Supporting Information

Heterolytic Activation of Dihydrogen by Platinum and Palladium Complexes

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Dihydrogen Bonding

Compounds **Pt2a-d** are potential candidates for dihydrogen bonding because they possess a protonated pyridyl moiety (hydrogen bond donor) and a metal hydride (hydrogen bond acceptor) in close proximity. The presence of a dihydrogen interaction has been characterized in the solid state by X-ray crystallography[1] and neutron diffraction,[2,3,4] and in solution by NMR and IR spectroscopy.[5] Normally, the infrared spectra of hydrogen bonded systems shows that the metal-hydride and the NH or OH vibration bands broaden and shift to lower frequencies compared to compounds in which no hydrogen bonding occurs.[6] The ^{1}H NMR spectrum usually displays low field shifts for the X–H resonance (X= O or N), low minimum T_1 values and sometimes even hydride-proton couplings.[7,8]

In order to investigate whether dihydrogen bonding occurred in the platinum compounds **Pt2a-d**, various NMR experiments were carried out**.** The ^{1}H NMR spectra of **Pt2a–d** did not change significantly with temperature and neither coupling nor coalescence between the NH and the hydride was observed. The T_1 of the two signals remained long at all temperatures ($T_{1min} \approx 500$ ms for the hydride) and no T_1 coalescence was observed. No exchange or through-space interactions could be detected using NOE and Spin Saturation Transfer experiments. It was therefore concluded that the protonated pyridine and the hydride do not interact with one another. An explanation for the lack of interaction may be the low hydridic character of the hydride ligand in complexes **Pt2a-d**. It is known that dihydrogen bonding is an electrostatic interaction between a negatively charged hydride and a positively charged proton. However, in some cases Pt(II)-hydrides are not considered to be negatively charged

or nucleophilic. Extended Hückel calculations by Wander *et al.* on $[Pd(PH_3)_3H]^+$ showed that the P–M–P angle has a large influence on the partial charge of the hydride. They calculated that when the P–M–P angle increases from 80° to 100°, the charge on the hydride decreases from –0.51 to –0.27.[9] The origin of this effect was attributed to a decrease of the energy of the LUMO of the $[Pd(PH_3)_3]^{2+}$ fragment as the bite angle increases, causing the electron density to shift from the hydride ligand into this orbital. This result implies that hydride complexes with phosphine ligands enforcing wide bite angles will be more acidic than analogous complexes with small bite angle ligands. Considering that all the ligands used enforce bite angles over 90 °, it is expected that the hydride complexes **Pt2a-d** have small negative charges and therefore the interaction with the pyridinium proton will be weak.

From the crystal structure of **Pt2a-Me** it can be seen that the pyridyl fragment of 2-(diphenylphosphino)-6-methylpyridine points away from the hydride. However, the Pt–P bond can rotate in solution and at some point the hydride and the pyridinium proton may be close enough to one another to establish an interaction. If this interaction is not strong enough to stabilize this particular conformation over the others, the potential dihydrogen bond will not be detectable by NMR.

Reactivity Studies

If dichloromethane solutions of the hydride complexes **Pt2b-d** are allowed to stand at room temperature, they lose dihydrogen slowly reforming the starting compounds **Pt1b-d**. When the solution is allowed to stand for a few days, precipitation of metallic platinum is also observed. The loss of dihydrogen is faster for complex **Pt2d** containing Xantphos, which reverts completely to **Pt1d** in 12h, even at 0 °C. If this solution is re-pressurised with 3 bar of dihydrogen for 16h, the hydride complex **Pt2d** is re-formed cleanly, showing that the loss of H_2 is reversible.

Complex **Pt2d** was tested as catalyst for the hydrogenation of several unsaturated substrates. **Pt2d** is able to hydrogenate 1-hexene under 3 bar of H_2 at 40 °C, but the reaction is very slow (ratio **Pt2d** : 1-hexene = 1:100). After 16 h reaction time, only 90 % conversion to hexane was observed. ^{1}H and ^{31}P NMR spectroscopy of the reaction mixture revealed the presence of mainly **Pt2d** in solution, in addition small amounts of **Pt1d** (both *cis* and *trans*) and free phosphine were observed. The hydride complex **Pt2d** is completely inactive towards acetone, acetophenone or heptaldehyde. As before, the NMR spectra of the solutions after reaction showed a mixture of **Pt2d** and **Pt1d**; but free phosphine was not observed. The stoichiometric reaction of 1-hexene with **Pt2d** (without dihydrogen) was followed by NMR. Immediately after the addition of 1-hexene to a solution of **Pt2d** in CD_2Cl_2, the ^{1}H NMR spectrum shows signals for hexane at 0.88 and 1.30 ppm, integration of these signals compared to those for the olefin indicates about 10 % conversion to hexane. In addition, small peaks for 2-hexene were identified. Heating the NMR tube to 35 °C leads to an increase of the signals for 2-hexene, and after 1 day at room temperature complete isomerisation of 1-hexene to 2-hexene was observed, while the signals for hexane did not change any further. Neither the proton nor the phosphorus spectra show important changes in the signals of **2d** during the reaction. Small peaks for **Pt1d** are visible after 24 h, but these may result from normal decomposition of **Pt2d** in solution.

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