# Characterisation of Hydridopalladium Complexes *

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The hydride complexes *trans*-$[PdH(X)(PPh_3)_2]$ (X = Cl or Br) have been prepared in good yield by hydrogenolysis of *trans*-$[PdX(COPh)(PPh_3)_2]$ or *trans*-$[PdXPh(PPh_3)_2]$. They have been fully characterised by NMR and IR spectroscopic measurements and shown to have the *trans* configuration. The mechanism of the hydrogenolysis reaction and the role of these hydride species in catalytic reactions are discussed.

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Hydride species of the type *trans*-$[MH(X)(PPh_3)_2]$ (M = Ni, Pd or Pt) are important because of their possible role as intermediates in many homogeneous catalytic reactions. The trend in stability of these hydrides Pt > Pd > Ni has been attributed in part to the variation in energy difference ($\Delta E$) between the highest-occupied and the lowest-unoccupied molecular orbitals, which decreases in the same order.[1-3] The nature of the phosphine ligand also affects the stability of the complexes. Good $\sigma$ donors reinforce the M–P bond, so trialkylphosphine complexes are more stable but also less reactive than analogues with aromatic phosphines.

Palladium is probably the most interesting metal in the triad, *vis-à-vis* metal hydride complexes and catalysis, because of the necessary compromise between reactivity and stability of its hydride complexes. Such complexes are of importance in the development of mechanistic concepts relating to the wide variety of organic transformations catalysed by palladium[4] and to the relationship between ionic and covalent palladium hydrides, exemplified by the current interest in water gas shift and ethylene hydrocarbonylation chemistry.[5]

Trialkylphosphine complexes of the type *trans*-$[PdH(X)(PR_3)_2]$ have been prepared previously by the action of reducing agents such as $GeMe_3H$ or *trans*-$[NiH(BH_4)\{P(C_6H_{11})_3\}_2]$ on $[PdX_2(PR_3)_2]$ (X = Cl or Br; R = Et, $Pr^i$ or $Bu^n$)[6,7] and analogous trialkyl/arylphosphine complexes have been prepared by oxidative addition of HX (X = Cl or Br) on $[Pd(PR_3)_4]$ ($R_3$ = $Me_2Ph$, $MePh_2$, $Pr^i{}_3$ or $Ph_3$).[8,9]

The direct oxidative addition of dihydrogen to palladium(II) complexes has not previously been reported. We now describe the preparation, in good yield, of *trans*-$[PdH(Br)(PPh_3)_2]$ by pressurising palladium(II) complexes with dihydrogen; the hydride complexes have been characterised by a combination of NMR and IR spectroscopic measurements.

## Results and Discussion

The hydrogenolysis reactions of *trans*-$[PdBr(COPh)(PPh_3)_2]$ **1b** and *trans*-$[PdBrPh(PPh_3)_2]$ **2b** have been investigated by high-pressure NMR spectroscopy and found to yield *trans*-$[PdH(Br)(PPh_3)_2]$ **3b** and benzaldehyde and benzene respectively, equations (1) and (2) (thf = tetrahydrofuran).† The complex *trans*-$[PdClPh(PPh_3)_2]$ **2a** reacts in a similar manner to give *trans*-$[PdH(Cl)(PPh_3)_2]$ **3a** and benzene, equation (3).

$$trans\text{-}[PdBr(COPh)(PPh_3)_2] \xrightarrow[{[^2H_8]thf,\ 60\,^{\circ}C}]{H_2(80\ atm)} trans\text{-}[PdH(Br)(PPh_3)_2] + PhCHO \quad (1)$$

$$trans\text{-}[PdBrPh(PPh_3)_2] \xrightarrow[{[^2H_8]thf,\ 60\,^{\circ}C}]{H_2(80\ atm)} trans\text{-}[PdH(Br)(PPh_3)_2] + PhH \quad (2)$$

$$trans\text{-}[PdClPh(PPh_3)_2] \xrightarrow[CDCl_3,\ 60\,^{\circ}C]{H_2(80\ atm)} trans\text{-}[PdH(Cl)(PPh_3)_2] + PhH \quad (3)$$

The reactions have been characterised by *in situ* high-pressure NMR and IR spectroscopies supported by ambient-pressure NMR and IR analyses of the reaction products to characterise further the new hydride species. The $^1H$ and $^{31}P$ NMR data for the new complexes are given in Table 1. The formation of both benzaldehyde and benzene, as required by equations (1)–(3) was confirmed by GC analysis of the reaction solution.

The hydride resonances in the $^1H$ NMR spectra of *trans*-$[PdH(X)(PPh_3)_2]$ (X = Cl or Br) appear as triplets at low temperature [Fig. 1(*b*)] indicating a *trans*-phosphine configuration for the square-planar complexes; at higher temperatures this resonance broadens presumably due to the onset of exchange processes. The $^1H$ chemical shifts and phosphorus–proton coupling constants for the new hydride complexes are consistent with those of analogous palladium hydride complexes in the literature, Table 1. Some $[PdX_2(PPh_3)_2]$ (X = Cl or Br) was also formed as evidenced by a weak signal in the respective $^{31}P$ NMR spectra (Fig. 2).

The reaction of toluene solutions of the benzoyl complex with dihydrogen (30 atm, 60 °C) has also been studied by *in situ* high-pressure IR spectroscopy. The progress of the reaction, equation (1), could easily be followed by monitoring the appearance and increase in intensity of a peak at 1707 $cm^{-1}$, characteristic of benzaldehyde, and the concomitant decrease in intensity of the peak at 1646 $cm^{-1}$ due to the co-ordinated benzoyl moiety. The appearance of an additional very weak peak at 2001 $cm^{-1}$ was also noted and tentatively assigned to $\nu$(Pd–H) of *trans*-$[PdH(Br)(PPh_3)_2]$. The variable (and sometimes vanishingly small) intensities of $\nu$(M–H) absorptions in the solution-phase IR spectra of transition-metal hydrides is

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* *Non-SI unit employed:* atm = 101 325 Pa.

† Throughout this paper, the complexes are labelled **a** when X = Cl and **b** when X = Br.

**Table 1** Infrared and NMR data for the complexes $[PdH(X)(PR_3)_2]$

| Complex | $\delta(^{31}P)$ | $\delta(^{1}H)$ | $^{2}J(H-P)/Hz$ | $\nu(Pd-H)/cm^{-1}$ | Ref. |
|---|---|---|---|---|---|
| *trans*-$[PdH(Cl)(PEt_3)_2]$ | | −13.6 | | 2029 | 6 |
| *trans*-$[PdH(Br)(PEt_3)_2]$ | | −12.5 | | 2035 | 6 |
| *trans*-$[PdH(Cl)(PBu^n{}_3)_2]$ | | −13.5 | | | 7 |
| *trans*-$[PdH(Br)(PBu^n{}_3)_2]$ | | −12.5 | | | 7 |
| *trans*-$[PdH(Cl)\{P(C_6H_{11})_3\}_2]$ | | −14.4 | 4.1 | 2002 | 7 |
| *trans*-$[PdH(Br)\{P(C_6H_{11})_3\}_2]$ | | −13.3 | 6.0 | 1991 | 7 |
| $[PdH(PPh_3)_3]^+$ | 21.9<br>27.9 | −7.0 | 13.5 (*cis*)<br>17.4 (*trans*) | | 10 |
| *trans*-$[PdH(Cl)(PPh_3)_2]$ | 27.4 | −13.2 | 7.3 | | This work |
| *trans*-$[PdH(Br)(PPh_3)_2]$ | 28.8 | −11.9 | 9.8 | 2024 | This work |

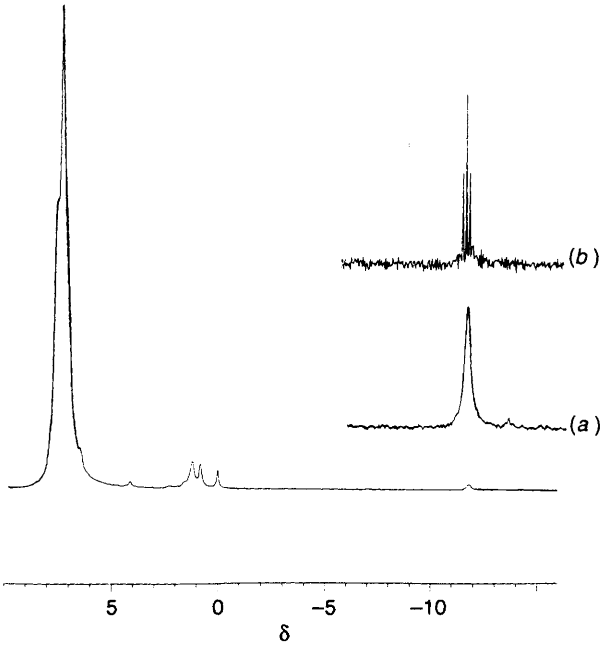

**Fig. 1** Proton NMR spectrum in $[^{2}H_8]$thf of the products of the reaction between *trans*-$[PdBrPh(PPh_3)_2]$ **2b** and $H_2(g)$ after depressurisation at −50 °C. Insert is an expansion of the metal hydride region at (*a*) 298, (*b*) 223 K

well established.[11] In order to seek confirmation of this band, a solid-state spectrum (Nujol mull) of the reaction product was measured after evaporation to dryness. An absorption at 2024 $cm^{-1}$ could be assigned to ν(Pd–H). It is well established that ν(M–H) varies significantly between solid and solution phases and even on varying the solvent.[11] This is particularly noticeable for square-planar complexes containing hydride *trans* to halide. The instability of the complex prevented elemental analysis. In solution the complex persists for a few hours at ambient temperature under an atmosphere of dinitrogen, and longer if kept under a pressure of dihydrogen, eventually decomposing to $[PdBr_2(PPh_3)_2]$ and palladium metal. The solid can survive for up to 48 h at −20 °C under dinitrogen.

The mechanism of formation of the complexes *trans*-$[PdH(X)(PPh_3)_2]$ may involve direct oxidative addition of dihydrogen to the palladium organyl complexes **1** and **2** to give a transient palladium(IV) species from which benzaldehyde or benzene respectively is eliminated to give **3**, equation (4).

$$[PdX(R)(PPh_3)_2] \xrightarrow{H_2} [PdH_2Br(R)(PPh_3)_2] \longrightarrow \textit{trans}\text{-}[PdH(X)(PPh_3)_2] + RH \quad (4)$$
$$R = Ph \text{ or } COPh$$

Alternatively, oxidative addition of dihydrogen to fortuitous palladium(0) species, followed by intermolecular hydride transfer, may occur, equation (5).

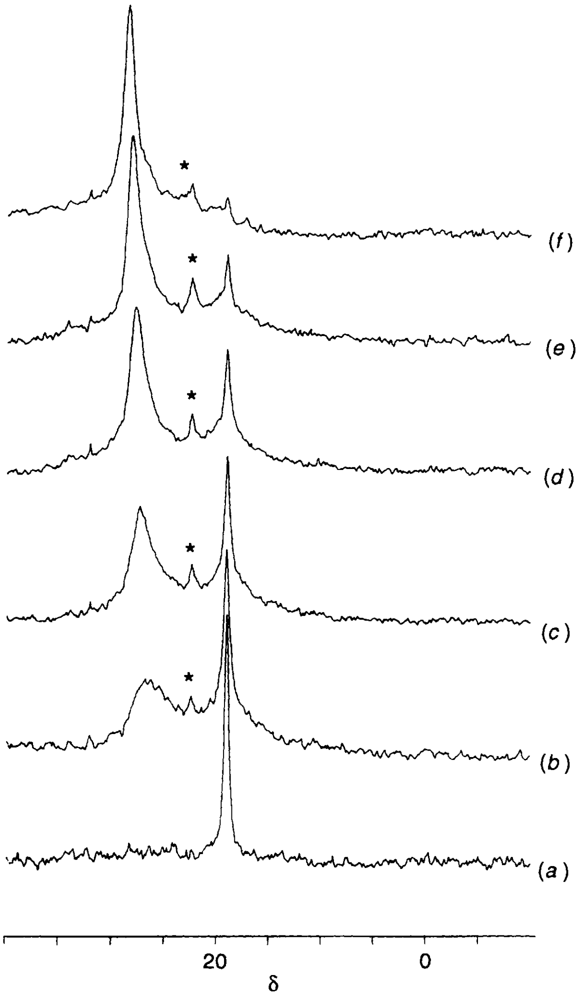

**Fig. 2** *In situ* $^{31}P$ NMR spectra of the reaction between *trans*-$[PdBr(COPh)(PPh_3)_2]$ **1b** and $H_2(g)$ (80 atm) at 60 °C to give *trans*-$[PdH(Br)(PPh_3)_2]$ **3b**. The asterisked peak is due to *trans*-$[PdBr_2(PPh_3)_2]$. *t* = 0 (*a*), 2 (*b*), 4 (*c*), 6 (*d*), 8 (*e*) and 10 h (*f*)

$$[Pd(PPh_3)_n] \xrightarrow{H_2} [PdH_2(PPh_3)_n] \xrightarrow{[PdX(R)(PPh_3)_2]} RH + [PdH(X)(PPh_3)_2] + [Pd(PPh_3)_n] \quad (5)$$
$$R = Ph \text{ or } COPh;\ X = Cl \text{ or } Br$$

The resonance due to the hydride complex **3b** in the $^{31}P$ NMR spectrum of the reaction solution at an early stage [Fig. 2(*b*)] is significantly broadened. As the reaction proceeds [Fig. 2(*b*) to 2(*f*)] it sharpens and shifts downfield. This may indicate

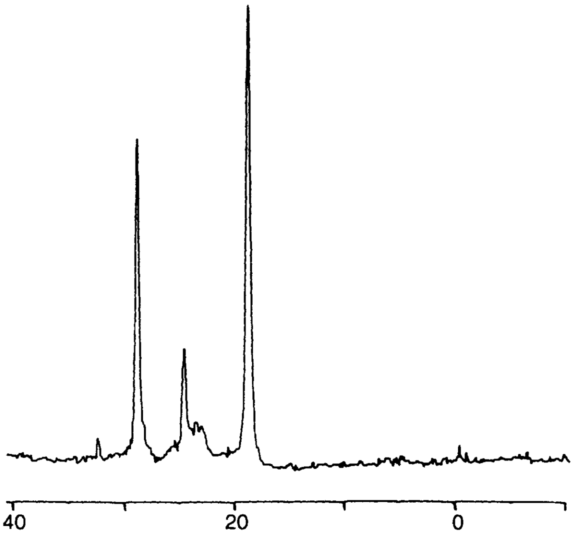

**Fig. 3** *In situ* $^{31}P$ NMR spectrum of the reaction between *trans*-$[PdBr(COPh)(PPh_3)_2]$ **1b** and $H_2(g)$, quenched to 228 K at *ca.* 30% conversion

exchange with a small amount of free phosphine and is consistent with the increase in the ratio **3b**:$PPh_3$ as **3b** is produced. The origin of the free $PPh_3$ may be dissociation from **1b**, the resonance of which also shows a slight broadening. In a separate experiment the reaction solution was cooled to −45 °C at *ca.* 30% conversion, Fig. 3. The resonances of the benzoyl and hydride complexes sharpen and less-intense resonances due to $OPPh_3$, $[PdBr_2(PPh_3)_2]$ and $[PdBr(R)(PPh_3)_2]$ are also observed, but there are no resonances due to free $PPh_3$ or $[Pd(PPh_3)_n]$ which suggests that dihydrogen adds directly to the benzoyl complex.

Finally, in a separate experiment, $[Pd(PPh_3)_4]$ was found not to react with dihydrogen under the conditions of temperature and pressure required for the hydrogenolysis of complexes **1** and **2**; this supports the preferential hydrogenolysis of the palladium(II) complexes, **1** or **2**, equation (4), *versus* the palladium(0) complex, equation (5).

These hydrogenolysis reactions are interesting since they have been proposed to take part in, for example, the palladium-catalysed hydrocarbonylation of bromobenzene described by Heck.[4] Reaction (1) corresponds to the stoichiometric hydrogenolysis of the benzoyl intermediate in this catalytic reaction.

The hydride complexes **3** produced by this hydrogenolysis, react cleanly with an excess of triphenylphosphine at 55 °C to give $[Pd(PPh_3)_n]$ and, initially, HX, equation (6). In the

$$[PdH(X)(PPh_3)_2] + 2PPh_3 \longrightarrow HX + [Pd(PPh_3)_n] + (4 - n)PPh_3 \quad (6)$$
$$n = 2\text{–}4$$

catalytic hydrocarbonylation reaction, $NEt_3$ is added to the reaction solution to remove the HBr as $[NEt_3H]Br$ which can be isolated and identified.

We have studied the hydrogenolysis of complex **1** (55 °C, 80 atm $H_2$) in the presence of an excess of $NEt_3$ and $PPh_3$ by high-pressure NMR spectroscopy. A broad coalesced resonance around δ 8 is seen in the $^{31}P$ NMR spectrum in addition to the resonance of the starting material. The reaction products were isolated and analysed by conventional NMR spectroscopy. On cooling to −95 °C the $^{31}P$ resonances of $PPh_3$ (δ −8.0) and $[Pd(PPh_3)_4]$ (δ 17.0) were resolved. No signal due to the palladium hydride species was observed in either the $^{31}P$ or the $^1H$ NMR spectrum during this experiment. Gas chromatographic analysis however revealed the formation of PhCHO and $[NEt_3H]X$, so the pathway (7) can be proposed. The

$$[PdX(COPh)(PPh_3)_2] \xrightarrow[-PhCHO]{+H_2} [PdH(X)(PPh_3)_2] \xrightarrow[-[NEt_3H]X]{+NEt_3\,+\,2PPh_3} [Pd(PPh_3)_4] \quad (7)$$

oxidative addition of HCl to $[Pd(PPh_3)_4]$ to produce $[PdH(Cl)(PPh_3)_2]$, essentially the reverse reaction of the last step in this scheme, has been reported.[9] We have observed a similar reaction (8) between $[Pd(PPh_3)_4]$ and HBr, but the yield of

$$[Pd(PPh_3)_4] \xrightarrow[-50\,°C]{HBr,\ EtOH} [PdH(Br)(PPh_3)_2] \quad (8)$$

the hydride complex was significantly lower than that obtained from hydrogenolysis of **1b** or **2b**.

The complex $[PdBr_2(PPh_3)_2]$ **4b** may be formed in the hydrogenolysis reactions described above *via* several routes but disproportionation of **3b** seems the most probable since we have observed that decomposition of **3b** occurs in solution when stored under dinitrogen, equation (9). Reaction of **3b** with **1b**

$$2[PdH(Br)(PPh_3)_2] \longrightarrow H_2 + [PdBr_2(PPh_3)_2] + [Pd(PPh_3)_2] \quad (9)$$

also gives **4b** and $[Pd(PPh_3)_n]$.[12] In the absence of $NEt_3$, oxidative addition of HX to **3** followed by reductive elimination of $H_2$ may also occur[13] and it is probable that more than one of these pathways is followed.

## Experimental

All syntheses and sample manipulations were carried out using standard Schlenk techniques under an atmosphere of dinitrogen.

The complexes $[PdBr(COPh)(PPh_3)_2]$ **1b** and $[PdBrPh(PPh_3)_2]$ **2b** were prepared by literature methods,[14,15] $[PdClPh(PPh_3)_2]$ **2a** was prepared by refluxing PhCl with $[Pd(PPh_3)_4]$. All other reagents were bought from Aldrich or BDH and were used without further purification.

Infrared spectra were recorded on a Perkin-Elmer 1720 spectrometer. Gas chromatography was carried out on a DANI 3800 gas chromatograph using an OV 351 WCOT column. The high-pressure NMR spectrometer and high-pressure IR cell have been described previously.[16]

The high-pressure NMR work was supplemented by experiments run in a Parr 4591 autoclave made of 316 stainless steel and spectra were recorded at ambient pressure on a Bruker WM250 instrument.

High-pressure NMR experiments were performed as follows. Typically, the starting material (80 mg) was dissolved in a deuteriated solvent, $CDCl_3$ or $[^2H_8]$thf (2–5 $cm^3$). The sample was then transferred under $N_2$ to the high-pressure NMR probe and pressurised with dihydrogen gas (80 atm). Heating the sample to 60 °C initiated reaction between $H_2$ and $[PdBr(COPh)(PPh_3)_2]$ **1b** or $[PdClPh(PPh_3)_2]$ **2a**, while the hydrogenolysis of $[PdBrPh(PPh_3)_2]$ **2b** proceeded at ambient temperature. The progress of the reaction was monitored every hour by *in situ* $^{31}P$ NMR spectroscopy until the resonances due to the starting material had disappeared. The sample was then cooled to −50 °C and depressurised slowly, followed by measurements of $^{31}P$ and $^1H$ NMR spectra under ambient pressure of dihydrogen. Finally, the sample was withdrawn under an atmosphere of dinitrogen, evaporated to dryness under vacuum, redissolved in $CDCl_3$ and monitored by conventional NMR techniques at ambient pressure.

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