

Activation of H₂ by halocarbonyl bis-phosphine and bis-arsine iridium(I) complexes. The use of parahydrogen induced polarisation to detect species present at low concentration and investigate their reactivity †

Sarah K. Hasnip,^a Simon A. Colebrooke,^a Christopher J. Sleigh,^a Simon B. Duckett,^{*a} Diana R. Taylor,^b Graham K. Barlow^b and Mike J. Taylor^b

^a Department of Chemistry, University of York, Heslington, York, UK YO10 5DD

^b BP Chemicals, BP Chemicals Limited, Salt End, Hull, UK HU12 8DS

Received 16th August 2001, Accepted 15th October 2001

First published as an Advance Article on the web 29th January 2002

The iridium phosphine complexes Ir(CO)Cl(L)₂ [L = PPh₃, PMe₃, AsPh₃ and PPh₂Cl, and L₂ = (PPh₂Cl)(PPh₃)] add H₂ to form the corresponding dihydrides IrH₂(CO)Cl(L)₂. These products are detected at enhanced levels of sensitivity through the ¹H NMR signatures of their hydride resonances *via* para-hydrogen (*p*-H₂) based spin state synthesis. Products corresponding to addition across both the Cl–Ir–CO and L–Ir–L axes are detected. For L = PPh₃, there is a 100 fold preference for the former pathway at 295 K, while for L = AsPh₃ the second product is favoured by a factor of 2.85. At elevated temperatures a third product corresponding to addition over the Cl–Ir–L axis is detected for L = AsPh₃ and PPh₂Cl. Under these conditions, the CO and HCl transfer products Ir(H)₃(CO)₂(AsPh₃), and IrH(CO)Cl₂(AsPh₃)₂ are also formed in a thermal reaction. When IrH₂(CO)Cl(L)₂ is warmed or photolysed with H₂ and CO, the corresponding products are produced for L = PPh₃ and PMe₃. However after photolysis with H₂ alone Ir(H)₃(CO)(L)₂ is the favoured product. Additional products detected during the photochemical studies include Ir(H)₂(PPh₃)(PPh₂C₅H₄CO), an unusual orthometallation product containing an η²-acyl ligand, and the binuclear products H(Cl)Ir(PMe₃)₂(μ-H)(μ-Cl)Ir(PMe₃)(CO) and (H)₂Ir(PMe₃)₂(μ-Cl)₂Ir(PMe₃)(CO).

Introduction

The examination of the oxidative addition of H₂ to d⁸ square-planar rhodium and iridium complexes has provided a number of key observations that have been essential to the development of organo-transition metal catalysis. *trans*-Ir(CO)Cl(PPh₃)₂, or Vaska's complex¹ has played a particularly important role in this process *via* studies of stoichiometric reactions with species such as H₂, O₂, SO₂, CO, HCl, CS₂ and CH₃I. These additions can generally be categorised as either coordinative addition or oxidative addition.^{2–4} For instance, the observation that *trans*-Ir(CO)Cl(PPh₃)₂ acts as a reversible oxygen carrier,⁵ led to a crystal structure of the oxygenated complex Ir(CO)Cl(O₂)(PPh₃)₂⁶ that revealed an O–O distance of 130 pm. Consequently this complex can be regarded as an example of either an Ir(III) peroxide or an Ir(I) O₂ adduct. The binding of H₂ to a transition metal centre provides another example of where the distinction of product type is blurred. In this case, dihydride and dihydrogen complexes with intact H–H bonds, mark the boundaries.⁷ Many workers have studied this phenomenon, with Jessop and Morris⁸ defining dihydrogen complexes as having the following characteristics: atomic distance, *d*(H–H) = 0.8–1.0 Å, IR stretches *ν*(H–H) = 3100–2400 cm^{–1}, *ν*(M–H₂) = 850–950 cm^{–1} and relaxation delay, *T*₁ (200 MHz) 5–22 ms. There are, however, still some complexes, such as [RhH₂(pp₃)]⁺ (where pp₃ = tetraphos-2, P(CH₂CH₂PPh₂)₃),⁹ whose characteristics lie on the edge of these boundaries.

As a result of early work by Vaska and others, the generally accepted mechanism of H₂ addition to square-planar Ir(CO)Cl(PPh₃)₂ proceeds *via* a concerted route and leads to the formation of an octahedral product with *cis* hydrides. Whilst two

possible isomers, *cis,trans*-IrH₂Cl(CO)(PPh₃)₂ and *cis,cis*-IrH₂Cl(CO)(PPh₃)₂, might result from this process, observations suggest that stereospecific addition across the Cl–Ir–CO axis leads to the former species. Many analogues of Vaska's complex have been synthesised in order to examine how the ligands affect this selectivity. Studies by Crabtree and co-workers demonstrated that when the Cl ligand of Vaska's complex is replaced by an alkyl group¹⁰ addition at low temperature occurs across the P–Ir–P axis. In the case of IrPh(CO)(PMe₃)₂ the corresponding low-temperature product isomerises at 25 °C to the *trans* isomer. Consequently, it can be deduced that when this reaction proceeds under kinetic control addition across the P–Ir–P axis results, with the thermodynamic product, corresponding to addition over the Ph–Ir–CO axis, being formed by subsequent isomerisation.

This trend has also been observed experimentally in a number of related systems. For example, Anton and Crabtree's synthesis of [(dct)Ir(PPh₃)₂]BF₄, where dct = dibenzo[*a,e*]cyclooctatetraene, enabled them to show that H₂ addition led to an all-*cis* kinetic product¹¹ which rearranged *via* a base catalysed deprotonation to the thermodynamically more stable *cis, trans*-phosphine isomer. Additionally, Eisenberg and co-workers investigated a series of complexes¹² containing the chelating ligand dppe (dppe = 1,2-bis(diphenylphosphino)ethane) that are constrained to have *cis* phosphine ligands. Electronic factors were demonstrated to control the H₂ addition pathway, with the *cis,cis*-isomer containing a hydride *trans* to CO forming initially with >99% selectivity. However, over a period of hours this isomer rearranged, *via* reversible H₂ addition, to place the hydride *trans* to chloride. In other words, whilst addition across the P–Ir–CO axis is kinetically preferred, addition the P–Ir–Cl axis leads to the more thermodynamically stable product.

† Based on the presentation given at Dalton Discussion No. 4, 10–13th January 2002, Kloster Banz, Germany.

Sargent, Hall and Guest investigated the oxidative addition of H₂ to IrCl(CO)(dppe) by *ab initio* MO techniques¹³ using two *cis* PH₃ groups to mimic the dppe ligand. They found that while addition over the P–Ir–Cl axis led to the formation of the more stable isomer, the more stable transition state involved reaction across the P–Ir–CO axis. They too concluded that strong σ - and π -donor ligands destabilise the associated five-coordinate transition state by increasing the electronic repulsion between the ligands and the metal.¹² In contrast, electron-withdrawing ligands stabilise the transition state by reducing this repulsion. Similar model calculations for Vaska's complex¹⁴ predicted that addition across the P–Ir–P axis proceeded *via* the more stable transition state for PH₃. However, upon improving the accuracy of the simulation by utilisation of PMe₃, the relative stabilities of the transition states were reversed. Sargent and Hall therefore predicted that complexes of the type IrCl(CO){P(OR)₃}₂ might give H₂ addition across the P–Ir–P axis due to the π -accepting ability of the phosphite ligand. However, when Crabtree, Hall and co-workers tested this prediction¹⁵ addition across the Cl–Ir–CO axis was still observed.

It has been shown that the addition of H₂ enriched in the *para* spin state to a transition metal centre leads to greatly enhanced hydride signals in associated ¹H NMR spectra.¹⁶ This phenomenon has resulted in the development of a powerful tool for the characterisation of minor reaction products such as all-*cis* Ru(H)₂(CO)₂(PMe₃)₂¹⁷ and the investigation of hydrogenation products and kinetics.¹⁸ Here we describe how parahydrogen has been used to probe the reactions of Vaska's complex and a number of analogues by NMR spectroscopy. In particular we report on the observation of *cis,cis*-Ir(H)₂(CO)Cl(L)₂ (L = PPh₃, PMe₃, AsPh₃, PPh₂Cl) and demonstrate that at elevated temperatures Ir(H)₂(CO)Cl(L)₂ reacts to form a series of iridium trihydride complexes such as IrH₃(CO)₂L *via* an HCl transfer process that is promoted by CO or UV irradiation. Complementary formation of the corresponding monohydride-dichloride complex Ir(H)(CO)(Cl)₂(L)₂ is also observed. Some of this work has been communicated.¹⁹

Results and discussion

Oxidative addition of H₂ to Ir(CO)Cl(PPh₃)₂, 1-[Cl-Ph]

It has been reported previously that when a 0.1 mM solution containing Ir(CO)Cl(PPh₃)₂, 1-[Cl-Ph], in toluene-d₈ under 3 atm *p*-H₂ is examined by ¹H NMR spectroscopy at 343 K the hydrogen addition product IrH₂(CO)Cl(PPh₃)₂, 2-[Cl-Ph], is produced and the associated hydride resonances at δ -7.02 and -17.6 are parahydrogen enhanced.²⁰ When this system is subsequently cooled to 295 K the hydride resonances no longer show parahydrogen-based enhancement and it can be concluded that hydrogen exchange at 295 K is very slow. In contrast, when H₂ addition to a 0.1 mM solution of 1-[Cl-Ph] in benzene-d₆ under 3 atm *p*-H₂ is observed directly by NMR spectroscopy at 295 K the associated reaction products are observed as they form and prior to nuclear spin relaxation. Consequently, the resulting ¹H NMR spectrum again contains enhanced hydride resonances that are due to 2-[Cl-Ph]. However, under these conditions a somewhat unexpected enhanced hydride resonance at δ -8.10 is also observed with substantially lower signal intensity. The appearance of the hydride resonance of this second product, 3-[Cl-Ph], (Fig. 1(a)) indicates that it arises from a pair of chemically equivalent protons that are magnetically distinct and belong to [AX]₂ spin system. This situation matches that which would exist in the isomer of H₂ addition that is generated by reaction across the P–Ir–P axis. ³¹P and ¹³C chemical shift information was determined for the CO and phosphine ligands of this product via suitable *p*-H₂ enhanced 2D NMR experiments.^{20b} These data confirm that 3-[Cl-Ph] corresponds to *cis,cis*-IrH₂(CO)Cl(PPh₃)₂. It should

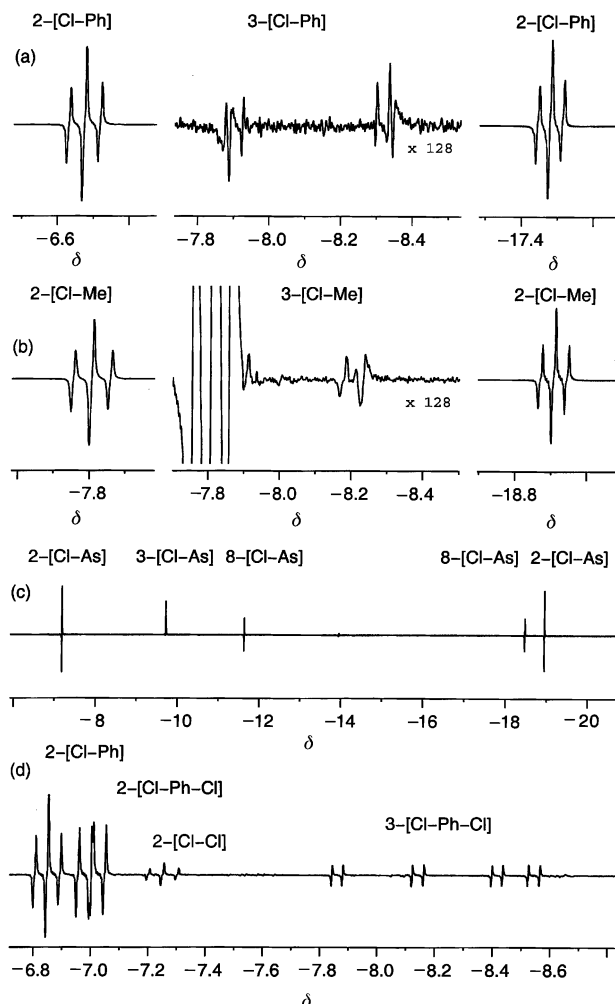
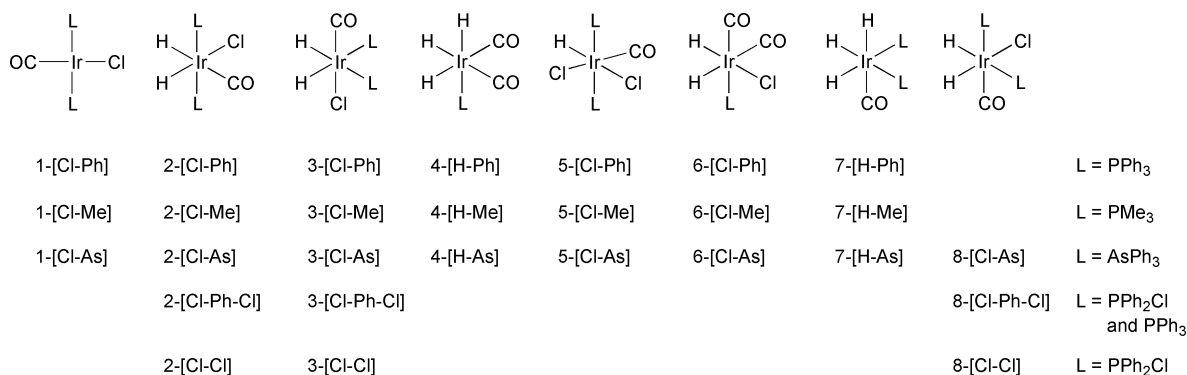


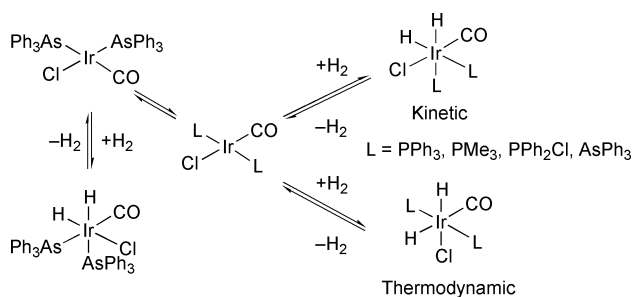
Fig. 1 (a) ¹H NMR spectrum (400 MHz, 295 K) of a 0.1 mM solution of 1-[Cl-Ph] in benzene-d₆ under 3 atm of *p*-H₂. The weak second order resonance arises from *cis,cis*-IrH₂(CO)Cl(PPh₃)₂ 3-[Cl-Ph]. (b) ¹H NMR spectrum (400 MHz, 333 K) of a 0.1 mM solution of 1-[Cl-Me] in benzene-d₆ under 3 atm of *p*-H₂ with resonances due to 2-[Cl-Me] and 3-[Cl-Me] indicated. (c) ¹H NMR spectrum (400 MHz, 338 K) of a 0.1 mM solution of 1-[Cl-As] in benzene-d₆ under 3 atm of *p*-H₂ showing resonances due to 2-[Cl-As], 3-[Cl-As] and 8-[Cl-As]. (d) ¹H NMR spectrum (400 MHz, 333 K) of a 0.1 mM solution of 1-[Cl-Ph] in benzene-d₆ in the presence of a four-fold excess of PPh₂Cl under 3 atm of *p*-H₂ showing resonances due to 2-[Cl-Ph], 2-[Cl-Ph-Cl], 2-[Cl-Cl] and 3-[Cl-Ph-Cl].

be noted at this point that the complexes described in this paper are referred to according to the designation X-[Y-Z] where X is the compound number, Y indicates whether the H₂ addition product contains additional chloride or hydride, and Z refers to the substituent on L, except for L = AsPh₃ where Z = As. These complexes are illustrated in Scheme 1 and the reaction is illustrated in Scheme 2.

In an attempt to quantify the ratios of these two products an NMR experiment was constructed that allowed the products of *p*-H₂ addition to be observed only once. This constraint was achieved by applying a 90° ¹H pulse to the sample followed by a pulsed field gradient to de-phase the initially coherent spin state. After a 100 ms delay a 45° ¹H read pulse was applied to enable the detection of any *p*-H₂ enhanced product formed during the 100 ms reaction time. The ratio of the hydride signal intensities for the two products under these conditions was 50 : 1. If similar enhancement levels are assumed for these two products, the ratio of 2-[Cl-Ph] : 3-[Cl-Ph] is 100 : 1 at 295 K. This equates to a difference in free energies of activation between the two H₂ addition pathways of 11 kJ mol⁻¹ at 295 K. We have already described how Sargent and Hall have investigated the oxidative addition of H₂ to Vaska's complex with *ab*



Scheme 1 Product identities.



Scheme 2 Reaction products detected by NMR spectroscopy when 1-[Cl-Ph], 1-[Cl-Me], 1-[Cl-As], 1-[Cl-Ph-Cl] and 1-[Cl-Cl] are warmed with *p*-H₂.

in MO techniques.²¹ They found that for PH₃ addition across the P–Ir–P axis proceeded *via* the more stable transition state whilst for PMe₃ this situation was reversed. In absolute terms, PH₃ addition across the P–Ir–P axis was favoured by 37.21 kJ mol⁻¹, while for PMe₃, addition across the CO–Ir–Cl axis was favoured by 9.51 kJ mol⁻¹. Consequently the value of 11 kJ mol⁻¹ estimated here for favouring addition over the CO–Ir–Cl axis of 1-[Cl-Ph] at 295 K would seem to be reasonable. In addition, we used a series of 1D EXSY NMR spectra to demonstrate that neither of these species interconvert over a 1-s reaction window. It can therefore be stated that 3-[Cl-Ph] corresponds to a minor addition product which is not observed at 333 K. NMR data for 2-[Cl-Ph] and 3-[Cl-Ph] is presented in Table 1.

Exchange of H₂ with IrH₂(CO)Cl(PPh₃)₂, 2-[Cl-Ph], in the presence of CO

In order to monitor the reaction of 2-[Cl-Ph] with *p*-H₂ in the presence of CO an NMR sample of ¹³C labelled 1-[Cl-Ph-¹³CO] was first converted to 2-[Cl-Ph-¹³CO] by reaction with H₂ in benzene-d₆. The sample of 2-[Cl-Ph-¹³CO] prepared in this way was then placed under 300 mm Hg of ¹³CO, the solution frozen, and the headspace of the NMR tube filled with 3 atm of *p*-H₂. The sample was then thawed and the subsequent reaction observed by multinuclear NMR spectroscopy at 313 K. The corresponding ¹H NMR spectrum contained evidence for 2-[Cl-Ph-¹³CO], and a number of new hydride containing species (Fig. 2(a)) The most significant of these extra species yielded a pair of hydride signals at δ -9.88 and -10.52 with overall intensity 2 : 1, respectively. The observation of hydride–hydride splittings for these two peaks of -2.4 and -4.8 Hz, respectively, suggested that these signals arise from a trihydride complex. This conclusion can be drawn on the basis that when trihydride complexes are examined with the *p*-H₂ the central feature of the triplet disappears due to cancellation of emission and absorption contributions and results in the apparent observation of two different couplings.²² The identification of this product is made relatively easy by the observation that these hydride signals are split by a single ³¹P nucleus, consequently

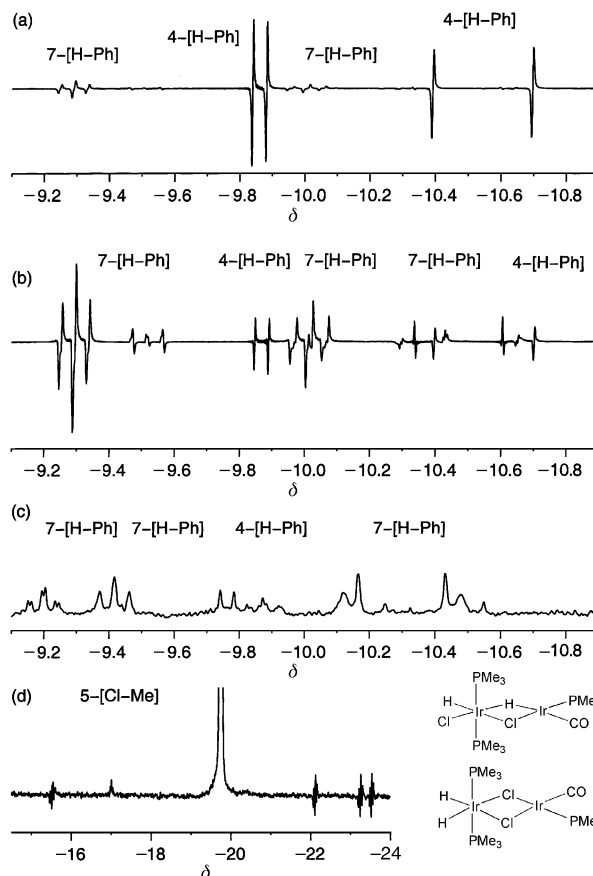


Fig. 2 (a) ¹H NMR spectrum (400 MHz, 333 K) of a 0.1 mM solution of 1-[Cl-Ph] in benzene-d₆ under CO and 3 atm of *p*-H₂ recorded after 5 minutes UV irradiation. Resonances for the *fac-cis* isomer of 4-[H-Ph] are clearly seen. (b) ¹H NMR spectrum (400 MHz, 338 K) of a 0.1 mM solution of 1-[Cl-Ph] in benzene-d₆ under 3 atm of *p*-H₂ recorded after 5 minutes of UV irradiation. Resonances for the *mer-trans* and *fac-cis* isomers of 7-[H-Ph] and the *fac-cis* isomer is 4-[H-Ph] is revealed. (c) ¹H NMR spectrum (400 MHz, 295 K) of the same sample used to record the spectrum shown in part (a). (d) ¹H NMR spectrum (400 MHz, 300 K) of a 0.1 mM solution of 1-[Cl-Me] in benzene-d₆ under 3 atm of *p*-H₂ after 5 minutes UV irradiation showing resonances due to H(Cl)Ir(PMe₃)₂(μ-H)(μ-Cl)Ir(PMe₃)₂(CO), and (H)₂Ir(PMe₃)₂(μ-Cl)₂Ir(PMe₃)₂(CO) (structures inset).

the product must correspond to IrH₃(CO)₂(PPh₃) 4-[H-Ph-¹³CO]. Furthermore, since these protons couple to a single ¹³CO environment that resonates at δ 172.2, and the hydride ligand providing the δ -10.48 signal is *trans* to phosphine, a *facial* ligand arrangement can be deduced. This information matches that previously reported for these complexes.²³

The formation of *fac*-4-[H-Ph] requires both the replacement of a phosphine ligand in 2-[Cl-Ph] by CO, and a chloride ligand by hydride. Notable features in these spectra also include the

Table 1 Selected NMR data for complexes 2–9 in benzene- d_6 unless specified

Complex, temp.	Nucleus	δ (multiplicity)	Assignment	Coupling constant/Hz, assignment
2-[Cl-Ph], 295 K	^1H	7.92 (m)	PPh_3 (<i>o</i> -H)	
		-6.69 (td)	Ir-H	$-4.6 \text{ } ^2J_{\text{HH}}$, $17.4 \text{ } ^2J_{\text{PH}} $, $43.7 \text{ } ^2J_{\text{CH}} $
	^{31}P	-17.48 (td)	Ir-H	$-4.6 \text{ } ^2J_{\text{HH}}$, $17.4 \text{ } ^2J_{\text{PH}} $, $4.1 \text{ } ^2J_{\text{CH}} $
2-[Cl-Me], 295 K ^a	^{13}C	9.9	PPh_3	$15 \text{ } ^2J_{\text{CH}} $
		177.8 (t)	CO	$5 \text{ } ^2J_{\text{CP}} $
	^1H	1.40 (m)	CH_3	$7.3 \text{ } ^2J_{\text{PH}} + ^4J_{\text{PH}} $
		-7.86 (td)	Ir-H	$-5.2 \text{ } ^2J_{\text{HH}}$, $20.8 \text{ } ^2J_{\text{PH}} $
2-[Cl-As], 295 K	^{31}P	-18.98 (td)	Ir-H	$-5.2 \text{ } ^2J_{\text{HH}}$, $14.7 \text{ } ^2J_{\text{PH}} $
		-41.1	PMe_3	$14.6 \text{ } ^2J_{\text{PCl}} $
	^{13}C	177.6 (t)	CO	$14.6 \text{ } ^2J_{\text{CP}} $
2-[Cl-Ph-Cl], 295 K	^1H	7.93 (m)	AsPh_3 (<i>o</i> -H)	
		7.01 (m)	AsPh_3 (<i>m,p</i> -H)	
	^{13}C	-7.11 (d)	Ir-H	$-5.0 \text{ } ^2J_{\text{HH}}$, $44.5 \text{ } ^2J_{\text{CH}} $
		-18.91 (d)	Ir-H	$-5.0 \text{ } ^2J_{\text{HH}}$, $3.7 \text{ } ^2J_{\text{CH}} $
2-[Cl-Ph-Cl], 295 K	^1H	177.2 (s)	CO	
		7.85 (m)	PPh_3 (<i>o</i> -H)	
	^{31}P	-6.81 (ddd)	Ir-H	$-4.7 \text{ } ^2J_{\text{HH}}$, $17.3 \text{ } ^2J_{\text{PH}} $, $19.7 \text{ } ^2J_{\text{PH}} $, $44.0 \text{ } ^2J_{\text{CH}} $
		-16.99 (td)	Ir-H	$-4.7 \text{ } ^2J_{\text{HH}}$, $17.3 \text{ } ^2J_{\text{PH}} $, $17.3 \text{ } ^2J_{\text{PH}} $, $4.4 \text{ } ^2J_{\text{CH}} $
2-[Cl-Cl], 333 K	^{31}P	9.0 (d)	PPh_3	$398.6 \text{ } ^2J_{\text{PP}} $
		66.2 (d)	PPh_2Cl	$398.6 \text{ } ^2J_{\text{PP}} $
	^{13}C	176.3 (t)	CO	$6 \text{ } ^2J_{\text{PCl}} $
3-[Cl-Ph], 295 K	^1H	-7.24 (td)	Ir-H	$-5.0 \text{ } ^2J_{\text{HH}}$, $20.3 \text{ } ^2J_{\text{PH}} $, $44 \text{ } ^2J_{\text{CH}} $
		-16.73 (td)	Ir-H	$-5.0 \text{ } ^2J_{\text{HH}}$, $15.0 \text{ } ^2J_{\text{PH}} $, $3.5 \text{ } ^2J_{\text{CH}} $
	^{31}P	65.1	PPh_2Cl	
3-[Cl-Me], 295 K	^{13}C	174.8 (t)	CO	$7 \text{ } ^2J_{\text{CP}} $
		-8.10 (2nd order)	Ir-H	$179 \text{ } ^2J_{\text{PH trans}} + ^2J_{\text{PH cis}} $
	^{31}P	-5.9	PPh_3	
3-[Cl-As], 295 K	^1H	167.1	CO	
		1.23	PMe_3	
	^{31}P	-8.00 (2nd order)	Ir-H	Obscured
3-[Cl-Ph-Cl], 333 K	^{13}C	-51.0	PMe_3	$14.6 \text{ } ^2J_{\text{PCl}} $
		173.7	CO	
	^1H	7.52 (m)	AsPh_3 (<i>o</i> -H)	
3-[Cl-Ph-Cl], 333 K	^1H	6.93 (m)	AsPh_3 (<i>m,p</i> -H)	
		-9.62 (s)	Ir-H	$6.4 \text{ } ^2J_{\text{CH}} $
	^{13}C	165.7 (s)	CO	
		-8.13 (ddd)	Ir-H	$-1.8 \text{ } ^2J_{\text{HH}}$, $15.0 \text{ } ^2J_{\text{PH}} $, $224.7 \text{ } ^2J_{\text{PH}} $, $6.5 \text{ } ^2J_{\text{CH}} $
3-[Cl-Cl], 333 K	^{31}P	-8.34 (ddd)	Ir-H	$-1.8 \text{ } ^2J_{\text{HH}}$, $160.8 \text{ } ^2J_{\text{PH}} $, $15.9 \text{ } ^2J_{\text{PH}} $, $6.7 \text{ } ^2J_{\text{CH}} $
		-4.0 (d)	PPh_3	$28.5 \text{ } ^2J_{\text{PP}} $
	^{13}C	65.2 (d)	PPh_2Cl	$28.5 \text{ } ^2J_{\text{PP}} $
3-[Cl-Cl], 333 K	^1H	165.3	CO	$6 \text{ } ^2J_{\text{PCl}} $
		-8.37	Ir-H	
	^{31}P	62.9 (s)	PPh_2Cl	
<i>mer-trans</i> -4-[H-Ph], 333 K	^1H	-8.8 (dd)	Ir-H	$5.2 \text{ } ^2J_{\text{HH}}$, $136.9 \text{ } ^2J_{\text{PH}} $
		-9.7 (dd)	Ir-H	$5.2 \text{ } ^2J_{\text{HH}}$, $14.8 \text{ } ^2J_{\text{PH}} $
	^{31}P	25.4 (s)	PPh_3	
<i>fac-cis</i> -4-[H-Ph], 333 K	^1H	-9.88 (dd)	Ir-H	$-2.4 \text{ } ^2J_{\text{HH}}$, $17.2 \text{ } ^2J_{\text{PH}} $, 39.5 , $5.8 \text{ } ^2J_{\text{CH}} $
		-10.52 (dd)	Ir-H	$-2.4 \text{ } ^2J_{\text{HH}}$, $121.6 \text{ } ^2J_{\text{PH}} $, $4 \text{ } ^2J_{\text{CH}} $
	^{31}P	3.29 (s)	PPh_3	
<i>mer-cis</i> -4-[H-Me], 333 K	^1H	172.2 (s)	CO	
		-10.06 (dd)	Ir-H	$-4.7 \text{ } ^2J_{\text{HH}}$, $21.4 \text{ } ^2J_{\text{PH}} $, $8.7 \text{ } ^2J_{\text{CH}} $
	^{31}P	-10.97 (dd)	Ir-H	$-4.7 \text{ } ^2J_{\text{HH}}$, $22.0 \text{ } ^2J_{\text{PH}} $, $31.3 \text{ } ^2J_{\text{CH}} $
<i>fac-cis</i> -4-[H-Me], 333 K	^1H	-50.7 (s)	PMe_3	
		-10.60 (dd)	Ir-H	$-2.9 \text{ } ^2J_{\text{HH}}$, $19.1 \text{ } ^2J_{\text{PH}} $, $40.6 \text{ } ^2J_{\text{CH}} $
	^{31}P	-10.64 (dd)	Ir-H	$-2.9 \text{ } ^2J_{\text{HH}}$, $116.5 \text{ } ^2J_{\text{PH}} $
<i>fac-cis</i> -4-[H-As], 338 K	^1H	-60.7 (s)	PMe_3	
		7.54	AsPh_3 (<i>o</i> -H)	
	^{31}P	-9.99 (d)	Ir-H	$-1.5 \text{ } ^2J_{\text{HH}}$, $45.2 \text{ } ^2J_{\text{CH}} $
<i>cis-trans</i> -5-[Cl-Ph], 295 K	^1H	-11.44 (d)	Ir-H	$-1.5 \text{ } ^2J_{\text{HH}}$, $4.9 \text{ } ^2J_{\text{CH}} $
		171.9 (s)	CO	
	^{31}P	-14.51 (t)	Ir-H	$11.6 \text{ } ^2J_{\text{PH}} $, $5.2 \text{ } ^2J_{\text{CH}} $
<i>trans-trans</i> -5-[Cl-Ph], 295 K	^1H	-2.9 (s)	PPh_3	$7.9 \text{ } ^2J_{\text{PCl}} $
		163.2 (br)	CO	
	^{31}P	-7.62 (td)	Ir-H	$13.7 \text{ } ^2J_{\text{PH}} $, $57.4 \text{ } ^2J_{\text{CH}} $
<i>trans-cis</i> -5-[Cl-Me], 295 K	^1H	4.0 (d)	PPh_3	$5.3 \text{ } ^2J_{\text{PCl}} $
		173.4 (s)	CO	
	^{31}P	-16.31 (dt)	Ir-H	$13.1 \text{ } ^2J_{\text{PH}} $, $5.8 \text{ } ^2J_{\text{CH}} $
<i>trans-cis</i> -5-[Cl-As], 295 K	^1H	-33.1 (s)	PMe_3	
		164.7 (t)	CO	$8.1 \text{ } ^2J_{\text{PCl}} $
	^{31}P	8.12	AsPh_3 (<i>o</i> -H)	
<i>cis-cis</i> -6-[Cl-Ph], 313 K (H <i>trans</i> to CO)	^1H	-15.06 (d)	Ir-H	$5.4 \text{ } ^2J_{\text{CH}} $
		162.4 (s)	CO	
	^1H	-7.97 (br dd)	Ir-H	$-5.0 \text{ } ^2J_{\text{HH}}$, $17.4 \text{ } ^2J_{\text{PH}} $, $45.5 \text{ } ^2J_{\text{CH}} $
		-16.51 (brdd)	Ir-H	$-5.0 \text{ } ^2J_{\text{HH}}$, $16.0 \text{ } ^2J_{\text{PH}} $, $2.9 \text{ } ^2J_{\text{CH}} $
^{31}P	5.2 (d)	PPh_3	$123.4 \text{ } ^2J_{\text{PCl}} $	
^{13}C	170.8 (d)	CO	$8 \text{ } ^2J_{\text{PCl}} $	
	166.1 (d)	CO	$123 \text{ } ^2J_{\text{PCl}} $	

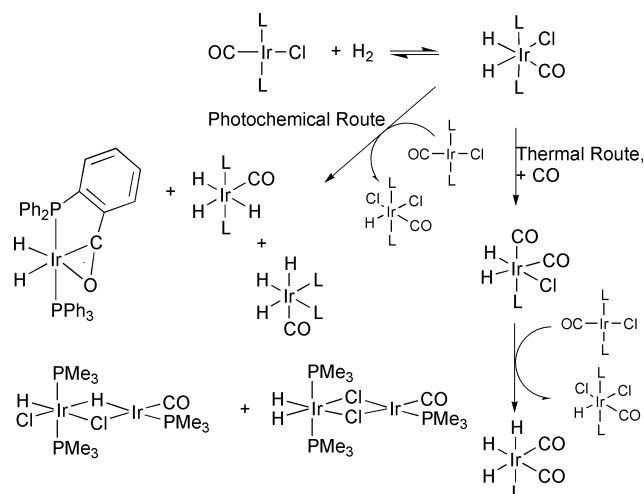
Table 1 (Contd.)

Complex, temp.	Nucleus	δ (multiplicity)	Assignment	Coupling constant/Hz, assignment
<i>cis-cis</i> - 6 -[Cl-Ph], 313 K (H <i>trans</i> to PPh ₃)	¹ H	-7.42 (dddd)	Ir-H	-7.0 ² J _{HH} , 14.5 ² J _{PH} , 56.6, 7 ² J _{CH}
		-8.37 (dtd)	Ir-H	-7.0 ² J _{HH} , 162.1 ² J _{PH} , 5 ² J _{CH}
	³¹ P	-5.7 (s)	PPh ₃	
	¹³ C	169.8 (d)	CO	8 ² J _{PCl}
<i>cis-trans</i> - 6 -[Cl-Ph], 313 K		161.7 (d)	CO	8 ² J _{PCl}
	¹ H	-9.43 (dd)	Ir-H	6.4 ² J _{HH} , 120.9 ² J _{PH}
		-17.03 (dd)	Ir-H	6.4 ² J _{HH} , 9.2 ² J _{PH}
	³¹ P	-2.6	PPh ₃	
<i>cis-cis</i> - 6 -[Cl-Me], 313 K	¹ H	-8.09	Ir-H	18.8 ² J _{PH} , 52.7 ² J _{CH} , 6 ² J _{CH}
	<i>cis-cis</i> - 6 -[Cl-Me], 333 K (H <i>trans</i> to PMe ₃)	¹ H	-9.12 (dd)	Ir-H
<i>cis-cis</i> - 6 -[Cl-As], 338 K		-9.15 (dd)	Ir-H	-4.1 ² J _{HH} 113.6 ² J _{PH}
	¹ H	-7.38 (d)	Ir-H	-2 ² J _{HH} , 56.5, 7.1 ² J _{CH}
		-9.49 (d)	Ir-H	-2 ² J _{HH} , 6.1, 4.2 ² J _{CH}
	¹³ C	169.7	CO	
<i>mer-trans</i> - 7 -[H-Ph], 323 K		161.2	CO	
	¹ H	7.91	PPh ₃ (<i>o</i> -H)	
		-9.26 (td)	Ir-H	-4.0 ² J _{HH} , 16.9 ² J _{PH} , 5 ² J _{CH}
		-9.97 (dtd)	Ir-H	-4.0 ² J _{HH} , 19.5 ² J _{PH} , 36 ² J _{CH}
<i>fac-cis</i> - 7 -[H-Ph], 323 K	³¹ P	18.0 (s)	PPh ₃	
	¹³ C	179.6 (t)	CO	10.3 ² J _{PCl}
	¹ H	7.90 (m)	PPh ₃ (<i>o</i> -H)	
		-9.51 (td)	Ir-H	+2.4 ² J _{HH} , 18.3 ² J _{PH} , 37.7 ² J _{CH}
<i>mer-cis</i> - 7 -[H-Ph], 333 K		-10.43 (2 nd order)	Ir-H	+2.4 ² J _{HH} , 106 ² J _{PH trans} + ² J _{PH cis}
	³¹ P	8.8 (s)	PPh ₃	
	¹³ C	179.3 (t)	CO	10.8 ² J _{PCl}
	¹ H	-9.08 (ddd)	Ir-H	4.6 ² J _{HH} , 17.6 ² J _{PH} , 136.4 ² J _{CH}
<i>mer-cis</i> - 7 -[H-Me], 333 K		-10.10 (obs)	Ir-H	5.8 ² J _{HH}
	³¹ P	20.5 (b)	PPh ₃	
		5.1 (b)	PPh ₃	
	¹ H	-10.82 (dt)	Ir-H	3 ² J _{HH} , 21.0 ² J _{PH}
<i>mer-trans</i> - 7 -[H-Ph], 333 K		-11.32 (2 nd order)	Ir-H	104.8 ² J _{PH trans} + ² J _{PH cis}
	³¹ P	-50.41 (s)	PMe ₃	
	¹ H	-10.95 (dt)	Ir-H	-5 ² J _{HH} , 22.0 ² J _{PH}
		-10.74 (dt)	Ir-H	-5 ² J _{HH} , 15.5 ² J _{PH}
<i>cis-cis</i> - 8 -[Cl-As], 338 K	³¹ P	-60.06 (s)	PMe ₃	
	¹ H	7.65	AsPh ₃ (<i>o</i> -H)	
		7.60	AsPh ₃ (<i>o</i> -H)	
		-11.69 (d)	Ir-H	-5.9 ² J _{HH} , 3.4 ² J _{CH}
<i>cis-cis</i> - 8 -[Cl-Ph-Cl], 333 K		-18.50 (d)	Ir-H	-5.9 ² J _{HH} , 4.7 ² J _{CH}
	¹³ C	170.3 (s)	CO	
	¹ H	-7.52 (ddd)	Ir-H	-2.9 ² J _{HH} , 17.0, 23.0 ² J _{PH} , 48.0 ² J _{CH}
		-9.50 (ddd)	Ir-H	-2.9 ² J _{HH} , 202, 23.0 ² J _{PH} , 4.4 ² J _{CH}
<i>cis-cis</i> - 8 -[Cl-Cl], 333 K	³¹ P	5.87 (s)	PPh ₃	(<i>trans</i> to chloride)
		65.3 (s)	PPh ₂ Cl	(<i>trans</i> to hydride)
		174.0	CO	
	¹ H	-7.25 (obs)	Ir-H	
<i>trans</i> - 9 -[Cl-As], IrClH ₂ (AsPh ₃) ₃ , 338 K		-9.72 (ddd)	Ir-H	-4.0 ² J _{HH} , 21.8 ² J _{PH} , 201.6 ² J _{PH}
	³¹ P	72.3 (br)	PPh ₂ Cl	
	¹ H	7.65	AsPh ₃ (<i>o</i> -H)	
		7.39	AsPh ₃ (<i>o</i> -H)	
H(Cl)Ir(PMe ₃) ₂ (μ -H)(μ -Cl)Ir(PMe ₃)(CO), 295 K ^a		-14.01 (d)	Ir-H	-5.7 ² J _{HH}
		-22.72 (d)	Ir-H	-5.7 ² J _{HH}
	¹ H	-15.53 (m)	Ir-H-Ir	-6.4 ² J _{HH} , 15.5 ² J _{PH}
		-22.13 (td)	Ir-H	-6.4 ² J _{HH} , 15.5 ² J _{PH}
(H) ₂ Ir(PMe ₃) ₂ (μ -Cl) ₂ Ir(PMe ₃)(CO), 295 K ^a	³¹ P	-37.3 (br)	PMe ₃	
	¹ H	-23.32 (dt)	Ir-H	-4.5 ² J _{HH} , 8.5, 22 ² J _{PH}
		-23.54 (dt)	Ir-H	-4.5 ² J _{HH} , 17.6 ² J _{PH}
	³¹ P	-32.71 (s)	PMe ₃	
Acylated metallation product, Scheme 3, 333 K	¹ H	-7.45 (m)	Ir-H	
		-18.49 (m)	Ir-H	
	³¹ P	14.7 (dd)	PPh ₃	380 ² J _{PP} , 11.9 ² J _{PCl}
	80.8 (d)	PPh ₂ PhCO	380 ² J _{PP}	

^a In toluene-d₈.

observation of weak signals for the hydride ligands of the dichloromonohydride complex, *trans,cis*-IrH(CO)(Cl)₂(PPh₃)₂ **5**-[Cl-Ph] at δ -14.51 and all four of the possible isomers of IrH₂(CO)₂Cl(PPh₃) **6**-[Cl-Ph] with *cis*-hydrides. Consequently, the formation of **5**-[Cl-Ph] when **2**-[Cl-Ph] is reacted with H₂ in the presence of CO suggests that HCl can be eliminated from **6**-[Cl-Ph]. (We note that the addition of HCl to a sample of **1**-[Cl-Ph] does indeed form **5**-[Cl-Ph].) Trapping of the resultant 16-electron intermediate IrH(CO)₂(PPh₃) with H₂ accounts

for the formation of **4**-[H-Ph]. The spectral characteristics of these new complexes are reported in Table 1. Since PPh₃ is liberated during the formation of **4**-[H-Ph] it would therefore seem sensible to suggest that IrH₂(PPh₃)₃Cl, a known *p*-H₂ active product, should also be detected.²⁰ We note that prior work has demonstrated that at this temperature the spectral features of IrH₂(PPh₃)₃Cl are not substantially enhanced, it is however observable in spectra recorded at higher temperatures. These reactions are summarised in Scheme 3.



Scheme 3 Reaction pathways evident when **2-[Cl-Ph]**, **2-[Cl-Me]** and **2-[Cl-As]** are warmed with *p*-H₂ in the presence of CO, or photolysed. Products specific to the PPh₃ and PMe₃ systems are expressly indicated.

Oxidative addition of H₂ to Ir(CO)₂Cl(PPh₃)₂

In order to explore the role of CO more fully, a sample of **1-[Cl-Ph]**, in benzene-d₆, was first placed under an atmosphere of CO in order to form the known complex Ir(CO)₂Cl(PPh₃)₂.² The solution was then placed under CO and 3 atm of *p*-H₂ according to the previous procedure. When the associated reaction at 295 K was monitored by multinuclear NMR spectroscopy, *p*-H₂ enhanced hydride resonances were readily detected for **2-[Cl-Ph]**, **3-[Cl-Ph]** and the facial isomer of **4-[H-Ph]**. Much weaker hydride signals were also present for the meridional isomer of IrH₃(CO)(PPh₃)₂ **7-[H-Ph]** and the *trans,cis* (major) and *trans,trans* (minor) isomers of the HCl addition product **5-[Cl-Ph]**. Upon warming this sample to 313 K the hydride signals for **3-[Cl-Ph]** were observed to disappear while those for **4-[H-Ph]** showed substantial enhancement. It can therefore be concluded that H₂ addition to Ir(CO)₂Cl(PPh₃)₂ leads to the generation of both IrH₂(CO)₂Cl(PPh₃) (minor) and IrH₂(CO)Cl(PPh₃)₂ (major). It can also be deduced that the former complex, IrH₂(CO)₂Cl(PPh₃), then reacts rapidly to form **4-[H-Ph]** via HCl elimination. These findings are summarised in Scheme 3.

Monitoring H₂ exchange within IrH₂(CO)Cl(PPh₃)₂, **2-[Cl-Ph]**, after UV irradiation of the precursor

In view of the ability of **1-[Cl-Ph]** to act as a photocatalyst for the carbonylation of benzene we decided to investigate how UV irradiation affected the identity of the species present in solution.²⁴ A solution of **2-[Cl-Ph]** under *p*-H₂ was therefore first exposed to UV light for 5 minutes and then observed by NMR spectroscopy. The corresponding ¹H NMR spectrum, recorded at 300 K, contained hydride resonances for **2-[Cl-Ph]** that were enhanced due to photochemically driven dihydrogen exchange. However, when this sample was heated to 333 K and re-examined enhanced hydride resonances were seen for both the *facial* and *meridional* isomers of **7-[H-Ph]**, the *facial* isomer of **4-[H-Ph]** and IrH₂(PPh₃)₃Cl as illustrated in Fig. 2(b). The observation of both isomers of the dichloromonohydride complex **5-[Cl-Ph]** accompanied these changes. UV irradiation therefore facilitates reaction pathways that lead to CO and HCl transfer products as indicated in Scheme 3.

More significantly, two highly complicated, and mutually coupled, hydride resonances were observed at δ -7.45 and -18.49 in these spectra. 2D ¹H-³¹P HMQC NMR spectroscopy showed that both these hydride resonances coupled to phosphorus signals resonating at δ 14.7 and 80.8 which were split into doublets of 380 Hz. This large coupling is typical of that seen in a complex that contains inequivalent *trans* phosphine

arrangements. An example of such a complex is given by IrH(PPh₃)₂(P(C₆H₅)₂(C₆H₄))Cl, **A**, where *J*_{PP} has been reported to be 376 Hz.²⁵ However, in such cases, the resonance due to the phosphorus centre of the four-membered ring is normally shifted considerably *upfield* (δ -69.6 (A)) relative to that of the simple phosphine (δ 3.1 and -2.5 in **A**). In contrast, the new product is characterised by a marked *downfield* shift of one of the phosphorus resonances. This situation is typical of that found in phosphorus centres that are located in *five*-membered rings.^{26,27} When these experiments were repeated with **2-[Cl-Ph-¹³C]** the corresponding hydride resonances of this product appeared to be unaffected by the presence of the ¹³C label. However, the corresponding phosphorus resonance at δ 14.7 contained an additional splitting of 11.9 Hz due to ¹³C. Although this requires the product to contain a ¹³CO unit we were unable to locate its chemical shift by 2D ¹H-¹³C HMQC experiments. This reaction product can therefore be deduced to contain the five-membered ring Ir(CO-C₅H₄-P), an acylated metallation product. A further key feature of this complex can be deduced on the basis of the chemical shifts of the two hydride ligands which resonate at δ -7.45 and -18.49. While the former is typical of a hydride *trans* to a soft donor, the latter is typical of a hydride *trans* to a hard group. The only hard ligand in this system is Cl, but filling the equatorial vacancy with a Cl ligand would lead to a paramagnetic product. In contrast Caulton *et al.*²⁸ have shown that when an iridium hydride is located *trans* to a vacant site, the corresponding resonance is dramatically shifted to high field which in the case of Ir(H)₂(P^tBuPh)₂I corresponds to δ -44.4. The hydride of our product resonates at δ -18.49 and is therefore unlikely to be *trans* to a vacant site, this suggests that η² binding of the acyl is required (a loosely bound solvent molecule is unlikely). The spectral evidence described here suggests that this product adopts the structure indicated in Scheme 3. NMR data for this product is presented in Table 1.

Using normal NMR methods to monitor the effect of UV irradiation on a sample of **2-[Cl-Ph]**

In order to explore whether **2-[Cl-Ph]** eliminates HCl that is subsequently trapped by **1-[Cl-Ph]** under photolysis a sample of **2-[Cl-Ph]** was first prepared in benzene-d₆. The large excess of H₂ present in the original solution was then reduced to 0.5 equivalents by degassing. At this point the solution of **2-[Cl-Ph]** was photolysed for 5 minutes before being re-examined by NMR spectroscopy. The ¹H spectrum shown in Fig. 2(c) was obtained. Evidence for conversion of 6% of **2-[Cl-Ph]** was obtained with detected products including *mer-trans*- and *fac-cis*-**7-[H-Ph]**, and *fac-cis*-**4-[H-Ph]** (ratio 5 : 5 : 1). In addition, equal amounts of both the *cis,cis* and *cis,trans* isomers of the HCl addition product **5-[Cl-Ph]** were observed.

When this sample was subsequently warmed to 338 K with *p*-H₂, the ratio of the enhanced hydride peak intensities for *mer-trans*- and *fac-cis*-**7-[H-Ph]**, and *fac-cis*-**4-[H-Ph]** corresponded to 1 : 0.2 : 0.35. However, on cooling to 300 K the ratio of the hydride peak intensities matched those obtained immediately after photolysis. It can therefore be concluded that at 338 K exchange of free H₂ into *fac-cis*-**4-[H-Ph]** proceeds at a faster rate than *mer-trans* isomer of **7-[H-Ph]**. Evidence was also observed for the conversion of the *cis,trans* isomer of the HCl addition product **5-[Cl-Ph]** into the *cis,cis* form.

Effect of UV irradiation of **2-[Cl-Ph]** in the presence of both CO and H₂

When a sample of **2-[Cl-Ph]** in the presence of H₂ and CO is irradiated, and subsequently monitored by NMR spectroscopy at 295 K enhanced resonances are observed initially due to **2-[Cl-Ph]**. Upon warming the formation of **4-[H-Ph]** became readily apparent. Surprisingly, however, at 333 K, the signals for *fac-cis*-**4-[H-Ph]** were around 1000-fold larger than those

observable in the absence of CO. In addition, the ratio of hydride signals for *fac-cis*-**4**-[H-Ph] and *mer-trans*-**7**-[H-Ph] under these conditions was 13 : 1 rather than the 1 : 5 observed without CO. It can therefore be concluded that in the presence of CO, IrH₃(CO)(PPh₃)₂ **7**-[H-Ph] readily converts into IrH₃(CO)₂(PPh₃) **4**-[H-Ph].

Oxidative addition of H₂ to Ir(CO)Cl(PMe₃)₂, **1**-[Cl-Me]

When the addition of hydrogen to the iridium(I) centre in **1**-[Cl-Me] was monitored at 295 K new polarised hydride resonances were initially seen at δ -7.86, -18.98 and -8.00 in the corresponding ¹H NMR spectrum that are indicative of the formation of the analogous products **2**-[Cl-Me] and **3**-[Cl-Me], respectively. In these spectra cross-relaxation between the hydrides, and the methyl protons of the phosphines, leads to the observation of enhanced signals for the methyl protons of **3**-[Cl-Me] at δ 1.23. When this sample was subsequently warmed to 333 K polarised hydride resonances could still be observed for both **2**-[Cl-Me] and **3**-[Cl-Me] in contrast to the situation described earlier for **1**-[Cl-Ph]. This suggests that the addition of H₂ to *trans*-**1**-[Cl-Me] is reversible at 333 K, with both isomers of H₂ addition being readily formed according to Scheme 2. The hydride resonances of **2**-[Cl-Me] and **3**-[Cl-Me] were present in the corresponding spectra in the ratio 93 : 1 at 333 K as revealed in Fig. 1(b).

Monitoring the exchange of H₂ with IrH₂(CO)Cl(PMe₃)₂, **2**-[Cl-Me], in the presence of CO

In order to monitor the effect of CO on the reaction of **2**-[Cl-Me] with *p*-H₂ a solution was made up that contained **2**-[Cl-Me], 3 atm *p*-H₂, and CO in a similar way to that described previously for **1**-[Cl-Ph]. At 333 K several new hydrides were observed by NMR spectroscopy of which the most intense appeared at δ -10.64 and -10.60. This product proved to be the *facial* isomer of the dicarbonyltrihydride complex IrH₃(CO)₂(PMe₃)₂, **4**-[H-Ph]. The NMR characteristics of this product are described in Table 1. Additional signals at δ -10.06 and -10.97 corresponding to the *meridional* isomer of **4**-[H-Ph] with 10% of the intensity of the facial peaks, and the dichloromonohydride complex **5**-[Cl-Me] were also observed in these spectra.¹⁰ The addition of CO therefore again enables the observation of a CO substituted HCl transfer product.

Monitoring the exchange of H₂ with IrH₂(CO)Cl(PMe₃)₂, **2**-[Cl-Me], after UV irradiation of the precursor

The role of photochemistry in enhancing ligand exchange was also investigated for **2**-[Cl-Me]. A solution of Ir(CO)Cl(PMe₃)₂, in benzene-*d*₆ was placed under 3 atm of *p*-H₂ in an NMR tube, left to react to form **2**-[Cl-Me], and then exposed to UV light for 5 minutes. The resulting solution was then observed by NMR spectroscopy. The hydride resonances of **2**-[Cl-Me] at δ -7.86 and -18.98 now showed enhancement in the corresponding ¹H NMR spectrum at 295 K in agreement with the observations made on **2**-[Cl-Ph]. Such an enhancement has not been seen previously at temperatures less than 333 K and demonstrates that photolysis causes the loss of H₂ from **2**-[Cl-Me]. In addition, pairs of enhanced resonances are also observed at δ -15.53, -22.13 and δ -23.32, -23.54 as shown in Fig. 2(d). The former pair appear as anti-phase doublet of doublet of triplets ($J_{\text{HH}} = -6.4$, $J_{\text{PH}} = 8.5$ and 22 Hz) and anti-phase doublet of triplets ($J_{\text{HH}} = -6.4$, and $J_{\text{PH}} = 14$ Hz), respectively, while the latter pair both appear with anti-phase doublet of triplet multiplicities ($J_{\text{HH}} = -4.5$, and $J_{\text{PH}} = 18.5$ and 17 Hz, respectively). The ¹H NMR chemical shifts of these products are consistent with those expected for a binuclear species containing bridging (δ -15) and terminal (δ -21) hydrides.²⁹ These resonances are therefore assigned to the binuclear species H(Cl)Ir(PMe₃)₂(μ -H)(μ -Cl)Ir(PMe₃)(CO) and (H)₂Ir(PMe₃)₂(μ -Cl)₂Ir(PMe₃)(CO), respectively. The observation of a triplet

at δ -16.31, due to the HCl transfer product IrH(CO)Cl₂(PMe₃)₂ **5**-[Cl-Me] and complex features in the region δ -9.5 and -11, accompanied these changes.¹⁰ On warming to 333 K, the hydride resonances due to (H)₂Ir(PMe₃)₂(μ -Cl)₂Ir(PMe₃)(CO) disappeared while those due to H(Cl)Ir(PMe₃)₂(μ -H)(μ -Cl)Ir(PMe₃)(CO) and the *mer-trans-P* isomer of **7**-[H-Ph] grew in intensity. Signals due to **3**-[Cl-Me] could also be picked out above the noise in the spectral baseline at this point. Interestingly, no evidence was obtained in these spectra to suggest that **4**-[H-Ph] was formed by photolysis.

When this reaction is repeated with ¹³CO labelled **1**-[Cl-Me] a new product resonance was observed at δ -9.56 that failed to couple to ³¹P. This signal has been tentatively assigned to the *facial* isomer of H₃Ir(CO)₃ and only becomes visible through the complex effects associated with the ¹³C labelling that enable the formation of a second-order spin system containing the H₃ group. NMR data for these species are listed in Table 1. Scheme 3 summarises the reaction products observed with the PMe₃ based system.

Oxidative addition of H₂ to Ir(CO)Cl(AsPh₃)₂, **1**-[Cl-As]

Addition of H₂ to the triphenylarsine analogue Ir(CO)Cl(AsPh₃)₂ **1**-[Cl-As] at 295 K produces three hydride resonances in the corresponding ¹H NMR spectrum at δ -7.11, -18.91 and -9.62 with relative intensities of 1 : 1 : 5.7. These correspond to **2**-[Cl-As] and **3**-[Cl-As] and are formed *via* addition over the Cl-Ir-CO and As-Ir-As axes, respectively. The initial ratio of **2**-[Cl-As] : **3**-[Cl-As] of 1 : 2.85 suggests that at 295 K the associated difference in free energy of activation corresponds to 2.5 kJ mol⁻¹ in favour of addition over the As-Ir-As axis. However, after five days at 295 K, these product equilibrate and the ratio of **2**-[Cl-As] : **3**-[Cl-As] changes to 1 : 0.1. This suggests that **2**-[Cl-As], the thermodynamic product, is 5.6 kJ mol⁻¹ lower in free energy than **3**-[Cl-As] at 295 K. Key resonances for **2**-[Cl-As] and **3**-[Cl-As] are listed in Table 1.

When this reaction was repeated with *p*-H₂ at 295 K, the hydride resonances for **2**-[Cl-As] were initially enhanced. However, once all the **1**-[Cl-As] was consumed normal signals were observed. H₂ addition is therefore irreversible on the NMR timescale. Furthermore, in this reaction, the isomer formed by H₂ addition over the As-Ir-As axis is not *p*-H₂ enhanced since the two hydrides are both chemically and magnetically equivalent. A significant consequence of this simplification is the lack of structural information associated with the corresponding hydride resonance. However, the identity of **3**-[Cl-As] was secured by a series of NMR measurements. For example, the corresponding hydride resonance for **3**-[Cl-As] connects to *ortho*-phenyl protons at δ 7.52 (strong connection), and coincident *meta* and *para* protons δ 6.93 (weaker connection), in a 2D nOe spectrum.

Interestingly, at 338 K observation with *p*-H₂ revealed the formation of a third H₂ addition product, **8**-[Cl-As] with hydride resonances at δ -11.69 and -18.50 (Fig. 1(c)). The corresponding 2D nOe NMR spectrum revealed that the hydride yielding the resonance at δ -11.69 connected to a single *ortho*-phenyl resonance at δ 7.65, while that at δ -18.50 was close to this group and a second whose *ortho* phenyl proton resonates at δ 7.60. This product must therefore contain two inequivalent arsine ligands that are *cis* to the hydride which resonates at δ -18.50. When ¹³CO **1**-[Cl-As] was employed, both the hydride resonances of **8**-[Cl-As] are split by an additional ¹³C coupling that is typical of a *cis* carbonyl-hydride arrangement. Consequently, the hydrides lie *trans* to arsine and halide, respectively, and the structure shown in Scheme 1 is supported.

Under these conditions, the nOe spectra also revealed that while **8**-[Cl-As] undergoes exchange with free H₂ no exchange with **2**-[Cl-As] or **3**-[Cl-As] occurs. This observation requires

the formation of **8-[Cl-As]** by direct H₂ addition to **1-[Cl-As]** and suggests that **1-[Cl-As]** can exist in both *cis* and *trans* configurations at this temperature (Scheme 1). Direct H₂ addition across the Cl–Ir–As axis of the *cis* isomer would be expected to yield **8-[Cl-As]**. At 338 K, four further hydride resonances are observed, corresponding to coupled pairs at $\delta = -14.01$, -22.72 and $\delta = -9.99$ and -11.44 . These resonances correspond to the complexes IrH₂(AsPh₃)₃Cl, **9-[Cl-As]**, and IrH₃(CO)₂(AsPh₃), **4-[H-As]**, with *meridional* and *facial* geometries respectively. Examination of the hydride and exchange peak integrals enabled the rate of reductive elimination of H₂ in **9-[Cl-As]** to be estimated at 343 K as 5.16 s⁻¹ which compares with that for IrH₂(PPh₃)₃Cl of 4.7 s⁻¹ under the same conditions.^{29c}

Monitoring the exchange of H₂ with IrH₂(CO)Cl(AsPh₃)₂, **2-[Cl-As]**, in the presence of CO

When the reaction of **2-[Cl-As]** with H₂ was monitored in the presence of CO, peaks due to Ir(H)₂Cl(CO)₂(AsPh₃), **6-[Cl-As]**, **4-[H-As]**, *cis,cis* **6-[Cl-H]**, and **5-[Cl-As]** were observed. These complexes have been characterised by nOe and ¹³C NMR measurements, key assignments are listed in Table 1.

Observation of H₂ exchange in IrH₂(CO)Cl(APh₃)₂, **2-[Cl-AsPh]**, after UV irradiation

A solution of IrH₂(CO)Cl(AsPh₃)₂ in benzene-d₆ was placed under 3 atm of *p*-H₂ and exposed to UV light for 5 minutes. At 333 K, the following products were observed: **2-[Cl-AsPh]**, **3-[Cl-As]**, **9-[Cl-As]**, **4-[H-As]**, **6-[Cl-As]** and **5-[Cl-As]**.

Utilisation of PPh₂Cl as a probe to explore the effect of phosphine on the addition of H₂ to Ir(CO)Cl(L)₂

In order to test the assertion of Sargent and Hall that increasing the π -acceptor ability of the phosphine in analogues of Vaska's complex would increase the proportion of addition of hydrogen across the P–Ir–P axis we also examined the reactivity of the complexes Ir(CO)Cl(PPh₃)(PPh₂Cl) **1-[Cl-Ph-Cl]** and Ir(CO)Cl(PPh₂Cl)₂ **1-[Cl-Cl]**. Here, **-[Cl-Ph-Cl]** is used to indicate the presence of both PPh₃ and PPh₂Cl, while **-[Cl-Cl]** corresponds to the fully substituted PPh₂Cl product. These complexes were formed *in situ* by taking a solution of **1-[Cl-Ph]** in benzene-d₆ under 3 atm *p*-H₂ and heating to 333 K with a four-fold excess of PPh₂Cl. This process inevitably led to the formation of a number of products. However, NMR spectroscopy enabled the reactivity profiles of **1-[Cl-Ph-Cl]** and **1-[Cl-Cl]** to be deduced.

Firstly, hydride resonances at $\delta = -6.81$ and -16.99 could be readily assigned to the mono-substituted product **2-[Cl-Ph-Cl]**, while those at $\delta = -7.24$ and -16.73 correspond to signals from **2-[Cl-Cl]**, the bis-substituted counterpart. However, of greater significance was the observation of strong signals at $\delta = -8.13$ and -8.34 due to **3-[Cl-Ph-Cl]**, the *cis,cis* isomer of the monosubstituted complex, and at $\delta = -8.37$ due to **3-[Cl-Cl]** respectively. These signals can be viewed in Fig. 1d. The former species is formed by H₂ addition across the P–Ir–P axis of Ir(CO)(PPh₃)(PPh₂Cl)Cl. Since **3-[Cl-Ph-Cl]** now contains inequivalent phosphines two hydride resonances result. Consequently, each resonance appears as doublet of doublet of doublets with couplings typical for *cis* and *trans* phosphine orientations. The ratio of hydride signals for **2-[Cl-Ph-Cl]** and **3-[Cl-Ph-Cl]** at 333 K suggests that these species are formed in the ratio 4 : 1; this corresponds to an activation barrier difference of 3.8 kJ mol⁻¹. Pairs of much weaker hydride resonances were observed, at $\delta = -7.52$, -9.50 and -7.25 , -9.72 due to the analogues of **8-[Cl-As]**, **8-[Cl-Ph-Cl]** and **8-[Cl-Cl]**, respectively. In **8-[Cl-Ph-Cl]**, the PPh₃ ligand lies *trans* to chloride. It should be noted that this is by no means a synthetic route to the PPh₂Cl substituted analogues of Vaska's complex since they react further to produce a multitude of hydride dichloride complexes.

Experimental

All sample preparations were completed using either a nitrogen filled glove box or a Schlenk line. Solvents were dried over potassium and degassed prior to use. NMR measurements were made using NMR tubes that were fitted with J. Young Teflon valves and solvents were added by vacuum transfer on a high vacuum line. Triphenylphosphine (Aldrich), trimethylphosphine (Aldrich) and hydrogen (99.99%, BOC) were used as received. Ir(CO)Cl(PPh₃)₂, **1-[Cl-Ph]** and Ir(CO)Cl(PMe₃)₂, **1-[Cl-Me]** were prepared according to established methods.³⁰ An attempt to prepare Ir(CO)Cl(AsPh₃)₂ **1-[Cl-As]** by the same synthetic route used to prepare Ir(CO)Cl(PPh₃)₂ gave only a low yield of Ir(AsPh₃)₃Cl. **1-[Cl-As]** was successfully synthesised by bubbling CO through a 2-methoxyethanol solution of Na₂IrCl₆·6H₂O for 3.5 hours.³¹ AsPh₃ was then added to the reaction mixture at room temperature and the solution was then refluxed for 15 minutes. The solution was filtered hot and crystals of **1-[Cl-As]** precipitated on cooling: ¹³C (CO) δ 207.0 in CD₂Cl₂, ν (CO) = 1950 cm⁻¹ (CH₂Cl₂).

For the parahydrogen experiments, hydrogen enriched in the para spin state was prepared by cooling H₂ to 77 K over a paramagnetic catalyst as described previously. An atmosphere of H₂ equivalent to *ca.* 3 atm. pressure at 298 K was introduced into the resealable NMR tube on a high vacuum line. The samples were thawed immediately prior to use and introduced into the NMR spectrometer at the pre-set temperature. Parahydrogen-enhanced NMR spectra were recorded on Bruker DRX-400 spectrometers with ¹H at 400.13, ³¹P at 161.92, ¹³C at 100, respectively. ¹H NMR chemical shifts are reported in ppm relative to residual ¹H signals in the deuterated solvents (benzene-d₆, $\delta = 7.13$, and toluene-d₈, $\delta = 2.13$). ³¹P{¹H} NMR data are reported in ppm downfield of an external 85% solution of phosphoric acid, ¹³C NMR data are reported relative to benzene-d₆, $\delta = 128.0$, and toluene-d₈, $\delta = 21.3$. Modified ¹H–¹H-COSY, HMQC and NOESY pulse sequences were used as previously described.^{20b,32,33}

Conclusions

Our studies of the complexes Ir(CO)Cl(L)₂ [L = PPh₃, PMe₃, AsPh₃ and PPh₂Cl, and L₂ = (PPh₂Cl)(PPh₃)] have revealed a strong dependence of the relative stabilities of the *cis,cis* and *cis,trans* isomers of the H₂ addition product, Ir(H)₂(CO)Cl(L)₂, on the nature of the phosphine ligand. For L = PPh₃, the *cis,trans* isomer produced by H₂ addition over the Cl–Ir–CO axis is the more stable by such a wide margin that the *cis,cis* was previously undetected. At 295 K, the difference in activation barriers between addition over the Cl–Ir–CO and L–Ir–L axes has been estimated to be at least 11 kJ mol⁻¹. For L = PMe₃, at 333 K the ratio of *cis,trans* to *cis,cis* addition products was 93 : 1. This corresponds to a difference in activation barriers of 12.5 kJ mol⁻¹. Both these values are consistent with that of 9.5 kJ mol⁻¹ calculated by Sargent and Hall for L = PMe₃.¹⁴ The gap narrows for L = AsPh₃, where both isomers can be detected without the need for *p*-H₂. At 295 K, the initially observed ratio of *cis,trans* and *cis,cis* addition products corresponds to a free energy of activation difference of 2.5 kJ mol⁻¹ in favour of the *cis,cis* form. However, on standing these two isomers equilibrate, with the equilibrium position interchanging the dominant form *via* a 5.6 kJ mol⁻¹ free energy difference in favour of the *cis,trans* product. Here matters are further complicated by the observation of a third isomer corresponding to addition over the Cl–Ir–As axis at 338 K. This suggests that the precursor, Ir(CO)Cl(AsPh₃)₂, can exist in both *cis* and *trans* isomers at high temperatures. Further reaction products corresponding to IrH₃(CO)₂(AsPh₃), IrH(CO)(Cl)₂(AsPh₃)₂ and IrH₂(AsPh₃)₃ are also observed to grow in under these conditions. These can be categorised as the products of CO and AsPh₃ exchange, and the product of HCl transfer to

Ir(CO)Cl(AsPh₃)₂. When Ir(CO)Cl(PPh₃)₂ was warmed in the presence of PPh₂Cl, products corresponding to H₂ addition to Ir(CO)Cl(PPh₃)(PPh₂Cl) were observed. In this case, the ratio of hydride signals for the *cis,trans* and *cis,cis* isomers of Ir(H)₂(CO)(Cl)(PPh₃)(PPh₂Cl) was 4 : 1 at 333 K. This corresponds to an activation barrier difference of 3.8 kJ mol⁻¹ and suggests that substituents on the phosphine that enhance its π accepting capabilities decrease the barrier to addition over the L–Ir–L axis in accordance with the suggestions of Sargent and Hall.¹⁴

We have obtained evidence to suggest that in the case of L = PPh₃ and PMe₃ the formation of IrH₃(CO)₂(L) occurs via the initial formation of IrH₂(CO)₂Cl(L). This reaction product is clearly formed when Ir(H)₂(CO)Cl(L)₂ is warmed under an atmosphere containing both H₂ and CO. Subsequently, IrH₂(CO)₂Cl(PPh₃) undergoes HCl elimination which accounts for the observation IrH(Cl)₂(CO)(PPh₃)₂. The 16-electron complex IrH(CO)₂(L) formed by this process rapidly reacts with H₂ to yield IrH₃(CO)₂(L). Additional products corresponding the *meridional* and *facial* isomers of IrH₃(CO)(L)₂ are also observed as minor reaction products in these reactions. However, when samples of Ir(H)₂(CO)Cl(L)₂ are subject to UV irradiation prior to warming with *p*-H₂ these species correspond to the dominant photo-products when L = PPh₃.

The photochemical studies are complicated by the observation of signals that we have attributed to Ir(H)₂(PPh₃)(PPh₂-C₅H₄CO) containing an unusual η²-acyl ligand when L = PPh₃. Furthermore, with L = PMe₃, signals for the binuclear products H(Cl)Ir(PMe₃)₂(μ-H)(μ-Cl)Ir(PMe₃)(CO) and (H)₂Ir(PMe₃)₂(μ-Cl)₂Ir(PMe₃)(CO) are detected after irradiation at 295 K. It has therefore been demonstrated that *p*-H₂ enhanced NMR studies can be used to provide experimental proof that complements theoretical investigations.

Acknowledgements

S. B. D. is grateful to the University of York, the EPSRC (C. J. S., S. A. C. and S. K. H.), the JREI scheme, Bruker UK (CASE award SAC and spectrometer) and BP Chemicals (CASE award SKH) for financial support. Discussions with Dr R. Watt, Dr M. Payne, Prof. R. N. Perutz and Dr R. J. Mawby are gratefully acknowledged.

References

- L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, 1961, **83**, 2784.
- L. Vaska, *Science*, 1966, **152**, 769.
- L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, 1966, **88**, 1333.
- S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 405.
- L. Vaska, *Science*, 1963, **140**, 809.
- S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, 1965, **87**, 2581.
- G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451.
- P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 155.
- C. Bianchini, C. Mealli, M. Peruzzini and F. Zanobini, *J. Am. Chem. Soc.*, 1987, **109**, 5548.
- M. J. Burk, M. P. McGrath, R. Wheeler and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 5034.
- D. R. Anton and R. H. Crabtree, *Organometallics*, 1983, **2**, 621.
- (a) C. E. Johnson, B. J. Fisher and R. Eisenberg, *J. Am. Chem. Soc.*, 1983, **105**, 7772; (b) C. E. Johnson and R. Eisenberg, *J. Am. Chem. Soc.*, 1985, **107**, 3148; (c) C. E. Johnson and R. Eisenberg, *J. Am. Chem. Soc.*, 1985, **107**, 6531; (d) P. P. Deutsch and R. Eisenberg, *Chem. Rev.*, 1988, **88**, 1147.
- A. L. Sargent, M. B. Hall and M. F. Guest, *J. Am. Chem. Soc.*, 1992, **114**, 517.
- A. L. Sargent and M. B. Hall, *Inorg. Chem.*, 1992, **31**, 317.
- X. Luo, D. Michos, R. H. Crabtree and M. B. Hall, *Inorg. Chim. Acta*, 1992, **200**, 429.
- C. R. Bowers and D. P. Weitekamp, *J. Am. Chem. Soc.*, 1987, **109**, 5541; R. Eisenberg, *Acc. Chem. Res.*, 1991, **24**, 110; J. Natterer and J. Bargon, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1997, **31**, 293; C. J. Sleight and S. B. Duckett, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1999, **34**, 71.
- S. B. Duckett, C. L. Newell and R. Eisenberg, *J. Am. Chem. Soc.*, 1994, **116**, 10548; S. B. Duckett and R. Eisenberg, *J. Am. Chem. Soc.*, 1993, **115**, 5292; S. B. Duckett, R. J. Mawby and M. G. Partridge, *Chem. Commun.*, 1996, 383; P. D. Morran, S. A. Colebrooke, S. B. Duckett, J. A. B. Lohmann and R. Eisenberg, *J. Chem. Soc., Dalton Trans.*, 1998, 3363.
- P. Hubler, R. Giernoth, G. Kummerle and J. Bargon, *J. Am. Chem. Soc.*, 1999, **121**, 5311.
- S. K. Hasnip, S. B. Duckett, C. S. Sleight, D. R. Taylor, G. K. Barlow and M. J. Taylor, *Chem. Commun.*, 1999, 1717.
- (a) C. J. Sleight, S. B. Duckett and B. A. Messerle, *Chem. Commun.*, 1996, 2395; (b) B. A. Messerle, C. J. Sleight, M. G. Partridge and S. B. Duckett, *J. Chem. Soc., Dalton Trans.*, 1999, 1429.
- A. L. Sargent and M. B. Hall, *Inorg. Chem.*, 1992, **31**, 317.
- (a) S. Hasnip, S. B. Duckett, D. R. Taylor and M. J. Taylor, *Chem. Commun.*, 1998, 923; (b) S. P. Millar, D. L. Zubris, J. E. Bercaw and R. Eisenberg, *J. Am. Chem. Soc.*, 1998, **120**, 5329.
- L. Malatesta, M. Angoletta and F. Conti, *J. Organomet. Chem.*, 1971, C43.
- A. J. Kunin and R. Eisenberg, *Organometallics*, 1998, **7**, 2124.
- M. A. Bennett and J. L. Latten, *Inorg. Synth.*, 1989, **26**, 202.
- P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
- C. A. Gilhardi, S. Midollini, S. Moneti and A. Oslandini, *J. Chem. Soc., Dalton Trans.*, 1988, 1833.
- K. Caulton, B. E. Hauger and D. Gusev, *J. Am. Chem. Soc.*, 1994, **116**, 208.
- (a) S. B. Duckett, R. Eisenberg and A. S. Goldman, *J. Chem. Soc., Chem Commun.*, 1993, 1185; (b) S. B. Duckett and R. Eisenberg, *J. Am. Chem. Soc.*, 1993, **115**, 5292; (c) P. D. Morran, S. A. Colebrooke, S. B. Duckett, J. A. B. Lohmann and R. Eisenberg, *J. Chem. Soc., Dalton Trans.*, 1998, 3363.
- J. P. Collman, C. T. Sears Jr. and M. Kubota, *Inorg. Synth.*, 1990, **28**, 92.
- G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, 1969, 725.
- (a) W. P. Aue, E. Bartholdi and R. R. Ernst, *J. Chem. Phys.*, 1976, **64**, 2229; (b) K. Nagayama, A. Kumar, K. Wüthrich and R. R. Ernst, *J. Magn. Reson.*, 1980, **40**, 321.
- A. Bax, R. H. Griffey and B. L. Hawkins, *J. Magn. Reson.*, 1983, **55**, 301.