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Preliminary communication

Formation and behaviour of stable *cis-fac* and *cis-mer* water-soluble rhodium(III) dihydrides

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Abstract

A mixture of the novel *cis-fac* dihydride (**3**) and the expected *cis-mer* dihydride (**2**) is obtained by oxidative addition of hydrogen to the water-soluble Rh^I coordination compound $RhCl(TPPTS)_3$ (**1**) (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$). Compound **2** is exclusively formed in the presence of HCl or NaCl and the *cis-fac* isomer **3** gives the *cis-mer* dihydride **2** upon addition of NaCl. The low catalytic activity of these compounds is considered.

The importance of homogeneous hydrogenation of olefins in organic solvents catalyzed by transition metal complexes has prompted numerous mechanistic studies [1] involving determination of kinetic characteristics, structures of intermediates, and the stereochemistry of transient species [2]. Recently, biphasic systems have attracted interest for industrial applications, and water-soluble phosphines have been prepared to below water-solubility on homogeneous catalysts, thus providing a means of separating them from organic products [3]. Water is not a solvent in which one expect persistence of reactive species, but we have now found that molecular hydrogen adds readily to water-soluble rhodium coordination compounds of TPPTS [4] and that $RhCl(TPPTS)_3$ (**1**) gives the expected *cis-mer* stereoisomer and a novel *cis-fac* dihydride.

When a solution of **1** [5 *] prepared in water containing either NaCl (1 mol l^{-1}) or HCl (1 mol l^{-1}) is placed under hydrogen (atmospheric pressure) there is quantitative formation of the *cis-mer* dihydride **2** (Scheme 1), which was characterized by comparison of its ^{31}P and ^{1}H NMR data [6 *] with those of the known $H_2RhCl(PPh_3)_3$ [7]. Well resolved spectra are obtained at 35 °C, showing that in addition to the stability of the dihydride in these media no configurational modifi-

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* Reference number with asterisk indicates a note in the list of references.

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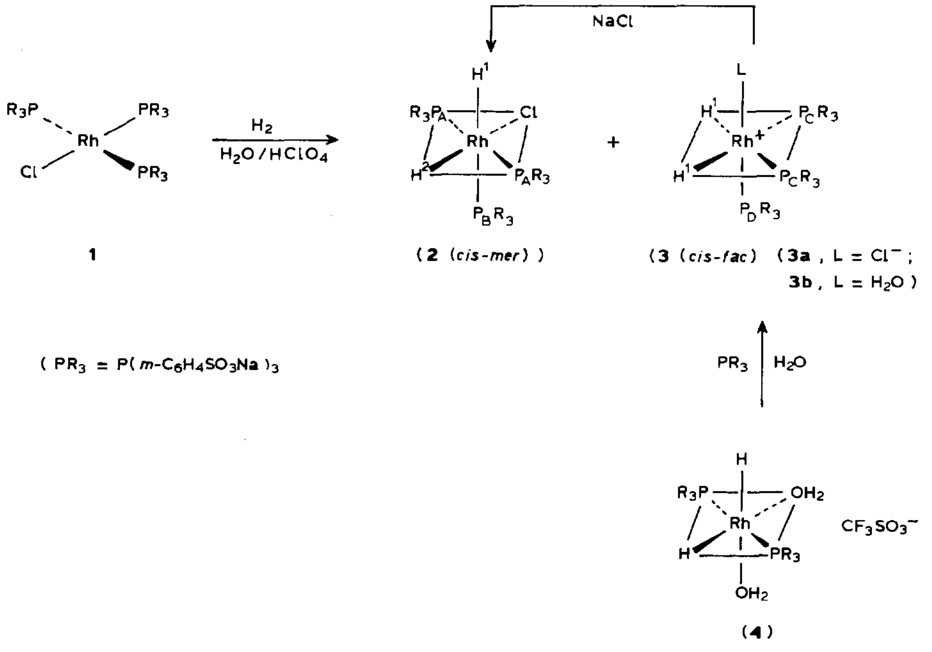
cations or dissociation equilibria take place at this temperature (which is not the case with $H_2RhCl(dpm)_3$) [8]). Surprisingly when compound **1** is dissolved in water containing $HClO_4$ (1 mol l^{-1}), the oxidative addition of H_2 gives a mixture of **2** and the new *cis-fac* dihydride **3a** or **3b** (Scheme 1). The stereochemistry of **3** was assigned from the ^{31}P NMR spectrum [9 *] (Fig. 1), and confirmed by an ^{1}H NMR study [9 *] of the mixture (60% of **2** and 40% of **3**). The two hydrido ligands of **3** are equivalent and *trans* to the equivalent phosphorus atoms P_C; in complex **2**, H^1 is exactly in the same environment. These three hydrogens give the doublet centered at δ −9.4 ppm ($^2J(P-H_{trans})$ 153 Hz), while the high field resonance at δ −17.4 ppm corresponds to H^2 in compound **2** [9 *].

The solution containing **2** and **3** may be kept for days under hydrogen without decomposition, but the proportion of **3** slowly increases up to 50%. However, if a few drops of saturated aqueous NaCl are added, the dihydride **3** is transformed instantaneously into complex **2** (Scheme 1) with the *cis-mer* stereochemistry considered to be the thermodynamically stable species in organic solvents [10]. This rapid displacement of the equilibrium accompanied by a ligand reorganization in the coordination sphere favours a cationic structure **3b** for the *cis-fac* dihydride; on the other hand its spectroscopic data are very similar to those of the authentic *cis-fac* cationic dihydride **3b** prepared independently by addition of TPPTS to dihydride **4** [11 *]. Recent studies in CH_2Cl_2/toluene have shown that PPh_3 dissociates from $H_2RhCl(PPh_3)_3$ to afford pentacoordinated species of various stereochemistries [2]. By contrast, in water, charged species are better stabilized than neutral ones, and in this polar solvent dissociation of the chloride ligand is preferred; the free coordination site can then be occupied by one molecule of water to afford the cationic



Scheme 1.

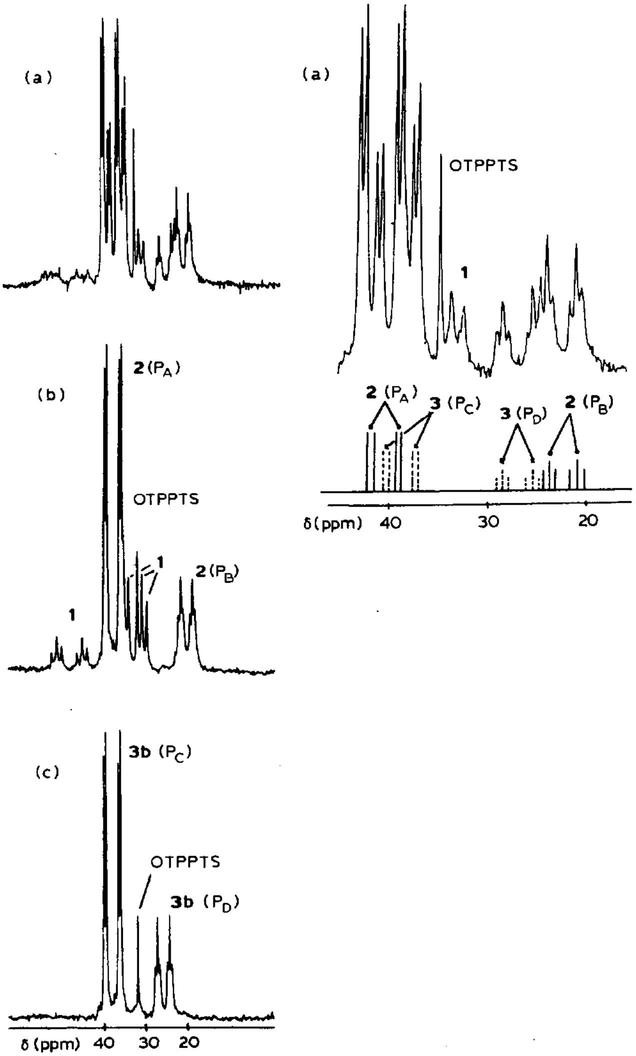


Fig. 1. ^{31}P {^1H} NMR spectra of the dihydrides (H_2O, 36° C, 32.38 MHz). (a) Mixture of **2** and **3** obtained after bubbling H_2 for 3 h into a $H_2O/HClO_4$(1 *M*) solution of **1** [13] (on the left: 250 Hz cm^{-1}; on the right: extended scale). (b) Spectrum recorded after addition of NaCl to the mixture **2**+**3** [18 *]. (c) Spectrum of the cationic dihydride **3b** obtained by addition of TPPTS on compound **4**.

complex **3b**. These findings are important because hydrogenation of olefins requires the liberation of a coordination site. Our studies show that in water with precursors such as **1**, the nature and the concentration of the ionic species in the solution must be carefully controlled, otherwise, dissociation of the phosphines is not observed and, since departure of the chlorine ligand is prevented, there is no point of attachment of the olefin to the metal. However even at low ionic strengths the dihydrides **2**, **3** and **4** show a very low reactivity either in the presence of water-soluble substrates or in biphasic conditions with liquid olefins. For instance, in the presence of an excess of cycloheptene, a ^{31}P NMR study shows that the dihydrides persist for several hours and that the rate of hydrogen absorption becomes significant only when a substantial quantity of phosphine oxide has been produced [12 *]. At this point large part of the rhodium is no longer characterizable by normal spectroscopic techniques, and it is probable that colloidal metallic dispersions are responsible for the catalytic activity [15–17].

This study reveals an aspect of transition-metal chemistry as yet little explored, and shows that with TPPTS very stable water-soluble Rh^{III} dihydrides are easily obtained. Their very low catalytic activities do not necessarily mean that other water-soluble transition metal dihydrides will be inefficient catalysts, and careful adjustment of the hydrophilic-hydrophobic balance of the phosphines may lead to efficient catalysts for biphasic hydrogenation systems.

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5 Complex **1** was prepared by addition of a solution of 6 equivalents of TPPTS in aqueous HCl, NaCl or $HClO_4$ to a THF solution of one equivalent of the dimer $[RhCl(cyclooctadiene)_2]_2$. After 2 h the ^{31}P NMR spectrum confirmed that the reaction was complete and the THF was removed under vacuum.

6 ^{31}P NMR (35 °C, H_2O/HCl, H_3PO_4 ext. {^{1}H}, δ (ppm)): P_A 39.8 ($J(Rh–P_A)$ 116 Hz) P_B 22.0 ($J(Rh–P_B)$ 93 Hz) ($J(P_A–P_B)$ 18 Hz); ^{1}H NMR (25 °C, H_2O/HCl, TMS ext., δ(ppm)): H^1 −9.3 ($J(P_B–H^1)$ 154 Hz) H^2 −17.4.

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8 A.F. Borowski, D.J. Cole-Hamilton and G. Wilkinson, Nouv. J. Chim., 2 (1978) 137; dpm = diphenyl *meta*-sulfophenyl phosphine.

9 ^{31}P NMR (35 °C, $H_2O/HClO_4$, H_3PO_4 ext., {^{1}H}, δ(ppm)): P_C 38.3 ($J(Rh–P_C)$ 115 Hz); P_D 26.7 ($J(Rh–P_D)$ 90 Hz) ($J(P_C–P_D$ 18 Hz); ^{1}H NMR (25 °C, $H_2O/HClO_4$, TMS ext.) the signals corresponding to the hydrides resonances are always broadened by the additional couplings (^2J(P–H-*cis*) and ^1J(Rh–H) are in the range 10–15 Hz).

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11 One equivalent of TPPTS was added to a water solution of **4** (prepared by conventional methods) to **3b**: ^{31}P NMR (35 °C, H_2, H_3PO_4 ext., {^{1}H}, δ (ppm)): P_C 37.9 ($J(Rh–P_C)$ 115 Hz); P_D 25.5 ($J(Rh–P_D)$ 93 Hz) ($JP_C–P_D$) 18 Hz); ^{1}H NMR (25 °C, H_2O, TMS ext., δ(ppm)): H_3 −10.1 (double multiplet with $J(P_C–H^3)$ 150 Hz).

12 After 6 h the ^{31}P spectrum showed that 30% of TPPTS oxide was formed. This oxidation of the phosphine must occur via Rh^{III} hydroxylated species [14] showing that the dihydrides decompose instead of reacting with the olefins to regenerate Rh^I.

13 A small amount of unchanged complex **1** remains in the solution. The production of phosphine oxide cannot be avoided, this oxidation of TPPTS has been described previously [14].

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18 A small amount of reductive elimination of H_2, leading to **1**, occurs when NaCl is added.