the solid-state. We report here such a system, that operates by a reversible acceptorless alkyl dehydrogenation in the solid-state to store and release up to three equivalents of H_2 per cycle.

We have recently reported the remarkably quick acceptorless dehydrogenation of one alkyl ring of *tris*-cyclopentylphosphine ($PCyp_3$) in the complex [Rh(dppe)Cl($PCyp_3$)] on addition of Na[BAr^F_4], to afford [Rh(dppe)($PCyp_2Cyp'$)][BAr^F_4] **1** in quantitative yield (Scheme 1, Ar^F = 3,5-$(CF_3)_2C_6H_3$).[8,9] This generates a hybrid phosphine–olefin ligand on a square planar Rh(I) centre. Addition of H_2 to **1** in CH_2Cl_2 solution results in hydrogenation of the alkene and the formation of the dihydrogen–dihydride complex **2**, [Rh(dppe)($PCyp_3$)$(\eta^2\text{-}H_2)(H_2)$][BAr^F_4]. This reaction is reversible, and placing **2** under a vacuum relatively rapidly (~1 h) regenerates **1**. Intermediates in this process have been observed spectroscopically and also studied using computational methods.[9] We now report that these reversible hydrogenation–dehydrogenation reactions also occur in the solid-state by solid–gas reactions. This represents not only a relatively rare example of an organometallic solid–gas reaction with small molecules [10–13] but also, as far as we are aware, the first example of reversible and acceptorless alkyl dehydrogenation to be reported in the solid-state. Alkene hydrogenation[11,14–16] and C–H activation[16,17] (an early mechanistic step in alkane dehydrogenation[2]) have been described in the solid-state and in one case dehydrogenation of cyclopentene has also been reported, although a hydrogen acceptor is required and the reaction was not reported to be reversible.[11]

Results and discussion

Addition of H_2 to light orange powder **1** at just above room temperature (40 °C) results in a subtle change in color to very pale yellow. This change can be followed spectroscopically by $^{31}P\{^1H\}$ solid-state NMR (SSNMR) spectroscopy (Scheme 2 and Fig. 1), which shows a change consistent with the complete conversion of **1** to a new complex. Although we were not successful in using ^1H SSNMR to resolve a bound dihydrogen ligand,[18] rapid vacuum transfer of CD_2Cl_2 at 78 K onto the pale yellow solid gave solution $^{31}P\{^1H\}$ and ^1H NMR spectra (at 180 K) that showed a ~1 : 1 mixture of [Rh(dppe)($PCyp_3$)$(\eta^2\text{-}H_2)(H_2)$][BAr^F_4] **2** and [Rh(dppe)($PCyp_3$)(L)(H_2)][BAr^F_4] **3**, the latter of which we have previously characterized as being a dihydride complex with a weakly bound ligand (C–H agostic or solvent) in the sixth coordination site.[9] We have demonstrated previously that the bound dihydrogen ligand in **2** is sufficiently labile so that it is easily lost in

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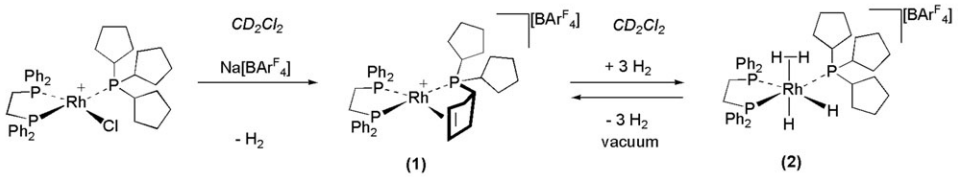
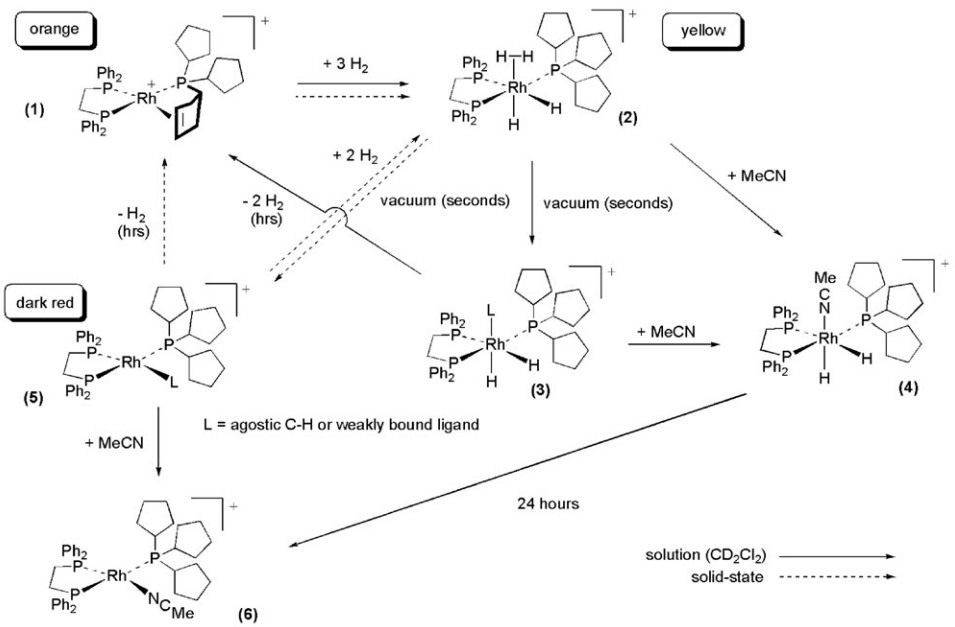


Scheme 1

solution under an Ar atmosphere at room temperature to form **3**,[9] meaning that we cannot definitively state whether **2** is formed exclusively in the solid-state or a mixture of **2** and **3** is formed. However, the overall close similarities between solution and solid state reactivity coupled with the observation that in the solid-state **2** loses H_2 to form a product *other* than **3** (*vide infra*), suggests that **2** is most likely formed exclusively, some of which then loses H_2 to form **3** on dissolving in CD_2Cl_2. Vacuum transfer of CD_2Cl_2 spiked with MeCN onto the yellow solid affords the acetonitrile adduct [Rh(dppe)-$(PCyp_3)$(NCMe)H_2][BAr^F_4] **4** as the only product. This mirrors the solution chemistry which shows that addition of MeCN to either **2** or **3** gives **4** cleanly.[9] The formation of labile dihydrogen complexes in the solid-state from hydrogenation of a bound alkene has been reported previously.[12,14]

Placing the pale yellow, "hydrogen charged", solid under a vacuum at room temperature results in a very rapid (seconds) darkening to deep red. This same transformation can be effected on replacing the H_2 atmosphere by flushing Ar over the solid. A slower (1 h) return to the pale orange of the starting material occurs either under vacuum or argon (as monitored by $^{31}P\{^1H\}$ SSNMR and solution NMR spectroscopies). The $^{31}P\{^1H\}$ SSNMR of the fully-cycled material show that **1** is returned unchanged, and the cycle can be repeated (five times) with no appreciable decomposition. Addition of H_2 to the red solid immediately regenerates the yellow powder which analyses by solution $^{31}P\{^1H\}$ NMR spectroscopy for **2** (along with **3** as observed previously). We have not been able to obtain a SSNMR of the red intermediate in the pure state, but monitoring the gradual loss of H_2 in the NMR probe from **2** shows the growth in and disappearance of new peaks at $\delta \sim 79$ and $\delta \sim 38$ ppm, which we assign to this intermediate complex, with the concomitant increase in the signals due to the dehydrogenated product **1** (Fig. 1). These peaks correlate reasonably well with those observed in solution for the red intermediate species (*vide infra*).

Solution trapping experiments suggest the identity of this dark red intermediate present in the solid-state. Vacuum transfer of CD_2Cl_2 onto the red solid results in a very broad room temperature solution $^{31}P\{^1H\}$ NMR spectrum suggesting a dynamic process (Fig. 2). Cooling to 200 K arrests this processes and, still broad, signals are observed at $\delta \sim 74$, 62 and 23 that demonstrate a new product has been formed, which we assign to [Rh(dppe)$PCyp_3$(L)][BAr^F_4] (L = agostic C–H, solvent or adventitious water) **5**. The hydride region of the ^1H NMR spectrum at low temperature is featureless showing that loss of the hydride ligands has occurred. The alkene region (δ 6.0–3.5) is also featureless, demonstrating that dehydrogenation of the $PCyp_3$ ligand has not occurred. Solutions of **5** slowly return to give **1** on standing at room



Scheme 2 Diagram showing the relationship between the final products and intermediates *observed* during the hydrogenation–dehydrogenation cycle in solution and the solid-state. Solid arrows indicate reactions in CD_2Cl_2 solution, some of which have been previously reported.[9] Dashed arrows show the solid-state reactions. This diagram makes no comment on the detailed mechanistic steps and only connects observed complexes. For example in solution **3** to **1** most likely proceeds through the intermediacy of **5**, which is not observed.

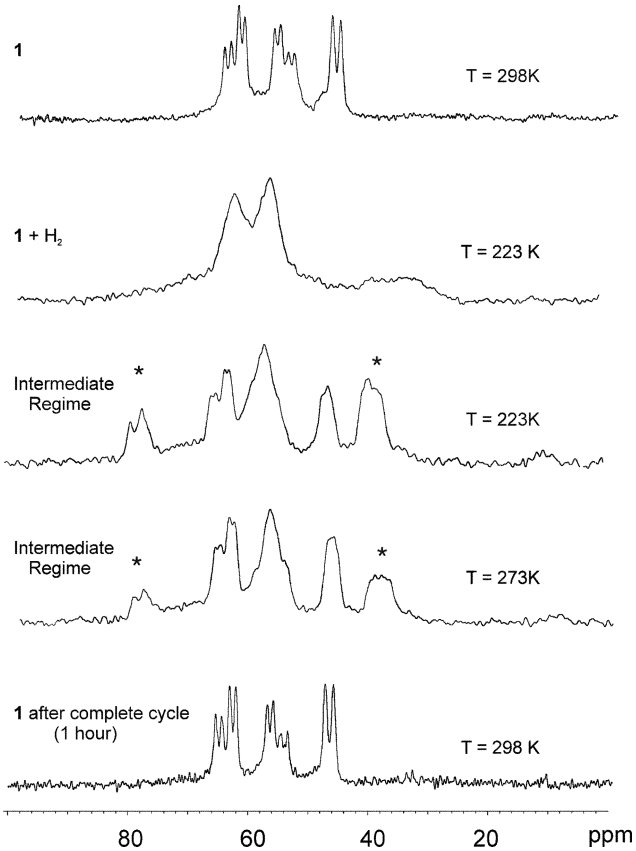


Fig. 1 Solid state $^{31}P\{^{1}H\}$ NMR (121.4 MHz) spectra of (a) **1**, (b) **1** + H_2 (*i.e.* complex **2**), (c, d) the intermediate regime demonstrating gradual H_2 loss from **2**, and (e) complex **1** after a complete cycle. * marks the peaks assigned to the intermediate species. The spin rate for all spectra was *ca.* 8000 Hz. Low temperature (223 K) used in an attempt to reduce the H_2 loss from complex **2**.

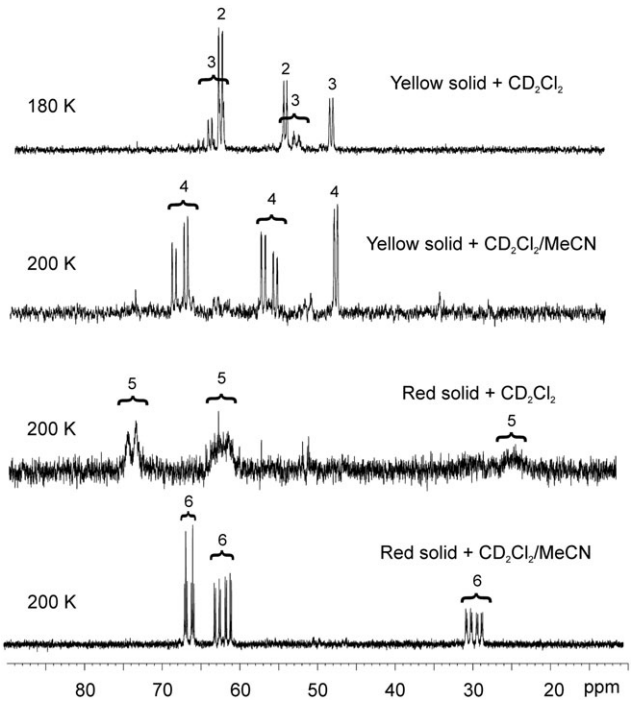


Fig. 2 $^{31}P\{^{1}H\}$ NMR (202.5 MHz) spectra of yellow and red solids after addition of CD_2Cl_2 or CD_2Cl_2/MeCN. Complex **2** (top spectrum) displays a tightly coupled ABMX coupling pattern and the outer AB lines are of low intensity. See ref. 9 for more details.

temperature. Vacuum transfer of CD_2Cl_2/MeCN to the deep red intermediate in the solid-state gives [Rh(dppe)$PCyp_3$(NCMe)][BAr^F_4] **6**, with no **4** observed. The same product is observed by addition of MeCN to a CD_2Cl_2 solution of **5** or slow (24 h) loss of H_2 from **4**.[9] No hydride signals were observed in the high field region. As complex **6** would result from addition of MeCN to a complex such as [Rh(dppe)$PCyp_3$(L)][BAr^F_4] **5** we suggest that placing **2** under vacuum results in the loss of 2 equivalents of H_2 in the solid-state to give **5**. This is in contrast to solution experiments that show that the dihydride **3** is initially formed on application of a vacuum to **2**.[9] Both solution and solid-state processes eventually give **1**—the dehydrogenated product. Thus although the solid-state and solution experiments follow the same overall transformation, they differ in the nature of the "low-hydride" intermediates that are observed (**5** *versus* **3**, respectively). Although the reasons for this are not completely clear at the present time we speculate that the structural change associated with stabilizing the vacant site in **3** is energetically less favorable in the solid state than for **5**. Changes between solution and solid-state reactivity with regard to hydrogen addition/ligand reorientation[13] and selectivity[19] have been noted previously.

In conclusion we have demonstrated that a remarkably undemanding reversible acceptorless dehydrogenation of a cyclic alkane aids the storage and release of up to 3 equivalents of H_2 per molecule occurs in the solid-state. Although this overall would result in a modest H_2 storage uptake and release of 0.35% (w/w), which is clearly impractical for mobile applications,[7] that this process occurs in the solid-state suggests that it might offer new opportunities in this technologically important area. Very recently a similar, solution only, process has been reported using $RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$ that stores 1.7% H_2 but this requires an acceptor (ethene) to promote transfer hydrogenation.[20]

Experimental

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk-line and glove-box techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. CD_2Cl_2 was distilled under vacuum from CaH_2 and stored over 3 Å molecular sieves. [Rh(dppe)($PCyp_2Cyp'$)][BAr^F_4] **1** was prepared by a published literature method.[8,9] Complexes **2**, **3**, **4** and **6** have previously been prepared.[9] ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ solution NMR spectra were recorded on Bruker Avance 400 MHz and Bruker Avance 500 MHz spectrometers. Residual protio solvent was used as the reference for ^{1}H NMR spectra (CD_2Cl_2: δ = 5.33). $^{13}C\{^{1}H\}$ spectra were referenced to the perdeuterio solvent signal. $^{31}P\{^{1}H\}$ spectra were referenced against 85% H_3PO_4 (external). $^{31}P\{^{1}H\}$ Solid State NMR spectra were recorded on a Varian Unity Inova spectrometer with a 4 mm rotor (o.d.) and MAS probe. Operating

frequency (121.4 MHz for ^{31}P). Spectra were recorded using cross polarization experiments and referenced against 85% H_3PO_4 for ^{31}P. Contact time = 1 ms, recycle delay = 10 s. Chemical shifts are quoted in ppm. Coupling constants are quoted in Hz.

Solid state NMR spectra for [(dppe)Rh(PCyp$_2$Cyp′)][BAr$^F_4$] (1)

$^{31}P\{^1H\}$ NMR (121.4 MHz, 298 K): δ 66.02 [dd, J(PP) 285 Hz, J(RhP) 120 Hz], 57.77 [dd, J(PP) 285 Hz, J(RhP) 115 Hz], 49.23 ppm [d, J(RhP) 159 Hz].

Preparation of [(dppe)(PCyp$_3$)Rh(η^2-H$_2$)(H)$_2$][BAr$^F_4$] (2) in the solid state

For solid state NMR. Finely powdered [(dppe)Rh(PCyp$_2$Cyp′)][BAr$^F_4$] (**1**) (30 mg, 1.87×10^{-2} mmol) was loaded into a 4 mm rotor (o.d.) which was then placed inside a J. Young's flask. The whole assembly was hydrogenated under 4 atm (298/77 = 3.8) at 40 °C overnight to give **2** as a very pale yellow solid. The rotor was stoppered with a close fitting plug, removed from the flask, and immediately put into an NMR spectrometer at low temperature (223 K) in an attempt to reduce the loss of H_2 from **2**. $^{31}P\{^1H\}$ NMR spectra were recorded over a 1 h period with slow warming to 298 K, this resulted in spectra consistent with complete conversion of **1** to **2**, the observation of an intermediate (**5**) and the recovery of complex **1**.

Solution trapping experiments. Finely powdered [(dppe)Rh(PCyp$_2$Cyp′)][BAr$^F_4$] (**1**) (5 mg, 3.13×10^{-3} mmol) was hydrogenated at ~4 atm H_2 pressure (298 K/77 K = 3.8) and heated at 40 °C overnight to give **2** as a very pale yellow solid. CD_2Cl_2 was vacuum transferred (at 77 K) into a sample of the pale yellow solid and the resulting solution was characterised by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy at 180 K, giving spectra fully consistent with a mixture of **2** and **3** in a 1 : 1 ratio.[9] Vacuum transfer of CD_2Cl_2/MeCN into a sample of the yellow solid gave spectra consistent with **4**[9] as the only product.

Preparation of [(dppe) Rh(PCyp$_3$)(L)][BAr$^F_4$] (5) (L = agostic interaction, vacant site or weakly bound adventitious ligand) in the solid state

A solid sample of **2** (5 mg, 3.11×10^{-3} mmol) was placed under vacuum at 298 K for 5 seconds giving a deep red solid. CD_2Cl_2 was vacuum transferred (at 77 K) into this red solid and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy of the resulting solution at 200 K tentatively identified the complex as [(dppe)Rh(PCyp$_3$)(L)][BAr$^F_4$] **5**. Vacuum transfer of CD_2Cl_2/MeCN into a sample of the red solid gave ^1H and $^{31}P\{^1H\}$ NMR spectra fully consistent with those previously reported for **6**.[9]

^1H NMR (500.1 MHz, CD_2Cl_2, 200 K): δ 7.92–7.31 (m, 20H, ArH), 7.70 (s, 8H, BAr$^F_4$), 7.51 (s, 4H, BAr$^F_4$), 2.88–0.85 (m, 31H, CH_2/CH). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2, 200 K): δ 73.90 (br m), 61.92 (br m), 23.52 ppm (v br m).

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