## New perspectives in hydroformylation : a para-hydrogen study<sup>†</sup>

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NMR studies on the reaction of  $Ir(CO)(PPh_3)_2(\eta^3-C_3H_5)$  with *para*-H<sub>2</sub> and CO enable the complete mapping of the hydroformylation mechanism for an iridium monohydride catalyst *via* the detection of species which include iridium acyl and alkyl dihydride intermediates.

Unravelling the mechanism by which a metal complex catalyses a reaction is a complicated process that requires the connection of kinetic, synthetic and theoretical studies.<sup>1</sup> The rewards of achieving a greater understanding of such mechanisms are dramatic, leading to significant improvements in atom efficiency and hence fulfilling the chemist's desire to make a positive contribution to today's greener world. Hydroformylation represents a key industrial process yielding millions of tonnes of aldehydes annually that feed into a wide range of end products.1 Both modified cobalt and rhodium systems containing phosphine donors are used as industrial catalysts.<sup>2</sup> It is generally accepted that such reactions involving iridium are slower than their congeners because of their reduced rates of migratory insertion.<sup>3</sup> These attributes commend themselves to model studies of the individual reaction steps.<sup>1,3</sup> Here we use  $Ir(CO)(PPh_3)_2(\eta^3-C_3H_5)$  **1** as the starting point to explore hydroformylation catalysis via a mono-phosphine based reaction path. We show that the  $\pi$ -allyl route allows the observation of key dihvdride intermediates when *para*-hvdrogen induced polarisation (PHIP)<sup>4</sup> is used to enhance the sensitivity of the NMR experiment.

Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) **1** was obtained by the addition of 10 equivalents of allyl magnesium bromide to Vaska's complex Ir(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl in THF at 273 K.<sup>5</sup> Crystals of **1** suitable for X-ray crystallography were obtained from a diethyl ether solution at room temperature.<sup>‡</sup> The structure of this complex, shown in Fig. 1(a), is similar to that previously reported for related complexes containing a substituted allyl ligand<sup>6</sup> with inequivalent phosphines and can be described as either a distorted tetrahedron, or a piano-stool with a capping  $\eta^3$ -allyl ligand. NMR data for **1** can be found in the supplementary information.<sup>†</sup>

In Wilkinson's paper<sup>5</sup>,  $H_2$  addition to 1 was reported to yield Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>(H)<sub>3</sub>. We re-examined this reaction using a toluene $d_8$  solution of 1 and 3 atm of pure *para*-hydrogen (*p*-H<sub>2</sub>). In the corresponding <sup>1</sup>H NMR spectrum at 273 K four sets of p-H<sub>2</sub> enhanced hydride resonances were detected at  $\delta - 10.80$ ,  $\delta - 11.20$ ,  $\delta$  -11.25 and  $\delta$  -11.55 that coupled to a single phosphorus centre. These signals arise from two previously unobserved species, isomeric forms of  $Ir(CO)(PPh_3)(\eta^3-C_3H_5)(H)_2$  (Fig. 1b, Scheme 1). A COSY spectrum connected the hydride resonances at  $\delta$  –10.80 (H<sub>a</sub>) and  $\delta$  -11.20 (H<sub>b</sub>), due to species 2, and those at  $\delta$  -11.25 (H<sub>c</sub>) and  $\delta$  -11.55 (H<sub>d</sub>) due to species 3, with the overall signal intensities suggesting that these products were formed in the ratio 1 : 1.8 respectively.<sup>†</sup> The formation of 2 and 3 was totally suppressed by the addition of a 5-fold excess of PPh<sub>3</sub> to the sample and they are therefore formed according to the reaction illustrated in Scheme 1. When this sample was warmed with p-H<sub>2</sub> to above 295 K, further reaction occurred and enhanced signals corresponding to the mer



**Fig. 1** (a) ORTEP diagram for  $Ir(CO)(PPh_3)_2(\eta^3-C_3H_5)$  **1**. Ellipsoids drawn at 50% probability level. (b) and (c) <sup>1</sup>H NMR spectra showing selected parts of the hydride region obtained from a sample of **1** in toluene-d<sub>8</sub>. (b) <sup>3</sup>IP-decoupled with *p*-H<sub>2</sub> at 275 K with resonances due to the two isomers of Ir(CO)(PPh\_3)(\eta^3-C\_3H\_5)(H)\_2 indicated; (c) with <sup>13</sup>CO and *p*-H<sub>2</sub> (ratio 1 : 2 total 3 atm). Enhanced resonances due to **8** and **9** are indicated with the left trace showing the enhanced Ir–CH<sub>2</sub> proton resonance of **9**.



Scheme 1 H<sub>2</sub> addition to  $Ir(CO)(PPh_3)_2(\eta^3-C_3H_5)$  1.

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† Electronic supplementary information (ESI) available: X-ray data for

and *fac* isomers of the trihydride species  $Ir(CO)(PPh_3)_2(H)_3^7$  and to both propane and propene were visible. In addition small amounts of the known complex  $Ir(CO)(PPh_3)_3(H)$  were detected.<sup>8</sup> In order for the propane and propene signals to exhibit *p*-H<sub>2</sub> enhancement, two protons that originate in a single *p*-H<sub>2</sub> molecule must be located in the product. This requires the transfer of a proton to the allyl terminus and the formation of a propene hydride complex, a reaction that has been observed previously.<sup>9</sup> The formation of an iridium propyl complex places a second *p*-H<sub>2</sub> derived proton into the substrate, and accounts for the observation of enhanced propane signals. Competitive  $\beta$ -hydride migration is necessary to account for the propene enhancement.

When a toluene-d<sub>8</sub> based sample of **1** was placed under a CO atmosphere, four species were formed immediately and fully characterised by NMR spectroscopy;  $Ir(CO)_2(PPh_3)(\eta^3-C_3H_5)$  **4**,  $Ir(CO)_3(PPh_3)(\eta^1-CH_2CH=CH_2)$  **5**,  $Ir(CO)_2(PPh_3)_2(COCH_2 CH=CH_2)$  **6** and  $Ir(CO)_3(PPh_3)(COCH_2 = CHCH_2)$  **7** (Scheme 2).† Species **6** and **7** correspond to reactive acyl complexes of the type that feature in proposed hydroformylation mechanisms.<sup>2</sup>

When the reaction of **1** with a mixture of  $CO / p-H_2$  (ratio 2 : 1, total 3 atm) is studied in toluene-d<sub>8</sub> at 295 K by <sup>1</sup>H NMR spectroscopy, neither 2 nor 3, nor propane nor propene, is observed but p-H<sub>2</sub> enhanced hydride signals are visible at  $\delta$  -8.91 and  $\delta$ -8.40 due to species 8 and 9 (Fig. 1c and Scheme 2).<sup>+ 13</sup>C information, obtained via HMQC methods, showed that the  $\delta$ -8.91 site connected to a single terminal carbonyl resonance at  $\delta$ 173.6 while the  $\delta$ -8.40 site connected to two signals at  $\delta$ 171.6 and  $\delta$  209.5 due to terminal carbonyl and acyl ligands respectively. The mono-phosphine dihydride acyl species 9, Ir(CO)<sub>2</sub>(PPh<sub>3</sub>)- $(COC_3H_5)(H)_2$ , can form from either 6 or 7 if PPh<sub>3</sub> or CO are appropriately lost. When <sup>13</sup>C labelling was introduced, the appearance of the single hydride resonances observed for 8 and 9 matched those expected for dihydrides with square planar cis, cis  $Ir(^{13}CO)_2(H)_2$  cores. The geometry of complex 9 matches that proposed for the analogous key intermediate in modified cobalt



Scheme 2 Reactivity of  $Ir(CO)(PPh_3)_2(\eta^3-C_3H_5)$  1 in the presence of 1 atm CO and 2 atm H<sub>2</sub> (R = CH<sub>2</sub>CH=CH<sub>2</sub>): Note 8 goes on to eliminate propene.

carbonyl catalysis.<sup>10</sup> A related complex,  $Ir(dppe)(CO)(COEt)(H)_2$  which mimics more closely the bisphosphine base rhodium catalysed system has been observed by Eisenberg.<sup>11</sup>

One striking observation that needs further comment relates to the observation of a *p*-H<sub>2</sub> enhanced signal at  $\delta$  3.05 (Fig. 1c) for **8** which arises from a proton that was originally in *p*-H<sub>2</sub> but now corresponds to a metal-bound CH<sub>2</sub> proton of an  $\eta^1$ -allyl ligand. Such an occurrence again requires the reversible generation of a propene hydride complex in order to obtain an  $\eta^1$ -allyl group where one *p*-H<sub>2</sub> derived proton is located on the C<sub>1</sub> atom. The spectral features associated with **8** therefore correspond to the observation of two distinct forms, one where both hydrides originate from the same *p*-H<sub>2</sub> molecule, and one where exchange has moved one of these ligands on to the allyl group. Upon warming such a sample to 318 K, the species *mer* and *fac* Ir(PPh<sub>3</sub>)<sub>2</sub>(CO)(H)<sub>3</sub>, and Ir-(CO)(PPh<sub>3</sub>)<sub>3</sub>(H) are again detected and GC-MS analysis reveals the formation of the hydroformylation products CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO and CH<sub>3</sub>CH(CH<sub>3</sub>)CHO.

In conclusion we have demonstrated that  $Ir(CO)(PPh_3)_2(\eta^3 C_3H_5$ ) 1 is a suitable precursor to study the hydroformylation reaction by NMR spectroscopy. Reaction of 1 with p-H<sub>2</sub> at 273 K revealed for the first time the formation of two isomers of the  $\eta^3$ allyl dihydride species  $Ir(CO)(PPh_3)(\eta^3-C_3H_5)(H)_2$  2 and 3 which upon warming to 295 K, yield propene, propane via reversible hydride transfer, and subsequently the fac and mer isomers of Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>(H)<sub>3</sub>. This confirms that the CO deficient atmosphere favours hydrogenation over carbonylation. When 1 reacts with CO alone, equilibria are established between 4, 5, 6 and 7 in which the latter two products result from CO insertion into an Ir-C bond (Scheme 2). When a mixture of CO and  $H_2$  was added to 1, hydrogenation is suppressed and the novel dihydride products, cis,cis Ir(CO)<sub>2</sub>(PPh<sub>3</sub>)(COCH<sub>2</sub>CHCH<sub>2</sub>)(H)<sub>2</sub> 8 and cis,cis Ir-(CO)<sub>2</sub>(PPh<sub>3</sub>)(η<sup>1</sup>-CH<sub>2</sub>CH=CH<sub>2</sub>)(H)<sub>2</sub> 9, are detected prior to the corresponding hydroformylation products. Collectively the observations correspond to the detection of all the key species required to complete the hydroformylation of a metal alkyl as shown in Scheme 2.

## Notes and references

‡ Crystal data for 1: C<sub>40</sub>H<sub>35</sub>IrOP<sub>2</sub>, FW 785.82, yellow blocks, crystal dimensions  $0.28 \times 0.14 \times 0.04$  mm, monoclinic,  $P2_1/n$ , a = 10.2878(7), b = 18.4100(12), c = 17.6432(11) Å,  $\beta = 91.633(2)^\circ$ , V = 3340.2(4) Å<sup>3</sup>, Z = 4,  $\mu$ (Mo-Kα) = 4.124 mm<sup>-1</sup>, T = 115(2) K; 26828 reflections measured,  $R_{int} = 0.0330$ .

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