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FULL PAPER

Activation of H_2 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 †

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The iridium phosphine complexes $Ir(CO)Cl(L)_2$ [L = PPh_3, PMe_3, $AsPh_3$ and PPh_2Cl, and L_2 = $(PPh_2Cl)(PPh_3)$] add H_2 to form the corresponding dihydrides $IrH_2(CO)Cl(L)_2$. These products are detected at enhanced levels of sensitivity through the ^1H NMR signatures of their hydride resonances *via* para-hydrogen (*p*-H_2) based spin state synthesis. Products corresponding to addition across both the Cl–Ir–CO and L–Ir–L axes are detected. For L = PPh_3, there is a 100 fold preference for the former pathway at 295 K, while for L = $AsPh_3$ 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 = $AsPh_3$ and PPh_2Cl. Under these conditions, the CO and HCl transfer products $Ir(H)_3(CO)_2(AsPh_3)$, and $IrH(CO)Cl_2(AsPh_3)_2$ are also formed in a thermal reaction. When $IrH_2(CO)Cl(L)_2$ is warmed or photolysed with H_2 and CO, the corresponding products are produced for L = PPh_3 and PMe_3. However after photolysis with H_2 alone $Ir(H)_3(CO)(L)_2$ is the favoured product. Additional products detected during the photochemical studies include $Ir(H)_2(PPh_3)(PPh_2C_5H_4CO)$, an unusual orthometallation product containing an η^2-acyl ligand, and the binuclear products $H(Cl)Ir(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Ir(PMe_3)(CO)$ and $(H)_2Ir(PMe_3)_2(\mu\text{-}Cl)_2Ir(PMe_3)(CO)$.

Introduction

The examination of the oxidative addition of H_2 to d^8 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*-$Ir(CO)Cl(PPh_3)_2$, or Vaska's complex[1] has played a particularly important role in this process *via* studies of stoichiometric reactions with species such as H_2, O_2, SO_2, CO, HCl, CS_2 and CH_3I. These additions can generally be categorised as either coordinative addition or oxidative addition.[2–4] For instance, the observation that *trans*-$Ir(CO)Cl(PPh_3)_2$ acts as a reversible oxygen carrier,[5] led to a crystal structure of the oxygenated complex $Ir(CO)Cl(O_2)(PPh_3)_2$[6] 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) O_2 adduct. The binding of H_2 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 Morris[8] 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}, $\nu(M–H_2)$ = 850–950 cm^{-1} and relaxation delay, T_1 (200 MHz) 5–22 ms. There are, however, still some complexes, such as $[RhH_2(pp_3)]^+$ (where pp_3 = tetraphos-2, $P(CH_2CH_2PPh_2)_3$),[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 H_2 addition to square-planar $Ir(CO)Cl(PPh_3)_2$ proceeds *via* a concerted route and leads to the formation of an octahedral product with *cis* hydrides. Whilst two possible isomers, *cis*,*trans*-$IrH_2Cl(CO)(PPh_3)_2$ and *cis*,*cis*-$IrH_2Cl(CO)(PPh_3)_2$, 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 group[10] addition at low temperature occurs across the P–Ir–P axis. In the case of $IrPh(CO)(PMe_3)_2$ 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 $[(dct)Ir(PPh_3)_2]BF_4$, where dct = dibenzo[*a*,*e*]-cyclooctatetraene, enabled them to show that H_2 addition led to an all-*cis* kinetic product[11] 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 complexes[12] 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 H_2 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 H_2 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.

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Sargent, Hall and Guest investigated the oxidative addition of H_2 to IrCl(CO)(dppe) by *ab initio* MO techniques[13] using two *cis* PH_3 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 complex[14] predicted that addition across the P–Ir–P axis proceeded *via* the more stable transition state for PH_3. However, upon improving the accuracy of the simulation by utilisation of PMe_3, 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 H_2 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 prediction[15] addition across the Cl–Ir–CO axis was still observed.

It has been shown that the addition of H_2 enriched in the *para* spin state to a transition metal centre leads to greatly enhanced hydride signals in associated ^{1}H 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* $Ru(H)_2(CO)_2(PMe_3)_2$[17] and the investigation of hydrogenation products and kinetics.[18] Here we describe how para-hydrogen 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 = PPh_3, PMe_3, $AsPh_3$, PPh_2Cl) and demonstrate that at elevated temperatures $Ir(H)_2(CO)Cl(L)_2$ reacts to form a series of iridium trihydride complexes such as $IrH_3(CO)_2L$ *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 H_2 to $Ir(CO)Cl(PPh_3)_2$, 1-[Cl-Ph]

It has been reported previously that when a 0.1 mM solution containing $Ir(CO)Cl(PPh_3)_2$, **1-[Cl-Ph]**, in toluene-d_8 under 3 atm *p*-H_2 is examined by ^{1}H NMR spectroscopy at 343 K the hydrogen addition product $IrH_2(CO)Cl(PPh_3)_2$, **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 H_2 addition to a 0.1 mM solution of **1-[Cl-Ph]** in benzene-d_6 under 3 atm *p*-H_2 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 ^{1}H 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 H_2 addition that is generated by reaction across the P–Ir–P axis. ^{31}P and ^{13}C chemical shift information was determined for the CO and phosphine ligands of this product via suitable *p*-H_2 enhanced 2D NMR experiments.[20b] These data confirm that **3-[Cl-Ph]** corresponds to *cis,cis*-$IrH_2(CO)Cl(PPh_3)_2$. It should

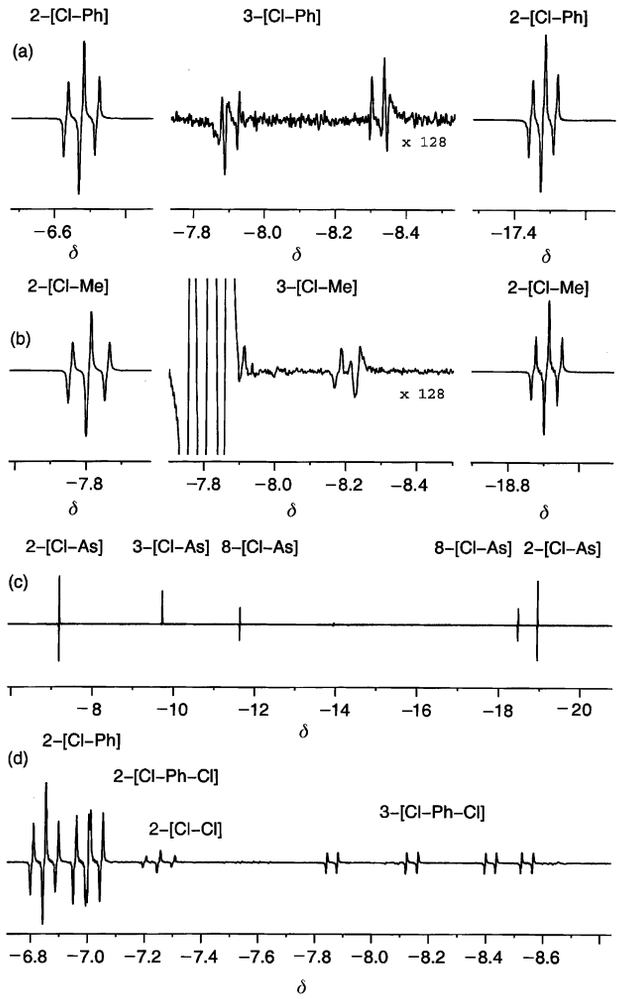
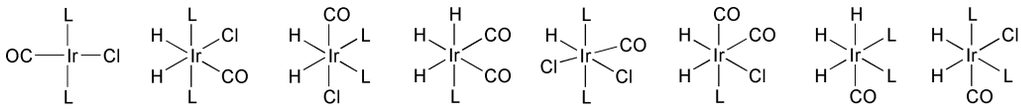


Fig. 1 (a) ^{1}H NMR spectrum (400 MHz, 295 K) of a 0.1 mM solution of **1-[Cl-Ph]** in benzene-d_6 under 3 atm of *p*-H_2. The weak second order resonance arises from *cis,cis*-$IrH_2(CO)Cl(PPh_3)_2$ **3-[Cl-Ph]**. (b) ^{1}H NMR spectrum (400 MHz, 333 K) of a 0.1 mM solution of **1-[Cl-Me]** in benzene-d_6 under 3 atm of *p*-H_2 with resonances due to **2-[Cl-Me]** and **3-[Cl-Me]** indicated. (c) ^{1}H NMR spectrum (400 MHz, 338 K) of a 0.1 mM solution of **1-[Cl-As]** in benzene-d_6 under 3 atm of *p*-H_2 showing resonances due to **2-[Cl-As]**, **3-[Cl-As]** and **8-[Cl-As]**. (d) ^{1}H NMR spectrum (400 MHz, 333 K) of a 0.1 mM solution of **1-[Cl-Ph]** in benzene-d_6 in the presence of a four-fold excess of PPh_2Cl under 3 atm of *p*-H_2 showing resonances due to **2-[Cl-Ph]**, **2-[Cl-Ph-Cl]**, **2-[Cl-Cl]** and **3-[Cl-Ph-Cl]**.

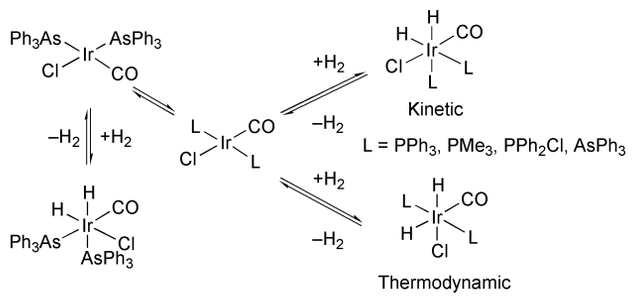
be noted at this point that the complexes described in this paper are referred to according to the designation X-[Y-Z] where X is the compound number, Y indicates whether the H_2 addition product contains additional chloride or hydride, and Z refers to the substituent on L, except for L = $AsPh_3$ where 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*-H_2 addition to be observed only once. This constraint was achieved by applying a 90° ^{1}H 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° ^{1}H read pulse was applied to enable the detection of any *p*-H_2 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 H_2 addition pathways of 11 kJ mol^{-1} at 295 K. We have already described how Sargent and Hall have investigated the oxidative addition of H_2 to Vaska's complex with *ab*



1-[Cl-Ph]	2-[Cl-Ph]	3-[Cl-Ph]	4-[H-Ph]	5-[Cl-Ph]	6-[Cl-Ph]	7-[H-Ph]		L = PPh_3
1-[Cl-Me]	2-[Cl-Me]	3-[Cl-Me]	4-[H-Me]	5-[Cl-Me]	6-[Cl-Me]	7-[H-Me]		L = PMe_3
1-[Cl-As]	2-[Cl-As]	3-[Cl-As]	4-[H-As]	5-[Cl-As]	6-[Cl-As]	7-[H-As]	8-[Cl-As]	L = $AsPh_3$
	2-[Cl-Ph-Cl]	3-[Cl-Ph-Cl]					8-[Cl-Ph-Cl]	L = PPh_2Cl and PPh_3
	2-[Cl-Cl]	3-[Cl-Cl]					8-[Cl-Cl]	L = PPh_2Cl

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*-H_2.

initio MO techniques.[21] They found that for PH_3 addition across the P–Ir–P axis proceeded *via* the more stable transition state whilst for PMe_3 this situation was reversed. In absolute terms, PH_3 addition across the P–Ir–P axis was favoured by 37.21 kJ mol^{-1}, while for PMe_3, 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 H_2 with $IrH_2(CO)Cl(PPh_3)_2$, 2-[Cl-Ph], in the presence of CO

In order to monitor the reaction of **2-[Cl-Ph]** with *p*-H_2 in the presence of CO an NMR sample of ^{13}C labelled **1-[Cl-Ph-^{13}CO]** was first converted to **2-[Cl-Ph-^{13}CO]** by reaction with H_2 in benzene-d_6. The sample of **2-[Cl-Ph-^{13}CO]** prepared in this way was then placed under 300 mm Hg of ^{13}CO, the solution frozen, and the headspace of the NMR tube filled with 3 atm of *p*-H_2. 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-^{13}CO]**, 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*-H_2 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 ^{31}P nucleus, consequently

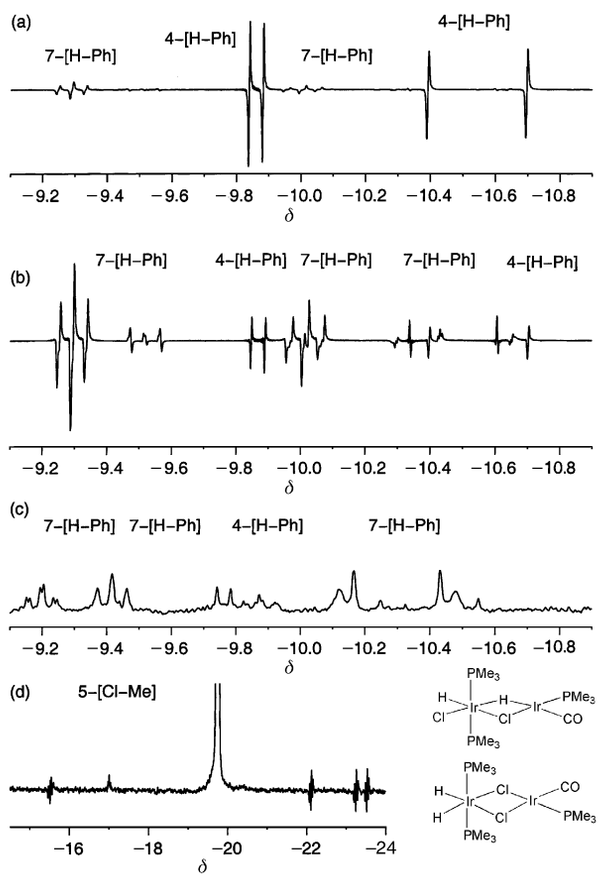


Fig. 2 (a) ^1H NMR spectrum (400 MHz, 333 K) of a 0.1 mM solution of **1-[Cl-Ph]** in benzene-d_6 under CO and 3 atm of *p*-H_2 recorded after 5 minutes UV irradiation. Resonances for the *fac-cis* isomer of **4-[H-Ph]** are clearly seen. (b) ^1H NMR spectrum (400 MHz, 338 K) of a 0.1 mM solution of **1-[Cl-Ph]** in benzene-d_6 under 3 atm of *p*-H_2 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-d_6 under 3 atm of *p*-H_2 after 5 minutes UV irradiation showing resonances due to $H(Cl)Ir(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Ir(PMe_3)(CO)$, and $(H)_2Ir(PMe_3)_2(\mu\text{-}Cl)_2Ir(PMe_3)(CO)$ (structures inset).

the product must correspond to $IrH_3(CO)_2(PPh_3)$ **4-[H-Ph-^{13}CO]**. Furthermore, since these protons couple to a single ^{13}CO 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

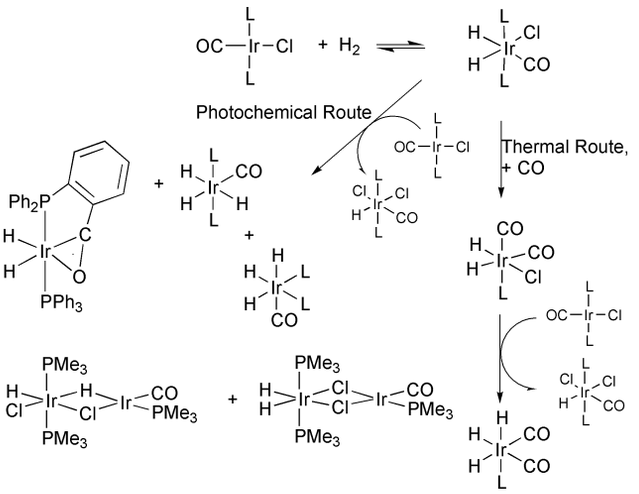
Complex, temp.	Nucleus	δ (multiplicity)	Assignment	Coupling constant/Hz, assignment
2-[Cl-Ph], 295 K	^{1}H	7.92 (m)	PPh_3 (*o*-H)	
		−6.69 (td)	Ir–H	−4.6 $^{2}J_{HH}$, 17.4 $\|^{2}J_{PH}\|$, 43.7 $\|^{2}J_{CH}\|$
		−17.48 (td)	Ir–H	−4.6 $^{2}J_{HH}$, 17.4 $\|^{2}J_{PH}\|$, 4.1 $\|^{2}J_{CH}\|$
	^{31}P]	9.9	PPh_3	15 $\|^{2}J_{CH}\|$
	^{13}C	177.8 (t)	CO	5 $\|^{2}J_{CP}\|$
2-[Cl-Me], 295 K [a]	^{1}H	1.40 (m)	CH_3	7.3 $\|^{2}J_{PH} + {}^{4}J_{PH}\|$
		−7.86 (td)	Ir–H	−5.2 $^{2}J_{HH}$, 20.8 $\|^{2}J_{PH}\|$
		−18.98 (td)	Ir–H	−5.2 $^{2}J_{HH}$, 14.7 $\|^{2}J_{PH}\|$
	^{31}P	−41.1	PMe_3	14.6 $\|^{2}J_{PC}\|$
	^{13}C	177.6 (t)	CO	14.6 $\|^{2}J_{CP}\|$
2-[Cl-As], 295 K	^{1}H	7.93 (m)	$AsPh_3$ (*o*-H)	
		7.01 (m)	$AsPh_3$ (*m,p*-H)	
		−7.11 (d)	Ir–H	−5.0 $^{2}J_{HH}$, 44.5 $\|^{2}J_{CH}\|$
		−18.91 (d)	Ir–H	−5.0 $^{2}J_{HH}$, 3.7 $\|^{2}J_{CH}\|$
	^{13}C	177.2 (s)	*C*O	
2-[Cl-Ph-Cl], 295 K	^{1}H	7.85 (m)	PPh_3 (*o-H*)	
		−6.81 (ddd)	Ir–H	−4.7 $^{2}J_{HH}$, 17.3 $\|^{2}J_{PH}\|$, 19.7 $\|^{2}J_{PH}\|$, 44.0 $\|^{2}J_{CH}\|$
		−16.99 (td)	Ir–H	−4.7 $^{2}J_{HH}$, 17.3 $\|^{2}J_{PH}\|$, 17.3 $\|^{2}J_{PH}\|$, 4.4 $\|^{2}J_{CH}\|$
	^{31}P	9.0 (d)	PPh_3	398.6 $\|^{2}J_{PP}\|$
		66.2 (d)	PPh_2Cl	398.6 $\|^{2}J_{PP}\|$
	^{13}C	176.3 (t)	CO	6 $\|^{2}J_{PC}\|$
2-[Cl-Cl], 333 K	^{1}H	−7.24 (td)	Ir–H	−5.0 $^{2}J_{HH}$, 20.3 $\|^{2}J_{PH}\|$, 44 $\|^{2}J_{CH}\|$
		−16.73 (td)	Ir–H	−5.0 $^{2}J_{HH}$, 15.0 $\|^{2}J_{PH}\|$, 3.5 $\|^{2}J_{CH}\|$
	^{31}P	65.1	PPh_2Cl	
	^{13}C	174.8 (t)	CO	7 $\|^{2}J_{CP}\|$
3-[Cl-Ph], 295 K	^{1}H	−8.10 (2nd order)	Ir–H	179 $\|^{2}J_{PH\ trans} + {}^{2}J_{PH\ cis}\|$
	^{31}P	−5.9	PPh_3	
	^{13}C	167.1	CO	
3-[Cl-Me], 295 K	^{1}H	1.23	PMe_3	
		−8.00 (2nd order)	Ir–H	Obscured
	^{31}P	−51.0	PMe_3	14.6 $\|^{2}J_{PC}\|$
	^{13}C	173.7	CO	
3-[Cl-As], 295 K	^{1}H	7.52 (m)	$AsPh_3$ (*o*-H)	
		6.93 (m)	$AsPh_3$ (*m,p*-H)	
		−9.62 (s)	Ir–H	6.4 $\|^{2}J_{CH}\|$
	^{13}C	165.7 (s)	CO	
3-[Cl-Ph-Cl], 333 K	^{1}H	−8.13 (ddd)	Ir–H	−1.8 $^{2}J_{HH}$, 15.0 $\|^{2}J_{PH}\|$, 224.7 $\|^{2}J_{PH}\|$, 6.5 $\|^{2}J_{CH}\|$
		−8.34 (ddd)	Ir–H	−1.8 $^{2}J_{HH}$, 160.8 $\|^{2}J_{PH}\|$, 15.9 $\|^{2}J$PH|, 6.7 $\|^{2}J_{CH}\|$
	^{31}P	−4.0 (d)	PPh_3	28.5 $\|^{2}J_{PP}\|$
		65.2 (d)	PPh_2Cl	28.5 $\|^{2}J_{PP}\|$
	^{13}C	165.3	CO	6 $\|^{2}J_{PC}\|$
3-[Cl-Cl], 333 K	^{1}H	−8.37	Ir–H	
	^{31}P	62.9 (s)	PPh_2Cl	
mer-trans-**4-[H-Ph]**, 333 K	^{1}H	−8.8 (dd)	Ir–H	5.2 $^{2}J_{HH}$, 136.9 $\|^{2}J_{PH}\|$
		−9.7 (dd)	Ir–H	5.2 $^{2}J_{HH}$, 14.8 $\|^{2}J_{PH}\|$
	^{31}P	25.4 (s)	PPh_3	
fac-cis-**4-[H-Ph]**, 333 K	^{1}H	−9.88 (dd)	Ir–H	−2.4 $^{2}J_{HH}$, 17.2 $\|^{2}J_{PH}\|$, 39.5, 5.8 $\|^{2}J_{CH}\|$
		−10.52 (dd)	Ir–H	−2.4 $^{2}J_{HH}$, 121.6 $\|^{2}J_{PH}\|$, 4 $\|^{2}J_{CH}\|$
	^{31}P	3.29 (s)	PPh_3	
	^{13}C	172.2 (s)	CO	
mer-cis-**4-[H-Me]**, 333 K	^{1}H	−10.06 (dd)	Ir–H	−4.7 $^{2}J_{HH}$, 21.4 $\|^{2}J_{PH}\|$, 8.7 $\|^{2}J_{CH}\|$
		−10.97 (dd)	Ir–H	−4.7 $^{2}J_{HH}$, 22.0 $\|^{2}J_{PH}\|$, 31.3 $\|^{2}J_{CH}\|$
	^{31}P	−50.7 (s)	*P*Me_3	
fac-cis-**4-[H-Me]**, 333 K	^{1}H	−10.60 (dd)	Ir–H	−2.9 $^{2}J_{HH}$, 19.1 $\|^{2}J_{PH}\|$, 40.6 $\|^{2}J_{CH}\|$
		−10.64 (dd)	Ir–H	−2.9 $^{2}J_{HH}$, 116.5 $\|^{2}J_{PH}\|$
	^{31}P	−60.7 (s)	PMe_3	
	^{13}C	171.9 (s)	CO	
fac-cis-**4-[H-As]**, 338 K	^{1}H	7.54	$AsPh_3$ (*o*-H)	
		−9.99 (d)	Ir–H	−1.5 $^{2}J_{HH}$, 45.2 $\|^{2}J_{CH}\|$
	^{31}P	−11.44 (d)	Ir–H	−1.5 2J_{HH}, 4.9 $\|^{2}J_{CH}\|$
	^{13}C	171.9 (s)	CO	
cis-trans-**5-[Cl-Ph]**, 295 K	^{1}H	−14.51 (t)	Ir–H	11.6 $\|^{2}J_{PH}\|$, 5.2 $\|^{2}J_{CH}\|$
	^{31}P	−2.9 (s)	PPh_3	7.9 $\|^{2}J_{PC}\|$
	^{13}C	163.2 (br)	CO	
trans-trans-**5-[Cl-Ph]**, 295 K	^{1}H	−7.62 (td)	Ir–H	13.7 $\|^{2}J_{PH}\|$, 57.4 $\|^{2}J_{CH}\|$
	^{31}P	4.0 (d)	PPh_3	5.3 $\|^{2}J_{PC}\|$
	^{13}C	173.4 (s)	CO	
trans-cis-**5-[Cl-Me]**, 295 K	^{1}H	−16.31 (dt)	Ir–H	13.1 $\|^{2}J_{PH}\|$, 5.8 $\|^{2}J_{CH}\|$
	^{31}P	−33.1 (s)	PMe_3	
	^{13}C	164.7 (t)	CO	8.1 $\|^{2}J_{PC}\|$
trans-cis-**5-[Cl-As]**, 295 K	^{1}H	8.12	$AsPh_3$ (*o*-H)	
		−15.06 (d)	Ir–H	5.4 $\|^{2}J_{CH}\|$
	^{13}C	162.4 (s)	CO	
cis-cis-**6-[Cl-Ph]**, 313 K (H *trans* to CO)	^{1}H	−7.97 (br dd)	Ir–H	−5.0 $^{2}J_{HH}$, 17.4 $\|^{2}J_{PH}\|$, 45.5 $\|^{2}J_{CH}\|$
		−16.51 (brdd)	Ir–H	−5.0 $^{2}J_{HH}$, 16.0 $\|^{2}J_{PH}\|$, 2.9 $\|^{2}J_{CH}\|$
	^{31}P	5.2 (d)	PPh_3	123.4 $\|^{2}J_{PC}\|$
	^{13}C	170.8 (d)	CO	8 $\|^{2}J_{PC}\|$
		166.1 (d)	CO	123 $\|^{2}J_{PC}\|$

Table 1 (*Contd.*)

Complex, temp.	Nucleus	δ (multiplicity)	Assignment	Coupling constant/Hz, assignment
cis-cis-**6-[Cl-Ph]**, 313 K (H *trans* to PPh_3)	^1H	−7.42 (dddd)	Ir–H	−7.0 $^2J_{HH}$, 14.5 $\|^2J_{PH}\|$, 56.6, 7 $\|^2J_{CH}\|$
		−8.37 (dtd)	Ir–H	−7.0 $^2J_{HH}$, 162.1 $\|^2J_{PH}\|$, 5 $\|^2J_{CH}\|$
	^{31}P	−5.7 (s)	PPh_3	
	^{13}C	169.8 (d)	CO	8 $\|^2J_{PC}\|$
		161.7 (d)	CO	8 $\|^2J_{PC}\|$
cis-trans-**6-[Cl-Ph]**, 313 K	^1H	−9.43 (dd)	Ir–H	6.4 $^2J_{HH}$, 120.9 $\|^2J_{PH}\|$
		−17.03 (dd)	Ir–H	6.4 $^2J_{HH}$, 9.2 $\|^2J_{PH}\|$
	^{31}P	−2.6	PPh_3	
cis-cis-**6-[Cl-Me]**, 313 K	^1H	−8.09	Ir–H	18.8 $\|^2J_{PH}\|$, 52.7 $\|^2J_{CH}\|$, 6 $\|^2J_{CH}\|$
cis-cis-**6-[Cl-Me]**, 333 K (H *trans* to PMe_3)	^1H	−9.12 (dd)	Ir–H	−4.1 $^2J_{HH}$ 16.7 $\|^2J_{PH}\|$
		−9.15 (dd)	Ir–H	−4.1 $^2J_{HH}$ 113.6 $\|^2J_{PH}\|$
cis-cis-**6-[Cl-As]**, 338 K	^1H	−7.38 (d)	Ir–H	−2 $^2J_{HH}$, 56.5, 7.1 $\|^2J_{CH}\|$
		−9.49 (d)	Ir–H	−2 $^2J_{HH}$, 6.1, 4.2 $\|^2J_{CH}\|$
	^{13}C	169.7	CO	
		161.2	CO	
mer-trans-**7-[H-Ph]**, 323 K	^1H	7.91	PPh_3 (*o*-H)	
		−9.26 (td)	Ir–H	−4.0 $^2J_{HH}$, 16.9 $\|^2J_{PH}\|$, 5 $\|^2J_{CH}\|$
		−9.97 (dtd)	Ir–H	−4.0 $^2J_{HH}$, 19.5 $\|^2J_{PH}\|$, 36 $\|^2J_{CH}\|$
	^{31}P	18.0 (s)	PPh_3	
	^{13}C	179.6 (t)	CO	10.3 $\|^2J_{PC}\|$
fac-cis-**7-[H-Ph]**, 323 K	^1H	7.90 (m)	PPh_3 (*o*-H)	
		−9.51 (td)	Ir–H	+2.4 $^2J_{HH}$, 18.3 $\|^2J_{PH}\|$, 37.7 $\|^2J_{CH}$ |
		−10.43 (2nd order)	Ir–H	+2.4 $^2J_{HH}$, 106 $\|^2J_{PH\ trans} + {}^2J_{PH\ cis}\|$
	^{31}P	8.8 (s)	PPh_3	
	^{13}C	179.3 (t)	CO	10.8$\|^2J_{PC}\|$
mer-cis-**7-[H-Ph]**, 333 K	^1H	−9.08 (ddd)	Ir–H	4.6 $^2J_{HH}$, 17.6 $\|^2J_{PH}\|$, 136.4 $\|^2J_{CH}\|$
		−10.10 (obs)	Ir–H	5.8 $\|^2J_{HH}\|$
	^{31}P	20.5 (b)	PPh_3	
		5.1 (b)	PPh_3	
mer-cis-**7-[H-Me]**, 333 K	^1H	−10.82 (dt)	Ir–H	3 $^2J_{HH}$, 21.0 $\|^2J_{PH}\|$
		−11.32 (2nd order)	Ir–H	104.8 $\|^2J_{PH\ trans} + {}^2J_{PH\ cis}\|$
	^{31}P	−50.41 (s)	PMe_3	
mer-trans-**7-[H-Ph]**, 333 K	^1H	−10.95 (dt)	Ir–H	−5 $^2J_{HH}$, 22.0 $\|^2J_{PH}\|$
		−10.74 (dt)	Ir–H	−5 $^2J_{HH}$, 15.5 $\|^2J_{PH}\|$
	^{31}P	−60.06 (s)	PMe_3	
cis-cis-**8-[Cl-As]**, 338 K	^1H	7.65	$AsPh_3$ (*o*-H)	
		7.60	$AsPh_3$ (*o*-H)	
		−11.69 (d)	Ir–H	−5.9 $^2J_{HH}$, 3.4 $\|^2J_{CH}\|$
		−18.50 (d)	Ir–H	−5.9 $^2J_{HH}$, 4.7 $\|^2J_{CH}\|$
	^{13}C	170.3 (s)	*C*O	
cis-cis-**8-[Cl-Ph-Cl]**, 333 K	^1H	−7.52 (ddd)	Ir–H	−2.9 $^2J_{HH}$, 17.0, 23.0 $\|^2J_{PH}\|$, 48.0 $\|^2J_{CH}\|$
		−9.50 (ddd)	Ir–H	−2.9 $^2J_{HH}$, 202, 23.0 $\|^2J_{PH}\|$, 4.4 $\|^2J_{CH}\|$
	^{31}P	5.87 (s)	PPh_3	(*trans* to chloride)
		65.3 (s)	PPh_2Cl	(*trans* to hydride)
		174.0	CO	
cis-cis-**8-[Cl-Cl]**, 333 K	^1H	−7.25 (obs)	Ir–H	
		−9.72 (ddd)	Ir–H	−4.0 $^2J_{HH}$, 21.8 $\|^2J_{PH}\|$, 201.6 $\|^2J_{PH}\|$
	^{31}P	72.3 (br)	PPh_2Cl	
trans-**9-[Cl-As]**, $IrClH_2(AsPh_3)_3$, 338 K	^1H	7.65	$AsPh_3$ (*o*-H)	
		7.39	$AsPh_3$ (*o*-H)	
		−14.01 (d)	Ir–H	−5.7 $^2J_{HH}$
		−22.72 (d)	Ir–H	−5.7 $^2J_{HH}$
$H(Cl)Ir(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Ir(PMe_3)(CO)$, 295 K [a]	^1H	−15.53 (m)	Ir–H–Ir	−6.4 $^2J_{HH}$, 15.5 $\|^2J_{PH}\|$
		−22.13 (td)	Ir–H	−6.4 $^2J_{HH}$, 15.5 $\|^2J_{PH}\|$
	^{31}P	−37.3 (br)	PMe_3	
$(H)_2Ir(PMe_3)_2(\mu\text{-}Cl)_2Ir(PMe_3)(CO)$, 295 K [a]	^1H	−23.32 (dt)	Ir–H	−4.5 $^2J_{HH}$, 8.5, 22 $\|^2J_{PH}\|$
		−23.54 (dt)	Ir–H	−4.5 $^2J_{HH}$, 17.6 $\|^2J_{PH}\|$
	^{31}P	−32.71 (s)	PMe_3	
Acylated metallation product, Scheme 3, 333 K	^1H	−7.45 (m)	Ir–H	
		−18.49 (m)	Ir–H	
	^{31}P	14.7 (dd)	PPh_3	380 $\|^2J_{PP}\|$, 11.9 $\|^2J_{PC}\|$
		80.8 (d)	PPh_2PhCO	380 $\|^2J_{PP}\|$

[a] In toluene-d_8.

observation of weak signals for the hydride ligands of the dichloromonohydride complex, *trans*,*cis*-$IrH(CO)(Cl)_2(PPh_3)_2$ **5-[Cl-Ph]** at δ −14.51 and all four of the possible isomers of $IrH_2(CO)_2Cl(PPh_3)$ **6-[Cl-Ph]** with *cis*-hydrides. Consequently, the formation of **5-[Cl-Ph]** when **2-[Cl-Ph]** is reacted with H_2 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 $IrH(CO)_2(PPh_3)$ with H_2 accounts for the formation of **4-[H-Ph]**. The spectral characteristics of these new complexes are reported in Table 1. Since PPh_3 is liberated during the formation of **4-[H-Ph]** it would therefore seem sensible to suggest that $IrH_2(PPh_3)_3Cl$, a known *p*-H_2 active product, should also be detected.[20] We note that prior work has demonstrated that at this temperature the spectral features of $IrH_2(PPh_3)_3Cl$ 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*-H_2 in the presence of CO, or photolysed. Products specific to the PPh_3 and PMe_3 systems are expressly indicated.

Oxidative addition of H_2 to $Ir(CO)_2Cl(PPh_3)_2$

In order to explore the role of CO more fully, a sample of **1-[Cl-Ph]**, in benzene-d_6, was first placed under an atmosphere of CO in order to form the known complex $Ir(CO)_2Cl(PPh_3)_2$.[2] The solution was then placed under CO and 3 atm of *p*-H_2 according to the previous procedure. When the associated reaction at 295 K was monitored by multinuclear NMR spectroscopy, *p*-H_2 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 meridonal isomer of $IrH_3(CO)(PPh_3)_2$ **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 H_2 addition to $Ir(CO)_2Cl(PPh_3)_2$ leads to the generation of both $IrH_2(CO)_2Cl(PPh_3)$ (minor) and $IrH_2(CO)Cl(PPh_3)_2$ (major). It can also be deduced that the former complex, $IrH_2(CO)_2Cl(PPh_3)$, then reacts rapidly to form **4-[H-Ph]** *via* HCl elimination. These findings are summarised in Scheme 3.

Monitoring H_2 exchange within $IrH_2(CO)Cl(PPh_3)_2$, 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 carbonlyation 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*-H_2 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 *meridonal* isomers of **7-[H-Ph]**, the *facial* isomer of **4-[H-Ph]** and $IrH_2(PPh_3)_3Cl$ as illustrated in Fig. 2(b). The observation of both isomers of the dichloromonohydride complex **5-[Cl-Ph]** accompanied these changes. UV irradiation therefore facilities 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–^{31}P 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 $IrH(PPh_3)_2(P(C_6H_5)_2(C_6H_4))Cl$, **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-^{13}CO]** the corresponding hydride resonances of this product appeared to be unaffected by the presence of the ^{13}C label. However, the corresponding phosphorus resonance at δ 14.7 contained an additional splitting of 11.9 Hz due to ^{13}C. Although this requires the product to contain a ^{13}CO unit we were unable to locate its chemical shift by 2D ^1H–^{13}C HMQC experiments. This reaction product can therefore be deduced to contain the five-membered ring $Ir(CO–C_5H_4–P)$, 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 ligand *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 $Ir(H)_2(P^tBu_2Ph)_2I$ 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 η^2 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-d_6. The large excess of H_2 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*-H_2, 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 preak intensities matched those obtained immediately after photolysis. It can therefore be concluded that at 338 K exchange of free H_2 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 H_2

When a sample of **2-[Cl-Ph]** in the presence of H_2 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, $IrH_3(CO)(PPh_3)_2$ **7-[H-Ph]** readily converts into $IrH_3(CO)_2(PPh_3)$ **4-[H-Ph]**.

Oxidative addition of H_2 to $Ir(CO)Cl(PMe_3)_2$, 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 ^{1}H 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 H_2 to *trans*-**1-[Cl-Me]** is reversible at 333 K, with both isomers of H_2 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 H_2 with $IrH_2(CO)Cl(PMe_3)_2$, 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*-H_2 a solution was made up that contained **2-[Cl-Me]**, 3 atm *p*-H_2, 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 $IrH_3(CO)_2(PMe_3)$, **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 *meridonal* 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 H_2 with $IrH_2(CO)Cl(PMe_3)_2$, 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 $Ir(CO)Cl(PMe_3)_2$, in benzene-d_6 was placed under 3 atm of *p*-H_2 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 ^{1}H 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 H_2 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_{HH} = −6.4, J_{PH} = 8.5 and 22 Hz) and anti-phase doublet of triplets (J_{HH} = −6.4, and J_{PH} = 14 Hz), respectively, while the latter pair both appear with anti-phase doublet of triplet multiplicities (J_{HH} = −4.5, and J_{PH} = 18.5 and 17 Hz, respectively). The ^{1}H 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 $H(Cl)Ir(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Ir(PMe_3)(CO)$ and $(H)_2Ir(PMe_3)_2(\mu\text{-}Cl)_2Ir(PMe_3)(CO)$, respectively. The observation of a triplet at δ −16.31, due to the HCl transfer product $IrH(CO)Cl_2(PMe_3)_2$ **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 $(H)_2Ir(PMe_3)_2(\mu\text{-}Cl)_2Ir(PMe_3)(CO)$ disappeared while those due to $H(Cl)Ir(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Ir(PMe_3)(CO)$ 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 ^{13}CO labelled **1-[Cl-Me]** a new product resonance was observed at δ −9.56 that failed to couple to ^{31}P. This signal has been tentatively assigned to the *facial* isomer of $H_3Ir(CO)_3$ and only becomes visible through the complex effects associated with the ^{13}C labelling that enable the formation of a second-order spin system containing the H_3 group. NMR data for these species are listed in Table 1. Scheme 3 summarises the reaction products observed with the PMe_3 based system.

Oxidative addition of H_2 to $Ir(CO)Cl(AsPh_3)_2$, 1-[Cl-As]

Addition of H_2 to the triphenylarsine analogue $Ir(CO)Cl(AsPh_3)_2$ **1-[Cl-As]** at 295 K produces three hydride resonances in the corresponding ^{1}H 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*-H_2 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. H_2 addition is therefore irreversible on the NMR timescale. Furthermore, in this reaction, the isomer formed by H_2 addition over the As–Ir–As axis is not *p*-H_2 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*-H_2 revealed the formation of a third H_2 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 ^{13}CO **1-[Cl-As]** was employed, both the hydride resonances of **8-[Cl-As]** are split by an additional ^{13}C 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 H_2 no exchange with **2-[Cl-As]** or **3-[Cl-As]** occurs. This observation requires

the formation of **8-[Cl-As]** by direct H_2 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 H_2 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 δ −14.01, −22.72 and δ −9.99 and −11.44. These resonances correspond to the complexes $IrH_2(AsPh_3)_3Cl$, **9-[Cl-As]**, and $IrH_3(CO)_2(AsPh_3)$, **4-[H-As]**, with *meridonal* and *facial* geometries respectively. Examination of the hydride and exchange peak integrals enabled the rate of reductive elimination of H_2 in **9-[Cl-As]** to be estimated at 343 K as 5.16 s^{-1} which compares with that for $IrH_2(PPh_3)_3Cl$ of 4.7 s^{-1} under the same conditions.[29e]

Monitoring the exchange of H_2 with $IrH_2(CO)Cl(AsPh_3)_2$, 2-[Cl-As], in the presence of CO

When the reaction of **2-[Cl-As]** with H_2 was monitored in the presence of CO, peaks due to $Ir(H)_2Cl(CO)_2(AsPh_3)$, **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 ^{13}C NMR measurements, key assignments are listed in Table 1.

Observation of H_2 exchange in $IrH_2(CO)Cl(APh_3)_2$, 2-[Cl-AsPh], after UV irradition

A solution of $IrH_2(CO)Cl(AsPh_3)_2$ in benzene-d_6 was placed under 3 atm of *p*-H_2 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 PPh_2Cl as a probe to explore the effect of phosphine on the addition of H_2 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 $Ir(CO)Cl(PPh_3)(PPh_2Cl)$ **1-[Cl-Ph-Cl]** and $Ir(CO)Cl(PPh_2Cl)_2$ **1-[Cl-Cl]**. Here, **-[Cl-Ph-Cl]** is used to indicate the presence of both PPh_3 and PPh_2Cl, while **-[Cl-Cl]** corresponds to the fully substituted PPh_2Cl product. These complexes were formed *in situ* by taking a solution of **1-[Cl-Ph]** in benzene-d_6 under 3 atm *p*-H_2 and heating to 333 K with a four-fold excess of PPh_2Cl. 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 δ −6.81 and −16.99 could be readily assigned to the mono-substituted product **2-[Cl-Ph-Cl]**, while those at δ −7.24 and −16.73 correspond to signals from of **2-[Cl-Cl]**, the bis-substituted counterpart. However, of greater significance was the observation of strong signals at δ −8.13 and −8.34 due to **3-[Cl-Ph-Cl]**, the *cis*,*cis* isomer of the monosubstiuted complex, and at δ −8.37 due to **3-[Cl-Cl]** respectively. These signals can be viewed in Fig. 1d. The former species is formed by H_2 addition across the P–Ir–P axis of $Ir(CO)(PPh_3)(PPh_2Cl)Cl$. 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 δ −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 PPh_3 ligand lies *trans* to chloride. It should be noted that this is by no means a synthetic route to the PPh_2Cl 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. $Ir(CO)Cl(PPh_3)_2$, **1-[Cl-Ph]** and $Ir(CO)Cl(PMe_3)_2$, **1-[Cl-Me]** were prepared according to established methods.[30] An attempt to prepare $Ir(CO)Cl(AsPh_3)_2$ **1-[Cl-As]** by the same synthetic route used to prepare $Ir(CO)Cl(PPh_3)_2$ gave only a low yield of $Ir(AsPh_3)_3Cl$. **1-[Cl-As]** was successfully synthesised by bubbling CO through a 2-methoxyethanol solution of $Na_2IrCl_6{\cdot}6H_2O$ for 3.5 hours.[31] $AsPh_3$ 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: ^{13}C (CO) δ 207.0 in CD_2Cl_2, ν(CO) = 1950 cm^{-1} (CH_2Cl_2).

For the parahydrogen experiments, hydrogen enriched in the para spin state was prepared by cooling H_2 to 77 K over a paramagnetic catalyst as described previously. An atmosphere of H_2 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, ^{31}P at 161.92, ^{13}C at 100, respectively. ^1H NMR chemical shifts are reported in ppm relative to residual ^1H signals in the deuterated solvents (benzene-d_6, δ = 7.13, and toluene-d_8, δ = 2.13). $^{31}P\{^1H\}$ NMR data are reported in ppm downfield of an external 85% solution of phosphoric acid, ^{13}C NMR data are reported relative to benzene-d_6, δ = 128.0, and toluene-d_8, δ = 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 = PPh_3, PMe_3, $AsPh_3$ and PPh_2Cl, and L_2 = $(PPh_2Cl)(PPh_3)$] have revealed a strong dependence of the relative stabilities of the *cis*,*cis* and *cis*,*trans* isomers of the H_2 addition product, $Ir(H)_2(CO)Cl(L)_2$, on the nature of the phosphine ligand. For L = PPh_3, the *cis*,*trans* isomer produced by H_2 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 = PMe_3, 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 = PMe_3.[14] The gap narrows for L = $AsPh_3$, where both isomers can be detected without the need for *p*-H_2. 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, $Ir(CO)Cl(AsPh_3)_2$, can exist in both *cis* and *trans* isomers at high temperatures. Further reaction products corresponding to $IrH_3(CO)_2(AsPh_3)$, $IrH(CO)(Cl)_2(AsPh_3)_2$ and $IrH_2(AsPh_3)_3$ are also observed to grow in under these conditions. These can be categorised as the products of CO and $AsPh_3$ exchange, and the product of HCl transfer to

$Ir(CO)Cl(AsPh_3)_2$. When $Ir(CO)Cl(PPh_3)_2$ was warmed in the presence of PPh_2Cl, products corresponding to H_2 addition to $Ir(CO)Cl(PPh_3)(PPh_2Cl)$ were observed. In this case, the ratio of hydride signals for the *cis*,*trans* and *cis*,*cis* isomers of $Ir(H)_2(CO)(Cl)(PPh_3)(PPh_2Cl)$ 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 = PPh_3 and PMe_3 the formation of $IrH_3(CO)_2(L)$ occurs via the initial formation of $IrH_2(CO)_2Cl(L)$. This reaction product is clearly formed when $Ir(H)_2(CO)Cl(L)_2$ is warmed under an atmosphere containing both H_2 and CO. Subsequently, $IrH_2(CO)_2Cl(PPh_3)$ undergoes HCl elimination which accounts for the observation $IrH(Cl)_2(CO)(PPh_3)_2$. The 16-electron complex $IrH(CO)_2(L)$ formed by this process rapidly reacts with H_2 to yield $IrH_3(CO)_2(L)$. Additional products corresponding the *meridonal* and *facial* isomers of $IrH_3(CO)(L)_2$ 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*-H_2 these species correspond to the dominant photo-products when L = PPh_3.

The photochemical studies are complicated by the observation of signals that we have attributed to $Ir(H)_2(PPh_3)(PPh_2C_5H_4CO)$ containing an unusual η^2-acyl ligand when L = PPh_3. Furthermore, with L = PMe_3, signals for the binuclear products $H(Cl)Ir(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Ir(PMe_3)(CO)$ and $(H)_2Ir(PMe_3)_2(\mu\text{-}Cl)_2Ir(PMe_3)(CO)$ are detected after irradiation at 295 K. It has therefore been demonstrated that *p*-H_2 enhanced NMR studies can be used to provide experimental proof that complements theoretical investigations.

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