

New perspectives in hydroformylation : a *para*-hydrogen study†Cyril Godard,^a Simon B. Duckett,^{*a} Céline Henry,^a Stacey Polas,^b Robert Toose^b and Adrian C. Whitwood^a^a Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: sbd3@york.ac.uk; Fax: +44 1904 432516^b Sasol Technology (UK) Ltd., Purdie Building, North Haugh, St Andrews, Scotland, UK KY16 9ST

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NMR studies on the reaction of Ir(CO)(PPh₃)₂(η³-C₃H₅) with *para*-H₂ 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.¹ 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.² It is generally accepted that such reactions involving iridium are slower than their congeners because of their reduced rates of migratory insertion.³ These attributes commend themselves to model studies of the individual reaction steps.^{1,3} Here we use Ir(CO)(PPh₃)₂(η³-C₃H₅) **1** as the starting point to explore hydroformylation catalysis via a mono-phosphine based reaction path. We show that the π-allyl route allows the observation of key dihydride intermediates when *para*-hydrogen induced polarisation (PHIP)⁴ is used to enhance the sensitivity of the NMR experiment.

Ir(CO)(PPh₃)₂(η³-C₃H₅) **1** was obtained by the addition of 10 equivalents of allyl magnesium bromide to Vaska's complex Ir(PPh₃)₂(CO)Cl in THF at 273 K.⁵ Crystals of **1** suitable for X-ray crystallography were obtained from a diethyl ether solution at room temperature. ‡ The structure of this complex, shown in Fig. 1(a), is similar to that previously reported for related complexes containing a substituted allyl ligand⁶ with inequivalent phosphines and can be described as either a distorted tetrahedron, or a piano-stool with a capping η³-allyl ligand. NMR data for **1** can be found in the supplementary information.†

In Wilkinson's paper⁵, H₂ addition to **1** was reported to yield Ir(CO)(PPh₃)₂(H)₃. We re-examined this reaction using a toluene-d₈ solution of **1** and 3 atm of pure *para*-hydrogen (*p*-H₂). In the corresponding ¹H NMR spectrum at 273 K four sets of *p*-H₂ enhanced hydride resonances were detected at δ -10.80, δ -11.20, δ -11.25 and δ -11.55 that coupled to a single phosphorus centre. These signals arise from two previously unobserved species, isomeric forms of Ir(CO)(PPh₃)₂(η³-C₃H₅)(H)₂ (Fig. 1b, Scheme 1). A COSY spectrum connected the hydride resonances at δ -10.80 (H_a) and δ -11.20 (H_b), due to species **2**, and those at δ -11.25 (H_c) and δ -11.55 (H_d) due to species **3**, with the overall signal intensities suggesting that these products were formed in the ratio 1 : 1.8 respectively. † The formation of **2** and **3** was totally suppressed by the addition of a 5-fold excess of PPh₃ to the sample and they are therefore formed according to the reaction illustrated in Scheme 1. When this sample was warmed with *p*-H₂ to above 295 K, further reaction occurred and enhanced signals corresponding to the *mer*

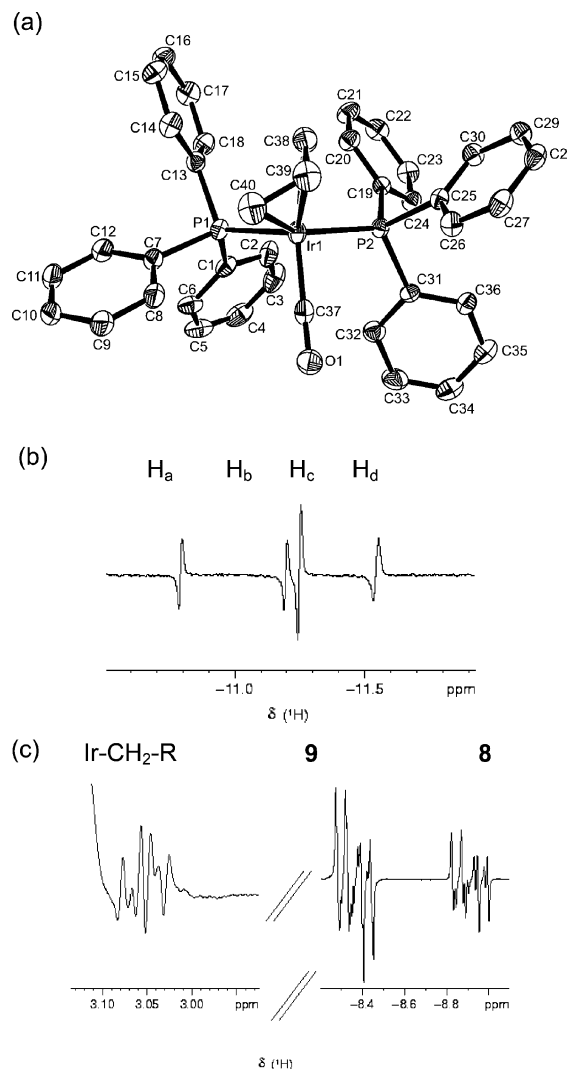
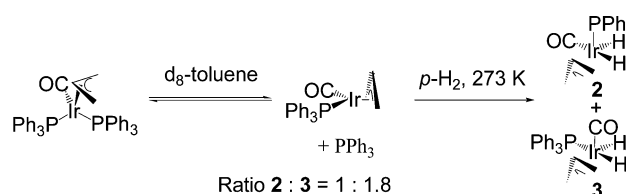


Fig. 1 (a) ORTEP diagram for Ir(CO)(PPh₃)₂(η³-C₃H₅) **1**. Ellipsoids drawn at 50% probability level. (b) and (c) ¹H NMR spectra showing selected parts of the hydride region obtained from a sample of **1** in toluene-d₈. (b) ³¹P-decoupled with *p*-H₂ at 275 K with resonances due to the two isomers of Ir(CO)(PPh₃)₂(η³-C₃H₅)(H)₂ indicated; (c) with ¹³CO and *p*-H₂ (ratio 1 : 2 total 3 atm). Enhanced resonances due to **8** and **9** are indicated with the left trace showing the enhanced Ir-CH₂ proton resonance of **9**.



Scheme 1 H₂ addition to Ir(CO)(PPh₃)₂(η³-C₃H₅) **1**.

† Electronic supplementary information (ESI) available: X-ray data for compound **1** and NMR data for compounds **1**–**9**. See <http://www.rsc.org/suppdata/cc/b4/b404547e/>

and *fac* isomers of the trihydride species $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{H})_3$ ⁷ and to both propane and propene were visible. In addition small amounts of the known complex $\text{Ir}(\text{CO})(\text{PPh}_3)_3(\text{H})$ were detected.⁸ In order for the propane and propene signals to exhibit *p*-H₂ enhancement, two protons that originate in a single *p*-H₂ 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.⁹ The formation of an iridium propyl complex places a second *p*-H₂ derived proton into the substrate, and accounts for the observation of enhanced propane signals. Competitive β -hydride migration is necessary to account for the propene enhancement.

When a toluene-d₈ based sample of **1** was placed under a CO atmosphere, four species were formed immediately and fully characterised by NMR spectroscopy; $\text{Ir}(\text{CO})_2(\text{PPh}_3)(\eta^3\text{-C}_3\text{H}_5)$ **4**, $\text{Ir}(\text{CO})_3(\text{PPh}_3)(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)$ **5**, $\text{Ir}(\text{CO})_2(\text{PPh}_3)_2(\text{COCH}_2\text{CH}=\text{CH}_2)$ **6** and $\text{Ir}(\text{CO})_3(\text{PPh}_3)(\text{COCH}_2=\text{CHCH}_2)$ **7** (Scheme 2).[†] Species **6** and **7** correspond to reactive acyl complexes of the type that feature in proposed hydroformylation mechanisms.²

When the reaction of **1** with a mixture of CO / *p*-H₂ (ratio 2 : 1, total 3 atm) is studied in toluene-d₈ at 295 K by ¹H NMR spectroscopy, neither **2** nor **3**, nor propane nor propene, is observed but *p*-H₂ enhanced hydride signals are visible at δ -8.91 and δ -8.40 due to species **8** and **9** (Fig. 1c and Scheme 2).[†] ¹³C information, obtained *via* HMQC methods, showed that the δ -8.91 site connected to a single terminal carbonyl resonance at δ 173.6 while the δ -8.40 site connected to two signals at δ 171.6 and δ 209.5 due to terminal carbonyl and acyl ligands respectively. The mono-phosphine dihydride acyl species **9**, $\text{Ir}(\text{CO})_2(\text{PPh}_3)(\text{COC}_3\text{H}_5)(\text{H})_2$, can form from either **6** or **7** if PPh₃ or CO are appropriately lost. When ¹³C 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* $\text{Ir}(\text{CO})_2(\text{H})_2$ cores. The geometry of complex **9** matches that proposed for the analogous key intermediate in modified cobalt

carbonyl catalysis.¹⁰ A related complex, $\text{Ir}(\text{dpe})(\text{CO})(\text{COEt})(\text{H})_2$ which mimics more closely the bisphosphine base rhodium catalysed system has been observed by Eisenberg.¹¹

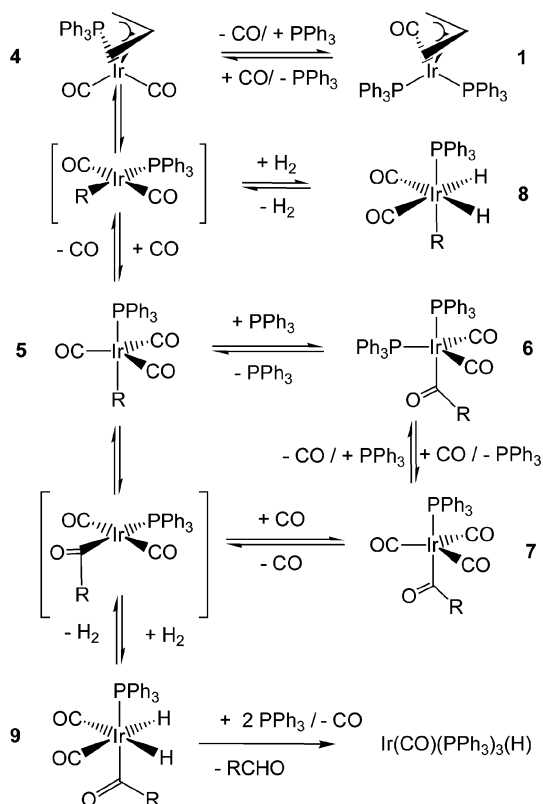
One striking observation that needs further comment relates to the observation of a *p*-H₂ enhanced signal at δ 3.05 (Fig. 1c) for **8** which arises from a proton that was originally in *p*-H₂ but now corresponds to a metal-bound CH₂ proton of an η^1 -allyl ligand. Such an occurrence again requires the reversible generation of a propene hydride complex in order to obtain an η^1 -allyl group where one *p*-H₂ derived proton is located on the C₁ 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*-H₂ 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* $\text{Ir}(\text{PPh}_3)_2(\text{CO})(\text{H})_3$, and $\text{Ir}(\text{CO})(\text{PPh}_3)_3(\text{H})$ are again detected and GC-MS analysis reveals the formation of the hydroformylation products $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ and $\text{CH}_3\text{CH}(\text{CH}_3)\text{CHO}$.

In conclusion we have demonstrated that $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\eta^3\text{-C}_3\text{H}_5)$ **1** is a suitable precursor to study the hydroformylation reaction by NMR spectroscopy. Reaction of **1** with *p*-H₂ at 273 K revealed for the first time the formation of two isomers of the η^3 -allyl dihydride species $\text{Ir}(\text{CO})(\text{PPh}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{H})_2$ **2** and **3** which upon warming to 295 K, yield propene, propane *via* reversible hydride transfer, and subsequently the *fac* and *mer* isomers of $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{H})_3$. 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 H₂ was added to **1**, hydrogenation is suppressed and the novel dihydride products, *cis,cis* $\text{Ir}(\text{CO})_2(\text{PPh}_3)(\text{COCH}_2\text{CHCH}_2)(\text{H})_2$ **8** and *cis,cis* $\text{Ir}(\text{CO})_2(\text{PPh}_3)(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)(\text{H})_2$ **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**: C₄₀H₃₅IrOP₂, FW 785.82, yellow blocks, crystal dimensions 0.28 × 0.14 × 0.04 mm, monoclinic, *P*2₁/*n*, *a* = 10.2878(7), *b* = 18.4100(12), *c* = 17.6432(11) Å, β = 91.633(2)°, *V* = 3340.2(4) Å³, *Z* = 4, $\mu(\text{Mo-K}\alpha)$ = 4.124 mm⁻¹, *T* = 115(2) K; 26828 reflections measured, *R*_{int} = 0.0330.

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Scheme 2 Reactivity of $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\eta^3\text{-C}_3\text{H}_5)$ **1** in the presence of 1 atm CO and 2 atm H₂ (*R* = CH₂CH=CH₂): Note **8** goes on to eliminate propene.