Photochemical Reactivity of $2[Ir^{III}HCl_2(PPr^i_3)_2]\cdot H_2$. Formation of Monohydrido Isomers of Ir^{III} and Evidence of Photoinduced Oxidative Addition of H_2 to Ir^{III}

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Photolysis in CH_2Cl_2 of the system $2[Ir^{III}HCl_2(PPr^i_3)_2]\cdot H_2$ (**A**), using light at 404 nm occurs with a quantum yield of 0.75 to give three new geometrical isomers of (**A**). N.m.r. spectroscopy and the chemical reactivity of the photoreaction mixtures have revealed the presence of equilibrium amounts of species containing molecular hydrogen. When (**A**) is irradiated in the presence of H_2 the complex $[Ir^VH_3Cl_2(PPr^i_3)_2]$ is formed by an oxidative-addition reaction.

There is much interest in the photochemistry of transition-metal hydrides in view of their catalytic potential.[1] Of particular relevance is the activation of molecular hydrogen and of saturated C–H bonds. The existence of molecular hydrogen complexes, the non-classical dihydrogen hydride formulation $[M(H_2)(H)]$ and the classical trihydride structure $[MH_3]$, is well established and, in some cases, both forms revert to an equilibrium mixture.[2,3]

Recently the preparation and structural and spectroscopic studies of the paramagnetic complex $[IrH_2Cl_2(PPr^i_3)_2]$ (**1**) have been reported.[4–6] Complex (**1**) is intensely coloured, nearly dark purple in solution. The solid is stable in the dark however n.m.r. spectroscopy clearly shows that solutions display dihydride $\rightleftharpoons$ dihydrogen dynamic equilibrium (1).[5,6]

$$2[Ir^{IV}H_2Cl_2(PPr^i_3)_2] \underset{\text{low temp.}}{\overset{20\,°C}{\rightleftharpoons}} \underset{(\mathbf{A})}{2[Ir^{III}HCl_2(PPr^i_3)_2]\cdot H_2} \quad (1)$$

The results reported herein demonstrate the potential of photoirradiation as a means of preparing (*i*) unstable hydridodihydrogen species of Ir^{III} and (*ii*) the iridium(v) trihydride complex $[Ir^VH_3Cl_2(PPr^i_3)_2]$ upon photolysis of (A) in the presence of H_2.

Results and Discussion

The characterization of the products of equation (1) has previously been described.[4–6] The equilibrium (1) is strongly shifted to the right at 20 °C and moves only slightly toward the paramagnetic species $[IrH_2Cl_2(PPr^i_3)_2]$ (1) on lowering the temperature.[5,6]

Photolysis (λ = 404 nm) of degassed CH_2Cl_2 solutions of (A) induces the electronic absorption spectral changes shown in Figure 1. As the photolysis proceeds the bands at 298, 338, 455, and 562 nm decrease and a new band grows at 358 nm with isosbestic points at 290, 349, and 415 nm. The presence of three isosbestic points in the optical region reflects a constant ratio of the reactant consumed to the photoproducts obtained. A quantum yield of 0.75 was determined for photoconversion of (A) according to the spectral changes at 335 nm recorded immediately upon conclusion of photolysis in CH_2Cl_2 solution (λ = 404 nm, 20 °C).

By maintaining the irradiated solutions in the dark the original u.v.–visible spectrum of (A) is re-established. Thermal and photochemical reactions can be cycled several times without decompositon of system (**A**). Irradiation of (**A**) gives rise to ^1H n.m.r. spectra much richer in lines than the original system (**A**). The relative intensity of the observed peaks strongly depends upon the time of observation after the irradiation has been stopped and the temperature at which the sample is kept during the n.m.r. observation. Even with the utmost speed, some return to the original (**A**) species always occurs. In order to keep this back reaction under control, the temperature and time for n.m.r. measurements were rigorously controlled.

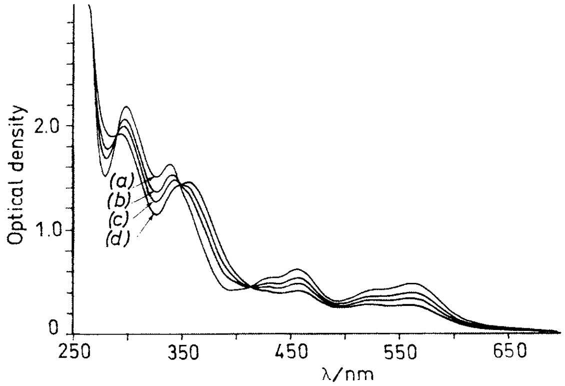


Figure 1. Electronic spectral changes accompanying photolysis at 404 nm of 1×10^{-2} mol dm^{-3} $[IrH_2Cl_2(PPr^i_3)_2]$ in CH_2Cl_2, with the following number of counts of irradiation: (*a*) = 0, (*b*) = 5′, (*c*) = 10′, and (*d*) = 15′

Photolysis of compound (**A**) in CD_2Cl_2 at room temperature, followed by quenching at 193 K and observation of the n.m.r. spectra within 5 min, gives rise to the spectrum in Figure 2. Here a strong loss of intensity of the peak at δ −49 is accompanied by a broadening of the same residual peak shifted to low field as previously reported.[5] Meanwhile three sharp triplets appear at δ −22.58, −24.70, and −28.12 (Figure 2 and Table). These new triplets can be assigned to three new iridium hydridic species (**P**), (**Q**), and (**R**) (Scheme).

The formation of the geometric isomers (**P**)—(**R**) of system (**A**) gains credence from the following spectroscopic observations.

(1) Complete reversibility, as evidenced by n.m.r. spectroscopy, of peaks (**P**)—(**R**) which return to species (**A**).

(2) Hydride peaks (**P**)—(**R**) are still triplets thus showing that *two* phosphines are present.

(3) Phosphorus-31 n.m.r. spectra not only show the complete

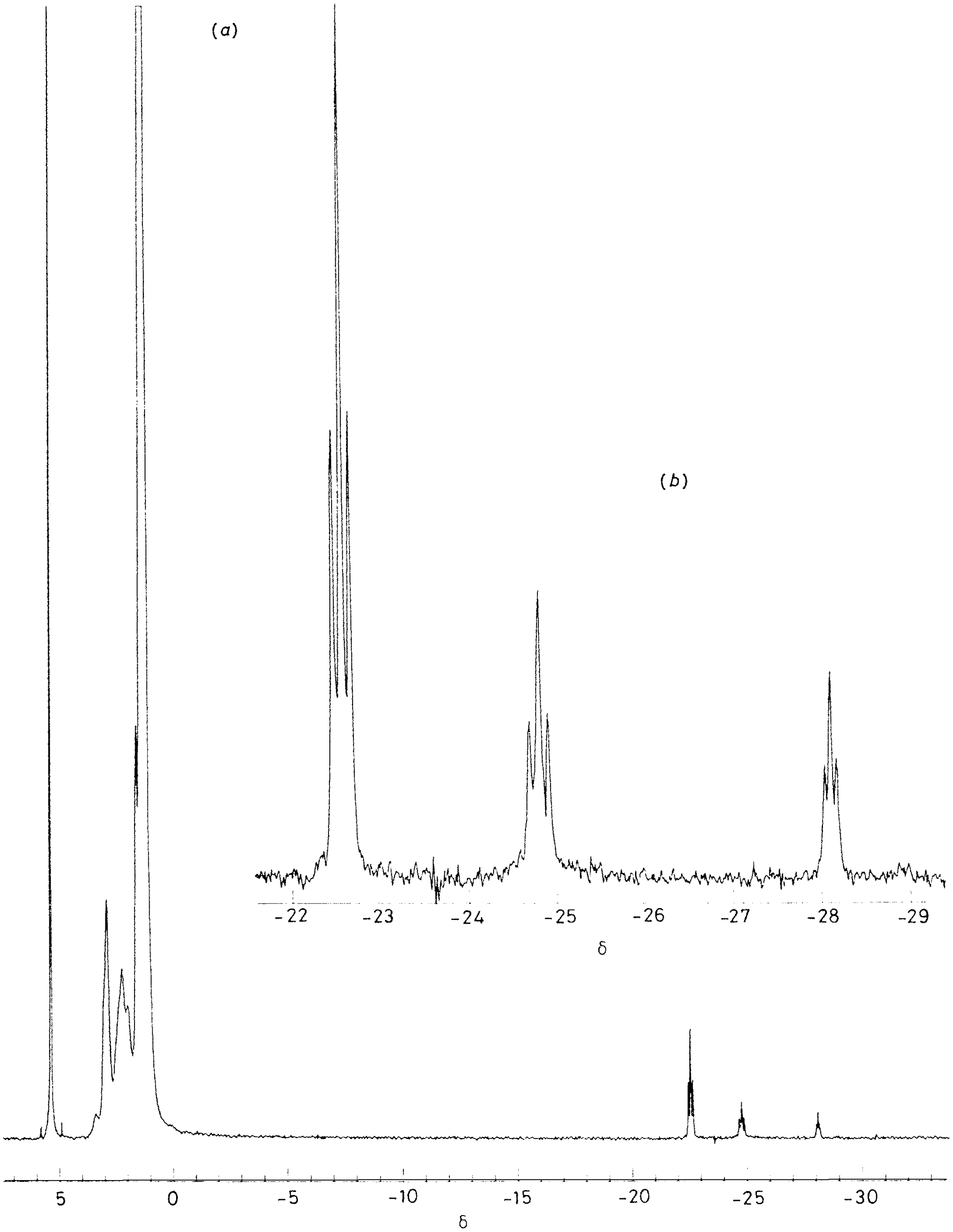


Figure 2. Proton n.m.r. spectrum of the photochemically generated hydrides (**P**)—(**R**): (*a*) full spectrum; (*b*) expanded view of the hydride signals

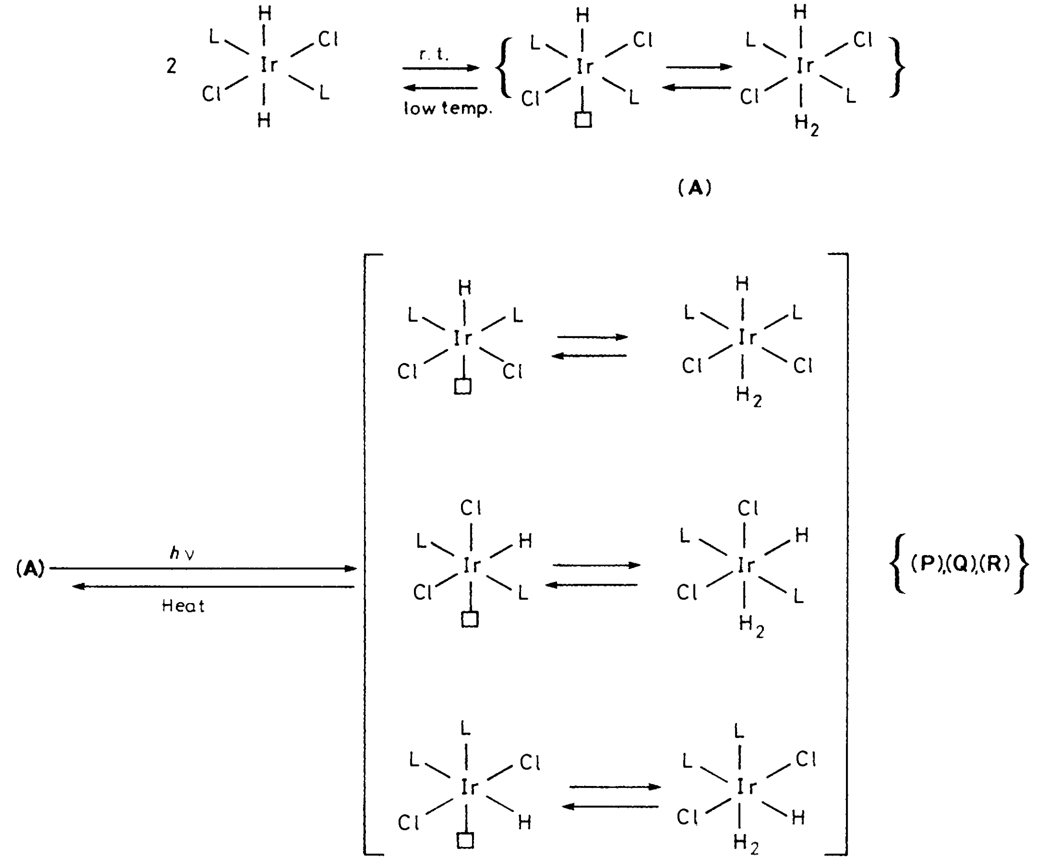
Table. N.m.r. data for the photochemically generated hydrido complexes of Ir$^{III\,a}$

^{1}H N.m.r. C shift, δ	J(PH)/ Hz	Relative intensity
−22.58	20.3	7.5
−24.70	23.0	3.3
−28.12	13.0	1.6
−49.00	11.0	traces^b

^{a} Solvent CD_2Cl_2. ^{b} Irradiation time 1 h ($\lambda > 400$ nm). Further conversion of (**A**) is very slow at this point because the generated hydrido species now absorb almost all the u.v. irradiation.

reversibility between the new species (**P**)—(**R**) and species (**A**), but likewise show that (**P**)—(**R**) interconvert at a high rate on the ^{31}P n.m.r. time-scale but slowly on the ^{1}H n.m.r. time-scale. At 253 K only one sharp signal is evident in the ^{31}P n.m.r. spectrum, shifted upfield by 2.23 p.p.m. with respect to the spectrum of (**A**) (32 p.p.m. from H_3PO_4). At 223 K this signal splits into two components, a sharp one at 2.35 p.p.m. from that of (**A**) and a broad one with lower intensity, shifted upfield by 3.4 p.p.m. Thus, even at low temperatures, where three hydride peaks appear, only two ^{31}P n.m.r. signals are present.

(4) The low-energy bands in the electronic spectra of the reaction mixtures (Figure 1) may be accounted for by the presence of five-co-ordinate species as in the Scheme. Such d^6 species have low-energy $e \longrightarrow a_1$ transitions as has been ob



Scheme. r.t. = Room temperature; L = PPr^i_3

served for $[M(CO)_5]$ (M = Cr, Mo, or W) and $[MnH(CO)_4]$ in low-temperature matrices.[1]

Therefore, all the above spectroscopic evidence would appear to confirm the formation of geometric isomers, although *cis*-phosphine ligands are obviously quite hindered.

The experimental evidence indicates that the new hydride system can be written as summarized in the Scheme with the hypothesis that (**P**)—(**R**) are geometrical isomers of (**A**) but no indication of which is which.

In the dark the new species decay quite rapidly and quantitatively to reform the system (**A**). Attempts to isolate the isomers (**P**)—(**R**) have resulted only in the near-quantitative recovery of (**A**). This cycle of photogeneration followed by thermal back reaction (Scheme) can be repeated several times without noticeable degradation of the system (**A**). The conversion yield [% of (**A**) consumed as measured by n.m.r. spectroscopy] is a function of the irradiation time and light intensity and approaches 80—90% upon prolonged irradiation with $\lambda > 400$ nm.

The exact nature of the photoproducts (**P**)—(**R**) is presently unclear. However, their chemical shifts and values of $J(P,H)_{cis}$ fall in the range observed[3] for monohydrido complexes of Ir^{III} in dynamic equilibrium with η^2 dihydrogen species. Further evidence for the chemistry summarized in the Scheme comes from the observation that the photoproducts (**P**)—(**R**) can be quantitatively converted into $[Ir^{III}HCl_2(PPr^i_3)_2(C_5H_5N)]$ simply by adding pyridine to the photoreaction mixture. Gas chromatographic analysis of the gas phase showed that 0.4 ± 0.1 mol of H_2 was formed for each mol of (**A**) decomposed. This demonstrates that the photoreaction occurs according to the stoicheiometry of the Scheme. Furthermore, ligands which are π acceptors such as CO and MeCN readily displace H_2 from the photoreaction mixture to produce the monohydride species $[IrHCl_2(PPr^i_3)_2L]$ (L = CO or MeCN).*

Photochemical Activation of H_2. *Formation of* $[IrH_3Cl_2(PPr^i_3)_2]$, (**B**).—The continuous photolysis of (**A**) in the presence of H_2 leads to the formation of the trihydride (**B**). A study of this photoreaction was carried out to determine the mechanism of the photoinduced oxidative addition of H_2 to the $2[IrHCl_2(PPr^i_3)_2]\cdot H_2$ system. Prolonged photolysis (4 h, $\lambda > 400$ nm) of (**A**) in CD_2Cl_2 under an atmosphere of H_2 induced a colour change from red to yellow. The irradiated solutions show a ^1H n.m.r. spectrum containing only one new, slightly broad triplet at −12.58 [$J(P,H) = 7.3$ Hz]. The coupling constant and intensity ratio indicate that the new triplet may be assigned to a trihydride species of Ir^V, $[IrH_3Cl_2(PPr^i_3)_2]$, (**B**). The corresponding broad-band decoupled $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a peak at 23.00 p.p.m. By selectively decoupling the region between 1 and 3 p.p.m. a broad quartet is observed [$J(P\text{–}H)$ 7 Hz] thus confirming the formation of (**B**).

In order to monitor the course of this reaction, hydrogen-purged solutions were irradiated in n.m.r. tubes and the ^1H n.m.r. spectra were recorded at successive stages of photolysis. These spectra showed the gradual conversion of hydrides (**P**)—(**R**) into the product (**B**). The reactions stopped in the absence of u.v.–visible irradiation. The course of this reaction can be explained by assuming that excitation induces the oxidative-addition reaction (2) of H_2 to the iridium(III) centre.

$$(\mathbf{A}) \xrightarrow{h\nu} (\mathbf{P})\text{—}(\mathbf{R}) \xrightarrow[\mathrm{H_2}]{h\nu} \underset{(\mathbf{B})}{[\mathrm{IrH_3Cl_2(PPr^i_3)_2}]} \qquad (2)$$

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* Characterization was carried out by i.r. spectroscopy: L = CO, ν(Ir–H) 2 190, ν(CO) 2 000 cm^{-1}; L = MeCN, ν(Ir–H) 2 180, ν(CN) 2 250 cm^{-1}.

Cleavage of the H–H bond would require electron donation from Ir metal into H σ* orbitals.[7] The electronic spectra of hydrides (**P**)—(**R**) show low-intensity shoulders in the 400—600 nm region typical of five-co-ordinate metal species.[1,8] These low-energy bands have no counterpart in the spectrum of any uncomplexed phosphines, suggesting that one or more metal orbitals are involved in the transition. It is likely that a rearrangement of electron density at the metal may lead to a different excited-state energy ordering. Thus, for iridium(III), low-energy ligand-field states may be the precursors of the oxidative addition of H_2, in agreement with theoretical arguments based on orbital topology considerations.[7,9]

Further studies involving other phosphine analogues of (**A**) are in progress including development of the catalytic properties of these materials for organic substrate hydrogenation.

Experimental

Preparation of $2[IrHCl_2(PPr^i_3)_2]_2$ (**A**).—The system (**A**) was prepared *in situ* by dissolving the iridium(IV) complex, $[IrH_2Cl_2(PPr^i_3)_2]$ (**1**) in CH_2Cl_2 or in $CHCl_3$.[4–6]

Formation of $[IrHCl_2(PPr^i_3)_2(C_5H_5N)]$.—A solution of (**A**) (10^{-2} mol dm^{-3}) in CH_2Cl_2 was deoxygenated by bubbling argon for 30 min. The solution was irradiated using $\lambda > 400$ nm. The photolysis was monitored by u.v.–visible spectroscopy. The reaction was stopped before completion [80% conversion of (**A**)]. To this irradiated solution pyridine (5 cm^3) was added *via* a syringe. A yellow colour developed immediately upon mixing, and very quickly faded as a yellow precipitate was formed. After filtration, washing with diethyl ether, and drying in a vacuum, the product $[IrHCl_2(PPr^i_3)_2(C_5H_5N)]$ was obtained (Found: C, 41.65; H, 7.30; Cl, 10.60; N, 2.15. Calc. for $C_{23}H_{48}Cl_2IrNP_2$: C, 41.60; H, 7.30, Cl, 10.70, N, 2.10%), and identified by i.r. [ν(Ir–H) 2 300 cm^{-1}] and ^{1}H n.m.r. spectroscopy [δ(IrH) −24.2, *J*(PH) = 14.65 Hz].

Studies of Hydrogen Evolution.—A deoxygenated solution of (**A**) (0.058 g, 10^{-2} mol) in CH_2Cl_2 (10 mol) was placed in a flat-sided Pyrex flask fitted with a side arm having a cuvette and containing pyridine (3 cm^3). After photolysis, as above, the pyridine was added. A sample of the gas phase (1 cm^3) was taken through a septum with a gas syringe and the H_2 determined by g.c. (after a preliminary calibration). The total H_2 formed was $(0.4 \pm 0.1) \times 10^{-2}$ mol.

Preparation of $[IrH_3Cl_2(PiPr^i_3)_2]$, (**B**).—A CH_2Cl_2 solution (10^{-2} mol dm^{-3}) of complex (**1**) was stirred under H_2 and irradiated with a 250-W Bruker medium-pressure mercury arc with output filtered for $\lambda > 400$ nm. The reaction was monitored by n.m.r. spectroscopy, following the growth of a peak at δ −12.58. The irradiation was discontinued after 4 h when the relative amount of product no longer increased. The solvent was subsequently removed in a vacuum and the residue dried overnight in the dark under vacuum (Found: C, 36.10; H, 7.20; Cl, 12.00; P, 10.45. Calc. for $C_{18}H_{45}Cl_2IrP_2$: C, 36.85; H, 7.75; Cl, 12.10; P, 10.55%). I.r. (in KBr); ν(Ir–H) 2 000 cm^{-1}. ^{1}H N.m.r.: δ −12.6 [t, *J*(P, H) 7.3 Hz].

Irradiation.—Photolysis experiments were carried out using the optical trains described previously using interference filters for wavelength selection.[10] Photosolution optical density changes were monitored using a Jasco Uvidec 650 spectrophotometer. Incremental quantum yields were extrapolated to zero time in order to correct for inner filter effects from absorbing products. Lamp intensities were measured with ferrioxalate, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$, actinometry.[10]

Materials.—Spectroscopic grade solvents were used without purification. Hydrogen was CP grade (minimum purity 99.9%). All chemical manipulations were carried out under an inert atmosphere in an argon-filled glove-box.

Instrumentation.—U.v.–visible spectra were recorded on a Cary-219 or a Jasco Uvidec-650 spectrophotometer, i.r. spectra on a Perkin-Elmer 323 spectrophotometer using KBr pellets, ^{1}H and ^{31}P n.m.r. spectra on a Bruker WP 200 spectrometer equipped with a variable-temperature unit belonging to C.N.R., Area Ricerca Roma. Analysis for H_2 by gas chromatography was carried out using a Perkin-Elmer F17 gas chromatograph with molecular sieve 5A column. Elemental analyses were performed by A. Bernard Mikroanalytisches Laboratorium, Elbach, Germany.

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