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# Observation of a stable *cis*-diphosphine solvate rhodium dihydride derived from PHANEPHOS

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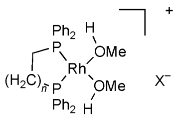
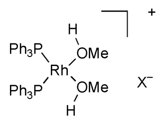
**The methanol solvate rhodium(PHANEPHOS) forms a stable dihydride which has been characterised in solution by NMR as a pair of equilibrating diastereomers.**

Early experiments designed to elicit the mechanism of asymmetric homogeneous hydrogenation provided a contrast between chelate diphosphine and bisphosphine rhodium complexes. The solvate **1a** showed no tendency to react with ambient hydrogen, whilst the solvate **2** formed a characterised dihydride;[1] the difference was attributed to a requirement for *trans*-diphosphine geometry in the stable solvate with H correspondingly *trans* to solvent oxygen. This observation has generally been sustained until recently. Aside from reversible *ortho–para* dihydrogen equilibration by complexes **1a** and **1b**,[2] and the likely mediation of a *cis*-dihydride in the formation of the dimeric species **3**,[3] no further progress had been made prior to the work of Gridnev, Imamoto and coworkers.[4] They demonstrated that the corresponding solvate **4** from a simple P-chiral alkylphosphine ligand formed significant quantities of the *cis*-dihydride **5** (20% at −95 °C and ambient pressure), with two diastereomers formed in a ratio of 10:1.[5] Further, this intermediate reacted with the catalytic substrate **6a** to form a Rh alkylhydride,[6] which then underwent reductive elimination at −50 °C to give the hydrogenated product. Taken together with labelling studies, the results are compatible with path **A** in Scheme 1, in contrast to the more generally accepted sequence **B**.[7]



**1a** *n* = 1
**1b** *n* = 3



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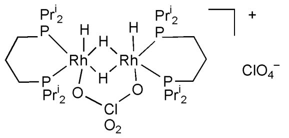

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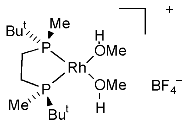

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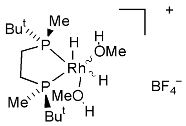

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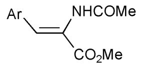
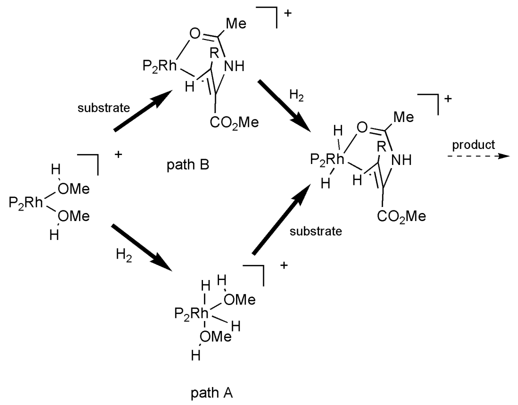
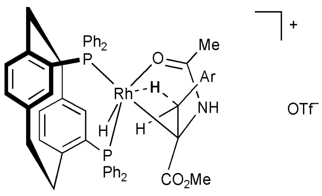


**6a** Ar = Ph
**6b** Ar = *p*-FC$_6$H$_4$

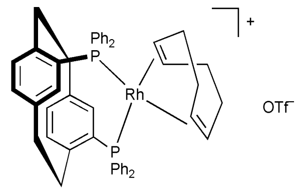
We recently demonstrated the presence of an agostic dihydride intermediate **7** in the hydrogenation cycle of compound **6a** by [PHANEPHOS]Rh$^+$, employing *para*-enriched hydrogen and the precursor complex **8** (or the NBD analogue) to identify the transient at −10 to −30 °C by $^1$H NMR.[8] When hydrogenation is complete and the substrate exhausted a second species can be observed, however. By carrying out the hydrogenation of the catalyst precursor in the absence of substrate the same intermediate is seen, optimally at −40 °C. The $\delta$ and $J$ values are entirely consistent with a *cis*-dihydride structure **9**, with one hydride *trans* to phosphorus ($\delta$ *ca.* −11) and one *trans* to one of the two solvent oxygens ($\delta$ *ca.* −20). Both the intensity and persistence of the signals indicate that it is a relatively robust species. There are two diastereomers **9a** and **9b** in 2:1 ratio, and their NMR spectra have been fully assigned using PHIP++ [Fig. 1(a)].[9] The chemical shifts are very different from the previous case[4] where the observed major diastereomer resonates at $\delta$ −7.7 and −23.0.



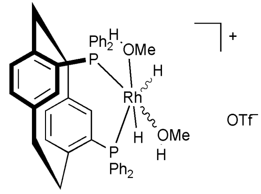
**Scheme 1** The possible paths for addition of dihydrogen to a dehydroamino ester; path **A**: H$_2$ addition prior to substrate (dihydride route). Path **B**: substrate addition prior to H$_2$ addition (unsaturate route).



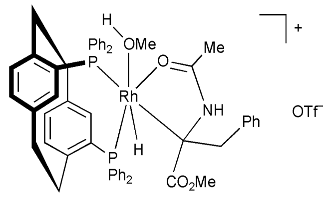
**7a** Ar = Ph
**7b** Ar = *p*-FC$_6$H$_4$



**8**



**9a, 9b**



**10**

When hydrogenation is carried out under conventional NMR conditions at −80 °C, the same dihydride **9** may be observed, along with small amounts of other Rh hydride resonances not seen in the PHIP spectrum. It is stable up to −40 °C [Fig. 1(b)], and a rough estimate based on integration of the high-field $^1$H NMR signals against the CH$_2$-region of the ligand indicates that 45% of species **9** is formed at equilibrium, making it more accessible than the previously observed case,[4,5] and to higher

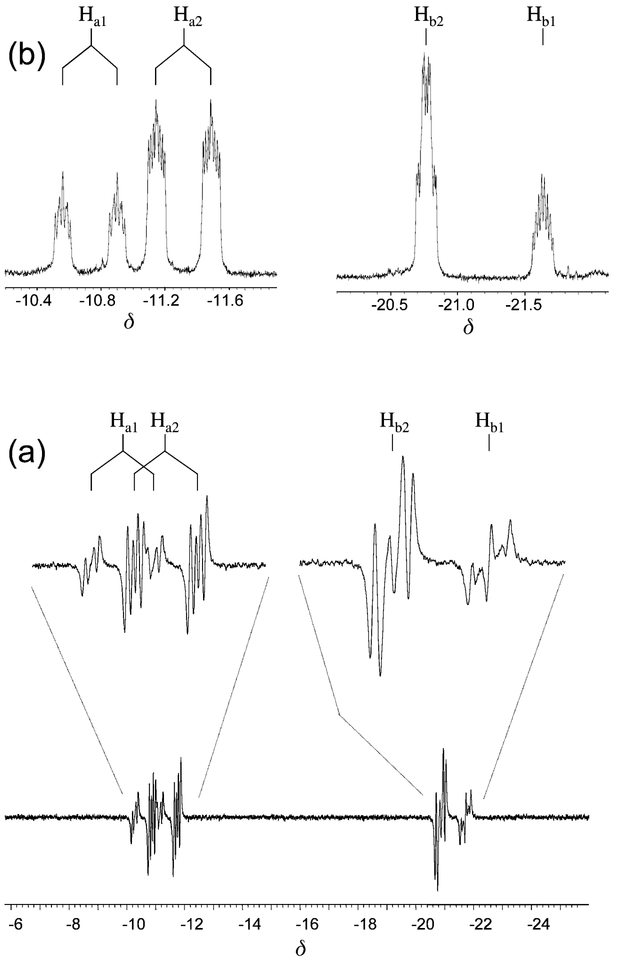


**Fig. 1** (a) The PHIP $^1H$ NMR spectrum ($CD_3OD$, 200 MHz) of dihydrides **9a** and **9b** taken after parahydrogen (98% enriched) passage through a solution of complex **8** in $CD_3OD$ at −40 °C. Minor diastereomer: $\delta$ −10.87 ($J_{HP}$ 170, 24, $J_{HRh}$ 14, $J_{HH}$ −9.0 Hz), −21.77, ($J_{HP}$ 32, 12, $J_{HRh}$ 21 Hz); major diastereomer : $\delta$ −11.46 ($J_{HP}$ 171, 28, $J_{HRh}$ 15.5, 15, $J_{HH}$ −7.5 Hz), −20.91, ($J_{HP}$ 29, 16, $J_{HRh}$ 22.5 Hz). (b) The $^1H$ NMR spectrum ($CD_3OD$, 500 MHz) of dihydrides **9a** and **9b** formed in the hydrogenation of complex **8** at −80 °C, taken at −40 °C, with comparable $J$ and $\delta$ values.

temperatures. This may be attributed to the high level of electron donation ensuing from the [2.2]paracyclophane backbone,[10] together with the large bite angle of PHANEPHOS,[11] which will favour the dihydride at equilibrium. The two diastereomers are in equilibrium by an unselective mechanism, as indicated by a selective homodecoupling experiment.[12]

When the solution containing complex **9** is held at −80 °C and a solution of compound **6a** in MeOH added, rapid formation of the agostic dihydride **7a** occurs. The signals at $\delta$ −2 and −19 are broad at that temperature, and at −70 °C they decay over time without formation of any further observable intermediates. The absence of a ‘classical’ alkylhydride **10** indicates that **7a** is the only accessible intermediate on the hydrogenation pathway. Further, it must be formed directly from an assumed dihydride precursor rather than by reinsertion of rhodium into the β-CH of **10** after formation of the latter, since the latter pathway would vitiate the earlier PHIP experiment by uncoupling the H–H spins.

In the earlier publication of Gridnev, Imamoto and coworkers,[4] it was suggested that path **A** could be a viable alternative to the accepted reaction mechanism of path **B** (Scheme 1). We observed that when the PHIP experiment was carried out with **6b** as substrate at the lower temperature of −27 °C, the solvate dihydride **9a**, **b** could be observed in significant amount, but only late in the reaction sequence when the substrate concentration was depleted (Fig. 2). This opens up the possibility that path **A** may contribute to catalytic turnover in the PHANEPHOS case. Earlier INEPT experiments demonstrated that the agostic intermediate **7a** is in reversible equilibrium with the solvate complex and substrate.[7] This makes the discrimination between the two pathways quite subtle. Given that both species **7** and **9** are observed in the same experiment under turnover conditions, the result is accessible in principle and a challenge for further work.

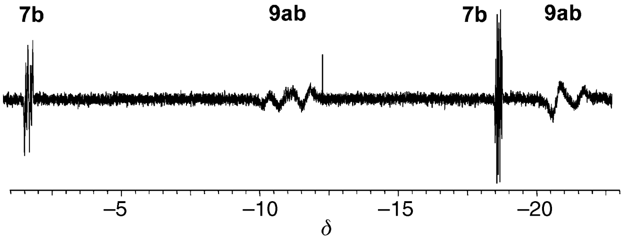


**Fig. 2** The PHIP $^1H$ NMR spectrum of the hydrogenation of reactant **6b** in $CD_3OD$ in the presence of Rh complex **8** at −27 °C, after 40 5 s pulses of parahydrogen (98%). Spectra taken earlier in the sequence after 16 pulses show only traces of complex **9**.

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## Notes and references

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