THE PREPARATION OF FLUXIONAL TETRAHYDRIDES, [ĪrH$_4$\{Bu$^t_2$ṖCH$_2$CH$_2$ĊHCHRCH$_2$ṖBu$^t_2$\}] (R = H OR Me) AND THEIR REACTIONS WITH CO, Bu^{t}NC OR HBr

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(Received April 30th, 1982)

Summary

The cyclometallated monohydrides [ĪrHCl\{Bu$^t_2$ṖCH$_2$CH$_2$ĊHCHRCH$_2$ṖBu$^t_2$\}] (R = H or Me) react with NaOPr^i/Pr^{i}OH/H$_2$ to give fluxional tetrahydrides, probably [ĪrH$_4$\{Bu$^t_2$ṖCH$_2$CH$_2$ĊHCHRCH$_2$ṖBu$^t_2$\}]. These are highly fluxional having magnetically equivalent hydridic hydrogens, even at —100°C. When treated with HBr, [ĪrH$_4$\{Bu$^t_2$ṖCH$_2$CH$_2$ĊHCH$_2$CH$_2$ṖBu$^t_2$\}], gives [ĪrHBr\{Bu$^t_2$ṖCH$_2$-CH$_2$CHCH$_2$CH$_2$ṖBu$^t_2$\}] and with CO it gives a mixture of complexes which are probably [ĪrH$_2$(CO)\{Bu$^t_2$ṖCH$_2$CH$_2$ĊHCH$_2$CH$_2$ṖBu$^t_2$\}] (2 isomers) and [Īr(CO)$_2$-\{Bu$^t_2$ṖCH$_2$CH$_2$CHCH$_2$CH$_2$ṖBu$^t_2$\}]. When treated with Bu^{t}NC this tetrahydride undergoes similar reactions but another (major) product is formed which appears to be binuclear and fluxional and is probably of type [Īr$_2$H$_4$\{Bu$^t_2$ṖCH$_2$-CH$_2$ĊHCH$_2$CH$_2$ṖBu$^t_2$\}$_2$], with four bridging hydrogens.

Iridium pentahydrides of the type [IrH$_5$L$_2$] (L = tertiary phosphine) are known for small phosphines, PEt$_3$, PEt$_2$Ph and PMe$_3$ but are rather labile [1,2]. They are made by treating R$_3$P— iridium chlorides with LiAlH$_4$ or NaBH$_4$ etc. With tertiary phosphine ligands, which are more bulky, iridium pentahydrides of this type are less labile and usually more easily isolated. We have shown that the five-coordinate hydride [IrHCl$_2$(PBu$^t_2$Pr^n)$_2$] reacts readily with dihydrogen in the presence of sodium propan-2-oxide to give the pentahydride [IrH$_5$-(PBu$^t_2$Pr^n)$_2$] [3]. The even more inert pentahydrides [IrH$_5$(PBu$^t_2$Ph)$_2$] and [IrH$_5$(PBu$^t_3$)$_2$] were similarly made from the dihydrides [IrH$_2$Cl(PR$_3$)$_2$] and dihydrogen/sodium propan-2-oxide [4]. We also showed that these penta-hydrides react with carbon monoxide to give, successively, mono- and di-carbonyl species of types [IrH$_3$(CO)L$_2$] and [IrH(CO)$_2$L$_2$] [3].

We have recently described cyclometallated hydrido complexes of the type [ĪrHCl\{Bu$^t_2$ṖCH$_2$CH$_2$ĊHCHRCH$_2$ṖBu$^t_2$\}] (1, R = H or CH$_3$) [5—7] and it seemed possible that these might react in a similar way with H$_2$/base to give tetrahydrides. It is also known that multihydrides of types [MH$_x$(PR$_3$)$_y$] (M =

Re; $x = 7$, $y = 2$; or $x = 5$, $y = 3$ [8,9]; M = Os, $x = 6$, $y = 2$; $x = 4$, $y = 3$ [10]; M = Ir, $x = 5$, $y = 2$ [1]) are highly fluxional and that the fluxional process is rapid on the NMR time scale even at $-100°C$. We hoped that the postulated iridium tetrahydrides containing the tridentate, cyclometallated diphosphine(s) depicted in **1** might be less fluxional.

When we treated a benzene solution of the cyclometallated hydride (**1**, R = Me) with sodium propan-2-oxide in a hydrogen atmosphere the initial deep orange colour paled and after ca. 30 min had become almost colourless. The solvent was removed under reduced pressure and the $^{31}P \{^1H\}$ NMR spectrum of the residue (in C_6D_6) showed a singlet at $\delta(P)$ 83.2 ppm, and a 1/4/6/4/1 quintet, when the t-butyl and methylene protons were selectively decoupled, leaving four hydridic hydrogens coupled to phosphorus. In the ^1H NMR spectrum, a single hydride resonance as a triplet at $\delta(H)$ -10.4 ppm, with $^2J(PH)$ 10.6 Hz, was observed, which shows that the four hydrides become magnetically equivalent by a fluxional process at room temperature, as are the five hydrides of the pentahydrides [IrH$_5$L$_2$]. The product is extremely soluble, even in pentane, and we were unable to isolate it. It is also air sensitive. However, the NMR evidence and method of synthesis shows that it is almost certainly the tetrahydride (**2a**). We hoped that the more rigid framework of the metallated diphosphine might make this tetrahydride **2a** less fluxional than complexes of type [IrH$_5$L$_2$] and that at low temperatures the fluxionality might be shown on the NMR time scale. The hydride resonance at $\delta(H)$ -10.4 ppm, however, only broadened when a solution of the tetrahydride **2a** in $C_6D_5CD_3$ was cooled to $-99.5°C$ and therefore this complex is still fluxional down to this temperature.

When a solution of the tetrahydride [IrH$_4\{$Bu$_2^t$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$_2^t\}$] in benzene was treated with carbon monoxide and the $^{31}P\{^1H\}$ NMR spectrum of the yellow-orange solution recorded, there were sharp singlet peaks at $\delta(P)$ 82.6, 85.3 and 94.4 ppm, present in the ratio of ca. 2/1/3, respectively. Selective decoupling of the t-butyl and methylene resonances showed these peaks as a double-doublet with $^2J(PH)$ 10 and 7.5 Hz, a triplet with $^2J(PH)$ 11 Hz, and a singlet respectively (Fig. 1). This indicates that the peaks at 82.6 and 85.3 ppm are dihydrido-complexes, probably [IrH$_2$(CO)$\{$Bu$_2^t$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$_2^t\}$], with the species showing the low frequency resonance containing non-equivalent hydride ligands. The singlet at $\delta(P)$ 94.4 ppm is probably due to a dicarbonyl complex [Ir(CO)$_2\{$Bu$_2^t$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$_2^t\}$] (**3**) (X = CO). When this reaction mixture was stirred for 18 h under carbon monoxide, the ^{31}P NMR spectrum showed only two products to be present; the dicarbonyl complex and the dihydro-complex with equivalent hydrides ($\delta(P)$ 85.3 ppm). We tentatively suggest that the species with $\delta(P)$ 85.3 ppm and which gives a 1/2/1 triplet ^{31}P NMR pattern when only the organic hydrogens are decoupled is **4a** and the species with $\delta(P)$ 82.6 ppm,is either **4b** or **4c**. We assign the structures in this way because with X or Z = H in **4** $^2J(PH)$ are more likely to be similar in magnitude than $^2J(PH)$ for a hydride in position Y (*trans* to carbon). The J-values are probably accurate to ± 2 Hz.

We thought that treatment of the tetrahydride **2a** with t-butyl isocyanide might go more slowly than treatment with carbon monoxide and products might be easier to isolate. However, we find that the reaction is even more
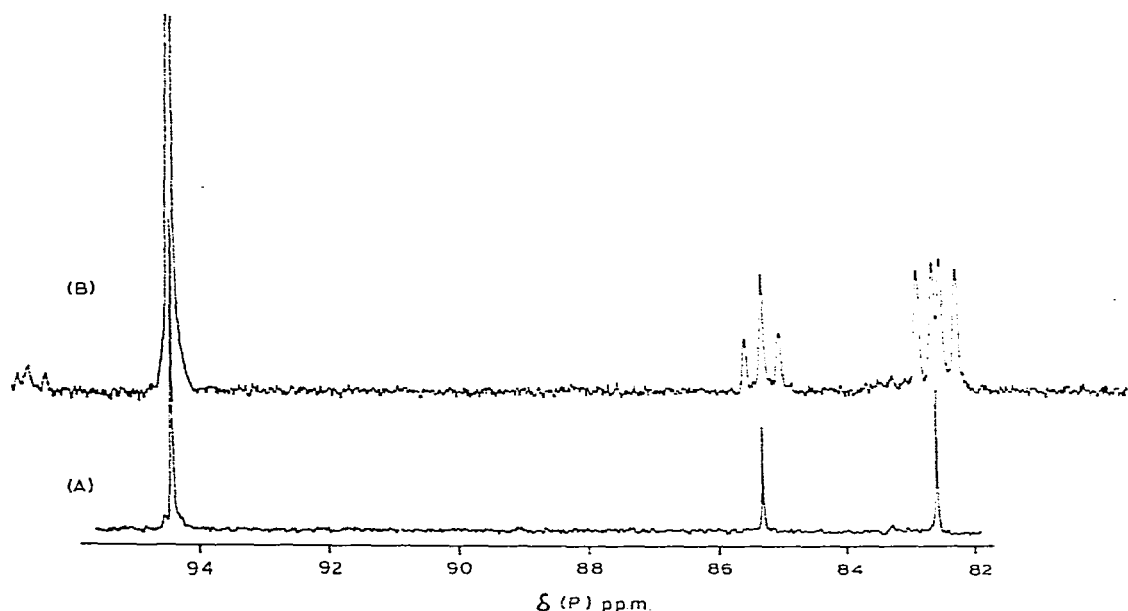
Fig. 1. ^{31}P NMR spectra of the products obtained by treatment of [IrH$_4$ {Bu$_2^t$PCH$_2$CH$_2$CHCH$_2$CH$_2$PBu$_2^t$}] with CO. (A) with all protons decoupled, (B) with Bu^t, CH$_2$ and CH protons selectively decoupled.

complex with t-butyl isocyanide than with carbon monoxide. Addition of one mole equivalent of Bu^{t}NC to a benzene solution of the tetrahydride 2a caused rapid conversion to a mixture of products. The fully proton-decoupled phosphorus-31 spectrum, and the corresponding phosphorus-31, resonances with only the organic hydrogens decoupled, are both shown in Fig. 2. The product, δ(P) 89.5 ppm, is thus shown not to be a hydride and is possibly of type 3b. Two dihydrides are formed, one at δ(P) 82.2 ppm has approximately equivalent hydride ligands and is possibly 4d whilst the other, giving a doublet of doublets ^{31}P pattern, is possibly 4e or 4f, i.e. completely analogous to the carbonyl dihydrides discussed above. There were also several small (unassigned) peaks in the ^{31}P {^{1}H} spectrum but another important product had δ(P) at 55.1 ppm. When only the organic hydrogens were selectively decoupled from this resonance the resultant pattern was complex and second order (see Fig. 2). This pattern is too complex to be due to a mononuclear species. We tentatively suggest that the pattern is of the [AX]$_4$ type and is produced by a fluxional binuclear hydride [Ir$_2$H$_4${Bu$_2^t$PCH$_2$CH$_2$CHCH$_2$CH$_2$PBu$_2^t$}$_2$] possibly with structure 5.

In this fluxional complex, the phosphorus nuclei are chemically but not magnetically equivalent. The ^{1}H {^{31}P} NMR spectrum of this mixture produced from 2a and Bu^{t}NC showed hydride resonances at −10.5, −12.9, and −13.8 ppm. Without ^{31}P-decoupling the hydride resonances were broad mainly with unresolved fine structure and we could not assign structures to the complexes responsible. Prolonged treatment of 2a with an excess of Bu^{t}NC gave a complex mixture which we did not separate.
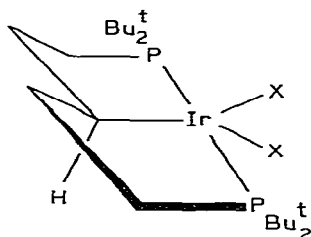
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SCHEME 1
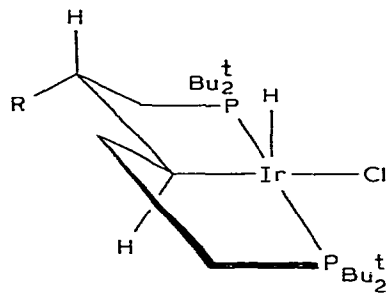
(1)
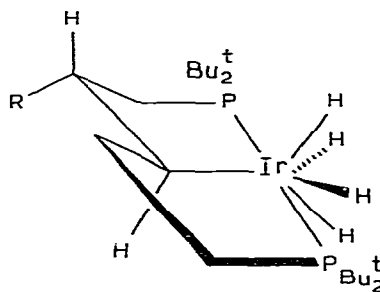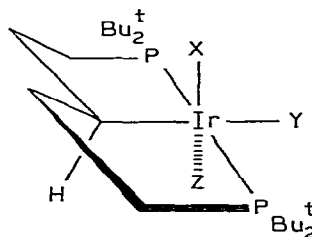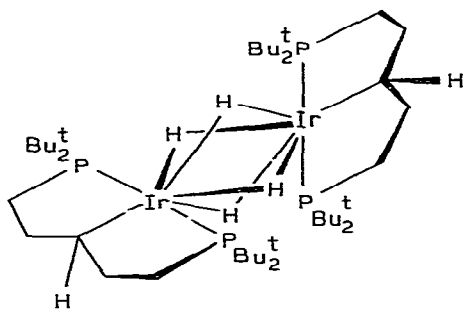
(2a, R = H;

2b, R = Me)

(3a, X = CO;

3b, X = CNBu^t)

(4a, X = Z = H, Y = CO;

4b, Y = Z = H, X = CO;

4c, X = Y = H, Z = CO;

4d, X = Z = H, Y = CNBu^t;

4e, Y = Z = H, X = CNBu^t;

4f, X = Y = H, Z = CNBu^t)

(5)

By treating a solution of the tetrahydride **3a** in benzene with one mol equivalent of HBr, an orange-red solution was obtained from which [IrHBr{Bu$_2^t$P-(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$_2^t$}] was obtained as red needles. The ^{31}P {^{1}H} NMR spectrum of this complex showed a singlet at δ(P) —75.2 ppm which resolved into a doublet when t-butyl and methylene protons were selectively decoupled.

We have also described the cyclometallated hydride [IrHCl{Bu$_2^t$PCH$_2$CH$_2$-CHCHMeCH$_2$PBu$_2^t$}] (**1**, R = Me) containing a pseudo-equatorial methyl group.
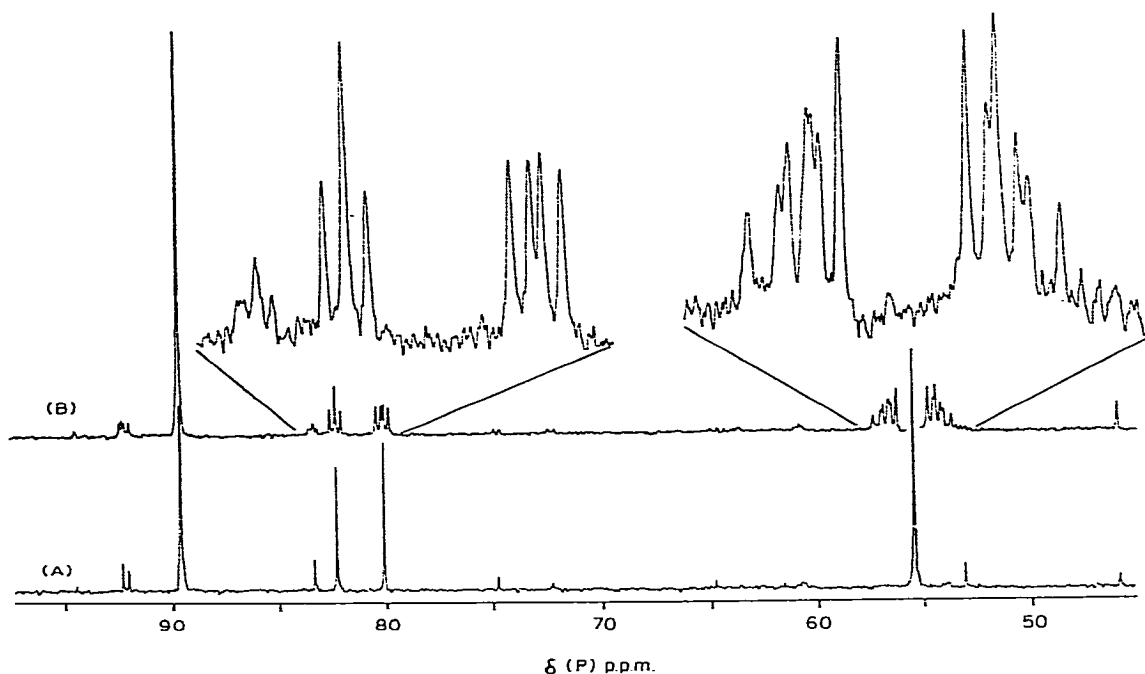
Fig. 2. ^{31}P NMR spectra of the products obtained by treatment of [IrH$_4$ {Bu$_2^t$PCH$_2$CH$_2$CHCH$_2$CH$_2$PBu$_2^t$}] with Bu^{t}NC. (A) with all protons decoupled, (B) with Bu^t, CH$_2$ and CH protons selectively decoupled.

We have now converted this hydride into a tetrahydride, probably **2b**, by treatment with H$_2$/NaOPr^i. The crude product was obtained as an air-sensitive and very soluble yellow solid which we did not purify. However, the ^{31}P {^{1}H}

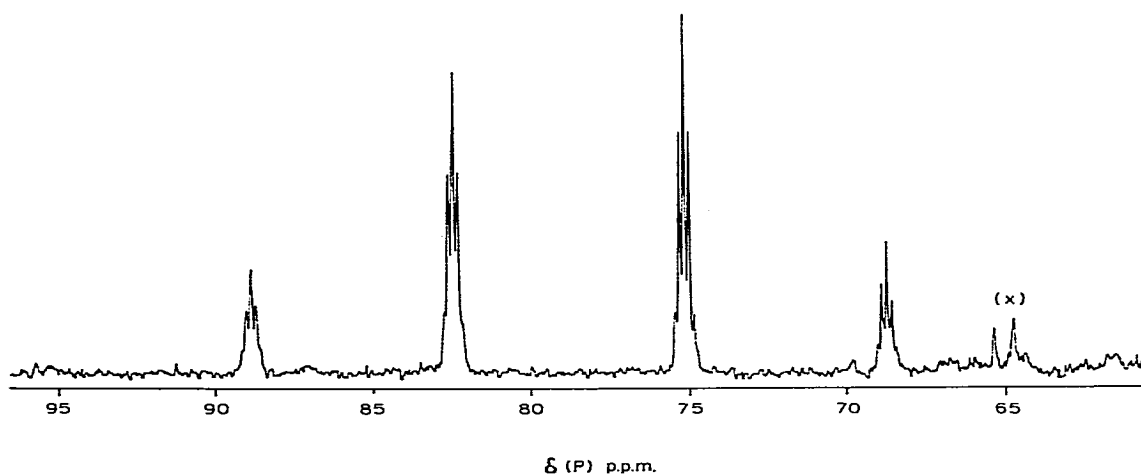Fig. 3. ^{31}P NMR spectrum (in C$_6$D$_6$) of [IrH$_4$ {Bu$_2^t$PCH$_2$CH$_2$CHCH(Me)CH$_2$PBu$_2^t$}] with Bu^t, CH$_2$ and CH protons selectively decoupled. δ(P$_1$) 68.7 ppm, δ(P$_2$) 83.8 ppm, ^{2}J(P$_1$P$_2$) 323 Hz. 'x' = impurity.

NMR spectrum showed an AB pattern uncontaminated by any other phosphorus-containing complex and the ^{31}P NMR pattern, with only the organic hydrogens decoupled, was of the ABX$_4$ type, see Fig. 3. The hydride resonance occurred at δ(H) —10.35 ppm as a triplet with ^2J(PH) 10.3 Hz. Hence we formulate the product as a fluxional tetrahydride [IrH$_4${Bu$^t_2$PCH$_2$CH$_2$CHCH-MeCH$_2$PBu$^t_2$}] (**2b**). At —99.5°C the ^{1}H NMR pattern consisted of two broad overlapping bands at δ(H) —10.0 and —10.6 ppm suggesting that the fluxional process, which causes apparent equivalence of the four hydrogens at 20°C, is slowing down. It is not possible to study NMR spectra below —100°C on our instrument.

Experimental

^{1}H, ^{1}H {^{31}P}, and ^{31}P {^{1}H} NMR spectra were recorded with a JEOL FX100Q spectrometer using an internal deuterium lock.

Preparation of [IrH$_4${Bu$^t_2$P(CH$_2$)$_2$CH(CH)$_2$PBu$^t_2$}] by treatment of [IrHCl-{Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$}] with NaOPr^i and H$_2$

A solution of [IrHCl{Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$}] (0.07 g, 0.11 mmol) in benzene (4 cm^3) was thoroughly degassed and stirred under hydrogen. A solution of sodium isopropoxide (0.113M, 1 cm^3, 0.11 mmol) was added and the mixture stirred for 1.5 h. The solvent was removed under pressure and the residue taken up in hexadeuteriobenzene for NMR spectroscopic studies. [IrHCl{Bu$^t_2$PCH$_2$CH$_2$CHCHMeCH$_2$PBu$^t_2$}] was similarly treated to give the corresponding tetrahydride (**2b**).

Treatment of [IrH$_4${Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$}] with CO or Bu^{t}NC

A solution of the tetrahydride was prepared as described above and the required amount of Bu^{t}NC added via a syringe or, in the case of CO, the gas was bubbled through the solution.

Preparation of [IrHBr{Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$}]

A solution of the corresponding chloride hydride (0.77 g, 0.131 mmol) in degassed C$_6$H$_6$ (2 cm^3) was stirred under H$_2$ and a solution of sodium propan-2-ol (1.4 cm^3, 0.113M, 0.136 mmol) added. The solution became almost colourless. An aqueous solution of hydrobromic acid (0.1 cm^3, 1.26M, 0.26 mmol) was added. A gas (hydrogen) was evolved and ^{31}P {^{1}H} NMR spectroscopy (C$_6$D$_6$ lock) established that only one phosphorus-containing species was present (i.e. the required product). This was isolated by evaporation, recrystallised from n-hexane and obtained as red-brown needles (0.050 g, 60%) which sublime above 170°C and melt with decomposition 195—205°C. Found: C, 40.2; H, 7.4; Br, 12.55. C$_{21}$H$_{48}$BrIrP$_2$ calcd.: C, 39.85; H, 7.35; Br, 12.65%.

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