Novel Iridium Complexes of an Azine Diphosphine: Very Reactive Iridium(I) Species formed by a Unique Isomerisation of an Iridium(III) Hydride. A New Method of creating Coordinative Unsaturation

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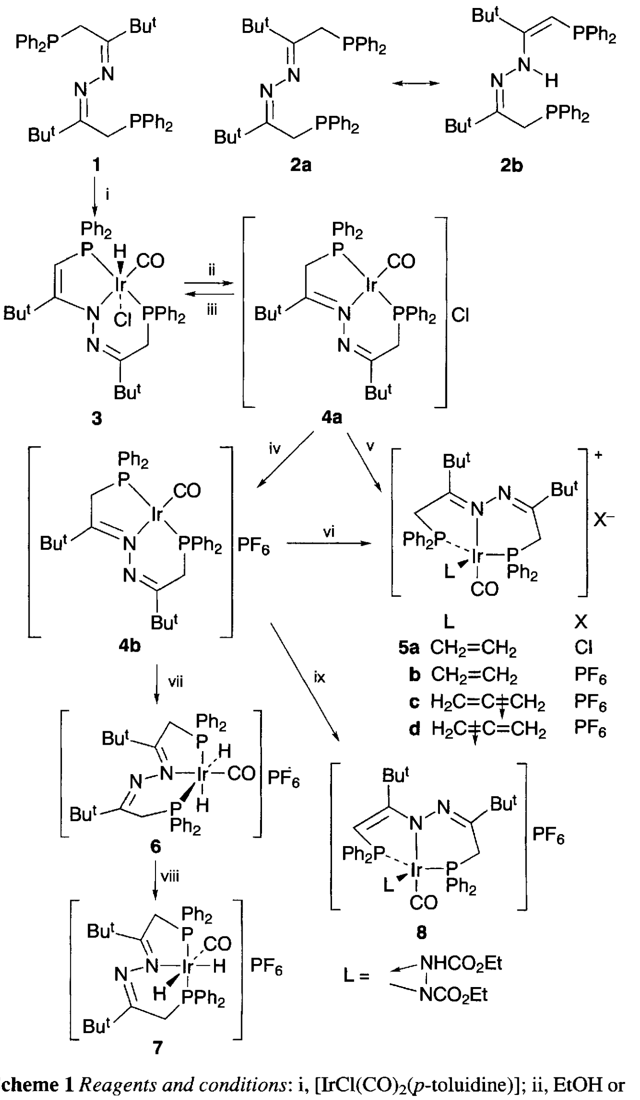
The coordinatively saturated iridium(III) hydride [IrHCl(CO){Ph$_2$PCH=C(Bu^t)N–N=C(Bu^t)CH$_2$PPh$_2$}] *containing an ene–hydrazone backbone isomerises reversibly in a polar solvent to give the reactive and coordinatively unsaturated iridium(I) salt* [Ir(CO){Ph$_2$PCH$_2$C(Bu^t)=N–N=C(Bu^t)CH$_2$PPh$_2$]Cl *which reacts rapidly with alkenes, acetylenes, dihydrogen, etc.*

Coordinative unsaturation is extremely important in transition metal chemistry and associated areas of catalysis; a classic illustration of this is the coordinatively unsaturated (16e) diethylene rhodium(I) complex [Rh(C_2H_4)$_2$(acac)] (acac = acetylacetonate), which exchanges complexed ethylene with free ethylene at 10^{14} times the rate which the coordinatively saturated (18e) complex [Rh(C_2H_4)$_2$(η^5-C_5H_5)] exchanges.[1,2] Here, we describe a new method of generating a labile, coordinatively unsaturated complex by the rapid and reversible isomerisation of a coordinatively saturated hydride complex. The isomerisation involves using an ene–hydrazone backbone of a diphosphine ligand as the sink for a hydrogen atom, thereby giving an azine backbone. An azine or ene–hydrazone forms an extremely stable backbone for a diphosphine, is easily prepared, very resistant to hydrolysis, and has not previously been used in this way. Iridium complexes, *e.g.* Vaska's complex, *trans*-[IrCl(CO)(PPh$_3$)$_2$], have proved to be excellent model systems for predicting the behaviour of many other tertiary phosphine–metal complexes, including their use in catalysis.

We have shown that the azine diposphine *Z,Z*-Ph$_2$PCH$_2$C(Bu^t)=N–N=C(Bu^t)CH$_2$PPh$_2$ **1**[3] cannot chelate through both phosphorus atoms because of the *Z,Z*-configuration,[3] but can bridge two metal centres to give binuclear or polynuclear species.[4] However, rotation around C=N can occur quite readily and the azine diphosphine in the *E,Z*-configuration **2a** can chelate to a metal giving a nine-membered ring or act as a terdentate ligand with *P,P* and *N* donor atoms.[3–5] We now find that **1** reacts with the labile iridium(I) carbonyl complex [IrCl(CO)$_2$(*p*-toluidine)] to give the coordinatively saturated (18e) iridium(III) hydride **3** (Scheme 1), in which a hydrogen atom has been lost from a methylene carbon and an iridium hydride has formed, presumably by oxidative addition of the N–H bond;[5,6] this could involve an azine ⟷ ene–hydrazone tautomerism, *i.e.* a 1,3-proton shift as shown, **2a** ⟷ **2b**. We formulate the stereochemistry of the iridium(III) hydride complex as **3**,‡ since $^2J_{PP}$ is large (312 Hz) and characteristic of *trans*-phosphines,[7] and the value of δ_H (−15.4) in the ^{1}H NMR spectrum is close to similar hydride ligands *trans* to chlorides for a range of iridium(III) hydrides derived from azine monophosphines.[6] Furthermore, oxidative addition of C–H, N–H, S–H, O–H, Si–H, B–H, or H_2 to iridium(I) is usually *cis* oriented.[6,8] In general, coordinatively saturated iridium(III) carbonyl hydrides show poor reactivity towards alkenes, *e.g.* [IrHCl$_2$(CO)(PPh$_3$)$_2$] or [IrH$_2$Cl(CO)(PPh$_3$)$_2$] or related species.[9,10] However, we find that **3** readily dissolves in methanol or ethanol to give an isomeric but coordinatively unsaturated iridium(I) complex salt **4a** in which a hydrogen atom has moved back to the methine carbon of the ene–hydrazone backbone and the iridium has lost its hydride ligand. This salt **4a** is readily isolated, and on dissolution in benzene or dichloromethane it immediately reverts back to the iridium(III) hydride **3**. The interconversion (or isomerisation) **3** ⟷ **4a** is rapid and can be readily followed by the characteristic ^{31}P{^{1}H] NMR, ^{1}H NMR or IR spectra of the two species. Treatment of **4a** with NH$_4$PF$_6$ in methanol gives the corresponding PF$_6$ salt **4b**.†

The salts **4a** or **4b** rapidly take up unsaturated molecules. A solution of **4a** in methanol reacts with ethylene to give **5a**;† **4b** in CD$_2$Cl$_2$ or CH$_2$Cl$_2$ reacts completely with ethylene in a few seconds to give a colourless adduct **5b**.† The ^{1}H{^{31}P} and ^{1}H NMR spectra of **5b** show that it is fluxional and most of the resonances are very broad at 25 °C ($w_{1/2}$ > 10 Hz). When the CD$_2$Cl$_2$ solution is cooled to −40 °C the resonances become sharp and the four ethylene protons give a well-defined ABMX pattern in the ^{1}H{^{31}P} spectrum, and the two CH_2P protons each give an AX pattern (at 400 or 600 MHz). We have formulated this five-coordinate ethylene complex as a trigonal bipyramid with the ethylene in an equatorial position and the double bond in the equatorial plane of the complex; other five-coordinate alkene–iridium(I) complexes have the alkene in the equatorial



Scheme 1 *Reagents and conditions*: i, [IrCl(CO)$_2$(*p*-toluidine)]; ii, EtOH or MeOH; iii, C$_6$H$_6$ or CH$_2$Cl$_2$; iv, NH$_4$PF$_6$; v, L or L/NH$_4$PF$_6$; vi, for **5b**–**5d**, L; vii, H$_2$; viii, 20 °C, 24 h; ix, EtO$_2$CN=NCO$_2$Et

plane[11] and it has been suggested by Rossi and Hoffmann that this is the preferred structure for five-coordinate iridium(I) alkene complexes.[12]

Allene reacted similarly with **4b** to give a mixture of two colourless adducts, in the approximate ratio of 4 : 1. These are probably complexes analogous to the ethylene complex **5b** with the allene pointing 'left' (**5c**) or 'right' (**5d**)[†] and are not fluxional at 25 °C. Other alkenes or acetylenes with electron-withdrawing substituents, such as dimethyl fumarate, diethyl fumarate, *N*-methylmaleimide, dimethyl acetylenedicarboxylate or methyl propriolate, also gave η^2-adducts of the type $[\mathrm{Ir(CO)(L)\{Ph_2PCH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2}\text{-}P,P,N\}][\mathrm{PF_6}]$ (L = alkene, acetylene) which were similarly characterised and probably have structures of type **5**.

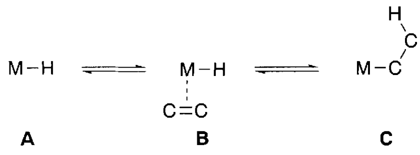
The iridium(I) salt **4b** reacted rapidly with H_2 to give an adduct of configuration **6**[†] with the phosphorus donor atoms mutually *cis* and each *trans* to H. In solution over a period of 24 h, **6** isomerised almost completely to give a dihydride **7**[†] with mutually *trans*-phosphines.

A key step in many organometallic and catalytic reactions is the migration of a hydride ligand from the metal to a coordinated alkene such as ethylene (**A** → **B** → **C** Scheme 2). Examples where this occurs include hydrogenation, hydroformylation, hydrosilylation, hydroboration, hydrocyanation, alkene oligomerisation; the reverse process (**C** → **B**, β-hydrogen elimination) is also important. For a hydride complex to react in this way, it must be coordinatively unsaturated so that it can accept the alkene. Hydrides which are not coordinatively unsaturated, such as *e.g.* complexes of the types $[\mathrm{IrHCl_2(CO)L_2}]$, $[\mathrm{IrH_2Cl(CO)L_2}]$ or $[\mathrm{IrH_2ClL_3}]$ (L = tertiary phosphine) react extremely slowly with alkenes, if at all.[9]

Our work suggests the possibility of a hydride ligand in 18-electron complexes migrating on to the diphosphine backbone, as in the conversion of **3** into **4a**, thus freeing a coordination site which could then take up a substrate such as an alkene or acetylene. The migration might be temporary in that a hydrogen atom from the azine diphosphine ligand backbone could then migrate to the coordinated unsaturated molecule. In support of our suggestion, we have found that the adduct formed between the iridium(I) salt **4b** and $\mathrm{EtO_2CN{=}NCO_2Et}$ has the structure **8**[†] in which a hydrogen atom has indeed moved from a CH_2 of the diphosphine to the nitrogen of the $\mathrm{EtO_2CN{=}NCO_2Et}$ substrate.

Iridium(I)/iridium(III)–tertiary phosphine complexes have been good models for catalytic systems including the reactions of more labile metals (*e.g.* rhodium) for which intermediates are not detected. We have done some preliminary work with rhodium and ligand **1** with encouraging results. We are also studying diphosphines and monophosphines generated from other ketones or aldehydes, including chiral molecules. Thus, we have made diphosphines from (1*R*)-(+)-camphor azine, which from preliminary work show a similar behaviour to **1**, although they react more slowly than **1** or **2** because of unfavourable steric effects. There is great current interest in organometallic and catalytic syntheses involving metals complexed to chiral phosphine ligands.[13]

We suggest that azine diphosphines should be very useful ligands for promoting organometallic and catalytic reactions which could have unique features because of the possibility of the phosphine backbone participating in the chemistry by acting as a temporary source and sink for a hydrogen atom.



Scheme 2

We thank the SERC for support including their University of Edinburgh High Field NMR Service for the 600 MHz spectrum and Dr J. D. Vessey for some of the 400 MHz NMR spectra. We thank Johnson Matthey plc for the generous loan of rare metal salts.

Received, 23rd January 1995; Com. 5/00391A

Footnotes

[†] New compounds were characterised by elemental analyses, and by IR, $^{31}P\{^1H\}$ NMR (36.2 MHz) and ^1H NMR (100, 400 or 600 MHz) spectroscopy.

[‡] *Selected NMR and IR data* for **3**: $\delta_P(C_6D_6$, ref. 85% $H_3PO_4)$ P_A 44.3, P_B 20.3, ^2J(PP) 312 Hz; δ_H ($CDCl_3$, TMS) −15.40 [1H, dd, ^2J(PH) 10.6, 11.4 Hz, IrH], 4.80 [1H, t, ^2J(PH) = ^4J(PH) = 4.9 Hz, PCH=]; IR ν/cm^{-1} (CH_2Cl_2) ν(C≡O) 2030 and ν(IrH) 2200. For **4a**: δ_P(MeOH–C_6D_6) P_A 60.6, P_B 56.0, ^2J(PP) 303 Hz; IR ν/cm^{-1} (MeOH) ν(C≡O) 2000. For **4b**: $\delta_P(CDCl_3)$ P_A 61.7, P_B 54.4, ^2J(PP) 308 Hz; δ_H ($CDCl_3$) 3.48 [2H, d, ^2J(PH) 10.0 Hz, CH_2], 4.17 [2H, dd, ^2J(PH) 7.8, ^4J(PH) 2.5 Hz, CH_2]; IR ν/cm^{-1} (CH_2Cl_2) ν(C≡O) 2000. For **5a**: δ_P(EtOH) P_A 39.5, P_B 10.6, ^2J(PP) 57 Hz; IR ν/cm^{-1} (EtOH) ν(C≡O) 2015. For **5b**: $\delta_P(CD_2Cl_2)$ P_A 38.4, P_B 10.4, ^2J(PP) 57 Hz; δ_H (600 MHz, CD_2Cl_2, −40 °C) 1.50 (1H, m, ethylene-H), 2.22 [1H, dd, ^2J(HH) 12.8, ^2J(PH) 12.2 Hz, CH_2], 2.41 (1H, m, ethylene-H), 2.83 (2H, m, ethylene-H), 3.59 [1H, ddd, ^2J(HH) 19.4, ^2J(PH) 7.0, ^4J(PH) 2.6 Hz, CH_2], 3.71 [1H, dd, ^2J(HH) 12.8, ^2J(PH) 12.6 Hz, CH_2], 4.38 [1H, dd, ^2J(HH) 19.4, ^2J(PH) 11.0 Hz, CH_2]; IR ν/cm^{-1} (CH_2Cl_2) ν(C≡O) 2015. For **5c**/**5d**: Major isomer **5c**; $\delta_P(CD_2Cl_2)$ P_A 32.5 P_B 14.5, ^2J(PP) 42 Hz; minor isomer **5d** δ P_A 41.2 P_B 6.7, ^2J(PP) 39 Hz. For **6**: $\delta_P(CD_2Cl_2)$ P_A 27.5, P_B 11.0, ^2J(PP) 11.0 Hz; δ_H (400 MHz, CD_2Cl_2) −8.76 [1H, ddd, ^2J(HH) 2.1, ^2J(PH) 138.0, 13.9 Hz, IrH], −7.56 [1H, ddd, ^2J(HH) 2.1, ^2J(PH) 132.6, 19.4 Hz, IrH]; IR ν/cm^{-1} (CH_2Cl_2) ν(C≡O) 2045, ν(IrH) 2100, 2070. For **7**: $\delta_P(CD_2Cl_2)$ P_A 37.5, P_B 20.5, ^2J(PP) 301 Hz; δ_H(400 MHz, CD_2Cl_2) −17.32 [1H, m, ^2J(HH) 3.7, ^2J(PH) 9.6 Hz, IrH], −8.87 [1H, m, ^2J(HH) 3.7, ^2J(PH) 20.1, ^4J(HH) 1.5 Hz, IrH]; IR ν/cm^{-1} (CH_2Cl_2) ν(C≡O) 2015, ν(IrH) 2110, 2160. For **8**: $\delta_P(CD_2Cl_2)$ P_A 3.7, P_B −17.5, ^2J(PP) 13.2 Hz; δ_H(400 MHz, CD_2Cl_2) 2.60 [1H, dd, ^2J(HH) 17.5, ^2J(PH) 12.0 Hz, PCH_2], 3.20 [1H, dd, ^2J(HH) 17.5, ^2J(PH) 13.5 Hz, PCH_2], 4.06 [1H, d, ^2J(PH) 7.0 Hz, PC*H*=], 10.61 (1H, s, br, N*H*); IR ν/cm^{-1} (CH_2Cl_2) ν(C≡O) 2065.

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