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Phosphine- and Pyridine-Assisted Rearrangement of (Ethene)iridium to Hydrido(vinyl)iridium Complexes[1]

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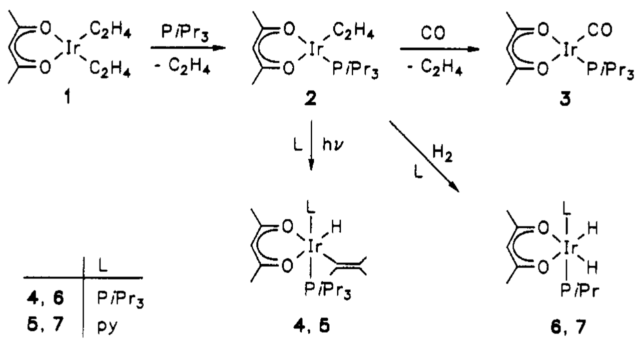
Summary: The (ethene)iridium complex $[Ir(acac)(C_2H_4)(P\mathit{i}Pr_3)]$ *(**2**), which is prepared from* $[Ir(acac)(C_2H_4)_2]$ *(**1**) and* $P\mathit{i}Pr_3$*, reacts on UV irradiation in the presence of triisopropylphosphine or pyridine to give the hydrido(vinyl) compounds* $[IrH(CH{=}CH_2)(acac)(L)(P\mathit{i}Pr_3)]$ *(**4**, **5**) in 85–90% yield. The X-ray crystal structure analysis of **4** (monoclinic, space group* $P2_1/c$ *(No. 14) with* $a = 10.690(5)$ Å, $b = 12.882(3)$ Å, $c = 21.66(1)$ Å, *and* $\beta = 90.95(2)°$*) reveals that the iridium is coordinated in a slightly distorted octahedral fashion with the two phosphine ligands in trans positions. On treatment of **2** with* H_2 *in the presence of* $P\mathit{i}Pr_3$ *or pyridine, the dihydridoiridium(III) complexes* $[IrH_2(acac)(L)(P\mathit{i}Pr_3)]$ *(**6**, **7**) are formed.*

Scheme I



Since the first report by Stoutland and Bergman,[2] that the 16-electron fragment $[C_5Me_5Ir(PMe_3)]$ which is generated on thermolysis of $[C_5Me_5IrH(C_6H_{11})(PMe_3)]$ reacts with ethene to give a mixture of $[C_5Me_5Ir(C_2H_4)(PMe_3)]$ and $[C_5Me_5IrH(CH{=}CH_2)(PMe_3)]$, the problem of both the *inter*- and the *intra*molecular activation of C–H bonds in simple olefins has become an area of great interest.[3] As far as iridium is concerned, we have shown recently[4] that non-Cp containing compounds of the general type *trans*-$[IrCl(C_2H_4)(PR_3)_2]$ rearrange photochemically to give $[IrHCl(CH{=}CH_2)(PR_3)_2]$ but that the equilibrium between the two isomers is strongly influenced by the nature of the coordinated phosphine. In this note we describe that the chelate complex $[Ir(acac)(C_2H_4)(P\mathit{i}Pr_3)]$ (**2**), which contains only one PR_3 ligand, upon photolysis can also be converted to a hydrido(vinyl)iridium compound. This transformation occurs provided that the formal insertion of the metal into one of the C—H bonds is supported by the addition of a Lewis base.

On treatment with $P\mathit{i}Pr_3$, the bis(ethylene)iridium(I) complex **1** (Scheme I) gives the phosphine derivative **2** in almost quantitative yield. The reaction proceeds at room temperature and does not lead to the displacement of the second olefin ligand even if a 10-fold excess of $P\mathit{i}Pr_3$ is used. **2** is a yellow air-sensitive solid which is stable for several hours if kept under argon at low temperature. The ^1H NMR spectrum indicates that the barrier for rotation around the Ir–C_2H_4 bond is rather high because the geminal H–H coupling can already be observed at −20 °C in toluene-d_8. The ethylene ligand is easily displaced by stronger π-acceptor ligands. Thus, by passing a slow stream of carbon monoxide through a hexane solution of **2**, the carbonyl complex **3** is quantitatively formed.

Whereas at room temperature compound **2** is inert toward $P\mathit{i}Pr_3$, a slow reaction takes place upon heating a solution of both substrates in C_6D_6 to 60 °C. The conversion of **2** to a hydridoiridium complex is indicated by the appearance of a sharp signal at δ −25.0 in the high-field region which owing to P–H coupling is split into a triplet. On UV irradiation, the reaction of **2** and $P\mathit{i}Pr_3$ is much faster and, after 1 h in C_6D_6, gives the hydrido(vinyl)iridium(III) derivative **4** in 88% yield. In contrast to the precursor complex **2**, the pale yellow crystalline compound **4** is not air-sensitive and can be stored at room temperature without decomposition. It is interesting to note that if a benzene solution of **2** is irradiated in the absence of $P\mathit{i}Pr_3$, a mixture of products is obtained which could not be separated either by chromatography or by fractional crystallization. According to the ^1H NMR spectrum, which shows a doublet in the high-field region at δ −23.3, the dominating species is presumably the five-coordinated hydrido(vinyl)iridium complex $[IrH(CH{=}CH_2)(acac)(P\mathit{i}Pr_3)]$. When the benzene solution is warmed to 60 °C for 2 h, the main product is reconverted to the starting material **2**.

The equilibrium between **2** and the isomeric hydrido(vinyl) compound can also be shifted to the side of the iridium(III) species if the photochemical reaction is carried out in the presence of pyridine. A yellow air-stable oil **5** is isolated in 86% yield and has been characterized by NMR spectroscopy. As none of the acac CH_3 resonances but one of the pyridine *C*H signals is split into a doublet due to P—C coupling, we propose a trans disposition of the phosphine and the pyridine ligands in **5**. We note that Vrieze et al. have studied the reaction of the bis(ethylene) complex **1** with $P\mathit{t}Bu_2(CH_2CH{=}CH_2)$ (in

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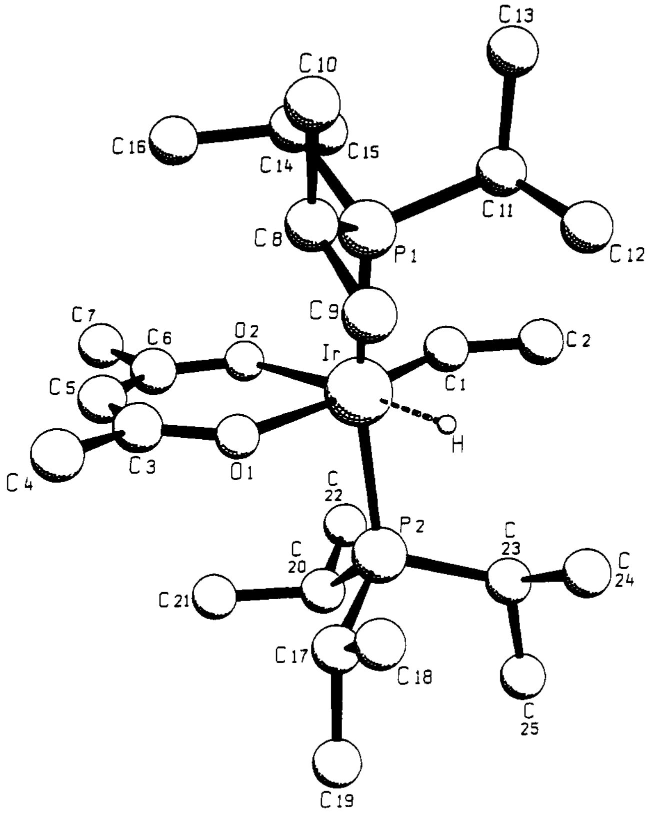

Figure 1. Molecular structure (SCHAKAL drawing) of complex **4** (with the hydride ligand in the calculated position).

Table I. Selected Bond Distances and Angles with Esd's for 4

Bond Distances (Å)			
Ir–P1	2.325(4)	C1–C2	1.34(2)
Ir–P2	2.339(4)	O1–C3	1.28(2)
Ir–O1	2.17(1)	O2–C6	1.28(2)
Ir–O2	2.185(9)	C3–C5	1.38(2)
Ir–C1	2.02(1)	C5–C6	1.38(2)
Bond Angles (deg)			
P1–Ir–P2	165.3(1)	C1–Ir–O2	86.5(4)
P1–Ir–O1	88.7(3)	O1–Ir–O2	87.0(3)
P1–Ir–O2	97.3(2)	Ir–C1–C2	135.0(1)
P1–Ir–C1	91.2(5)	Ir–O1–C3	125.0(1)
P2–Ir–O1	90.0(3)	Ir–O2–C6	125.2(9)
P2–Ir–O2	97.2(2)	O1–C3–C5	126.0(1)
P2–Ir–C1	91.7(4)	O2–C6–C5	126.0(1)
C1–Ir–O1	173.4(4)	C3–C5–C6	131.0(1)

hexane at 60 °C) and trapped the primary intermediate $[IrH\{PtBu_2(CH_2CH{=}CH)\}(acac)]$ as a 1:1 adduct with γ-picoline.[5]

The result of the X-ray structural analysis of compound **4** is shown in Figure 1. Although the position of the hydride ligand was calculated (see the hatched circle), on the basis of the positions of the Ir-bound atoms O1, O2, and C1 and the bond angles (see Table I), there is no doubt that the metal center is octahedrally coordinated. The bending of the phosphorus–metal–phosphorus axes (angle 165.3(1)°) in the direction of the smallest ligand (hydride) is comparable to that found in $[IrH(CH{=}CH_2)Cl(CO)(PiPr_3)_2]$.[4] The distance between the iridium and the α-carbon atom of the vinyl group (2.02(1) Å) is significantly smaller than that in the related complex $[IrH(CH{=}CH_2)Cl(CO)(PiPr_3)_2]$ (2.06(1) Å)[4] and reflects the different influence of the chloro and the acac ligands.

The starting material **2** can be used not only for C–H activation but also for oxidative addition reactions. Whereas (as mentioned above) the ethylene complex at room temperature does not react with $PiPr_3$ and pyridine, the dihydrido compounds **6** and **7** are easily formed by passing a slow stream of H_2 through a solution of **2**/$PiPr_3$ or **2**/py. Both are yellow, only moderately air-sensitive solids for which correct elemental analyses have been obtained. As the acac CH_3 resonances in the ^{13}C NMR spectra of **6** and **7** show no P–C coupling, we assume that in both compounds the two hydrides are in the same plane as the acac ligand, while the two neutral ligands occupy the apical positions. We are presently investigating the reactivity of the dihydrido- and the hydrido(vinyl)iridium complexes to find out in particular whether they can be used like other iridium hydrides (e.g., $[IrH_2Cl(PiPr_3)_2]$ and $[IrH_5(PiPr_3)_2]$) for alkyne insertion reactions and the preparation of vinylideneiridium species.[6]

Experimental Section

All experiments were carried out under an atmosphere of argon using Schlenk tube techniques. The starting material **1** was prepared as described in the literature.[7] Melting points were determined by DTA.

Preparation of $[Ir(acac)(C_2H_4)(PiPr_3)]$ (2). A solution of **1** (80 mg, 0.23 mmol) in 10 mL of hexane was treated with $PiPr_3$ (44 μL, 0.23 mmol) and stirred for 5 min at room temperature. The solvent was removed in vacuo, and a yellow crystalline solid was isolated. It can be stored for some hours at –60 °C without decomposition; yield 105 mg (95%); mp 72 °C dec. Anal. Calcd for $C_{16}H_{32}IrO_2P$: C, 40.07; H, 6.72. Found: C, 40.31; H, 7.00. IR (THF): ν(acac) 1575, 1522 cm^{-1}. ^1H NMR (400 MHz, $C_6D_5CD_3$, –20 °C): δ 5.21 (s, C*H* of acac), 2.78 and 2.28 (both dd, *J*(HH) = 7.9 and 3.5 Hz, C_2H_4), 2.02 (m, $PCHCH_3$), 1.73 and 1.63 (both s, CH_3 of acac), 1.17 (dd, *J*(PH) = 12.7, *J*(HH) = 7.2 Hz, $PCHCH_3$). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 186.43 and 181.54 (both s, *C*O of acac), 100.98 (s, *C*H of acac), 28.28 (d, *J*(PC) = 5.5 Hz, one CH_3 of acac), 26.73 (s, one CH_3 of acac), 26.20 (s, C_2H_4), 21.89 (d, *J*(PC) = 30.3 Hz, $PCHCH_3$), 19.66 (s, $PCHCH_3$). ^{31}P NMR (36.2 MHz, C_6D_6, 25 °C): δ 15.44 (s).

Preparation of $[Ir(acac)(CO)(PiPr_3)]$ (3). A slow stream of CO was passed for 5 min through a solution of **2** (72 mg, 0.15 mmol) in 15 mL of hexane. After the solvent was removed, the yellow-green air-stable residue was washed with pentane (0 °C) and dried in vacuo; yield 69 mg (96%); mp 98 °C. Anal. Calcd for $C_{15}H_{28}IrO_3P$: C, 37.57; H, 5.88. Found: C, 37.38; H, 5.83. IR (KBr): ν(CO) 1940, ν(acac) 1581, 1525 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 5.27 (s, C*H* of acac), 2.27 (m, $PCHCH_3$), 1.72 and 1.58 (both s, CH_3 of acac), 1.16 (dd, *J*(PH) = 13.8, *J*(HH) = 7.2 Hz, $PCHCH_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ 35.55 (s).

Preparation of $[IrH(CH{=}CH_2)(acac)(PiPr_3)_2]$ (4). A solution of **2** (62 mg, 0.13 mmol) in 0.4 mL of C_6D_6 was treated with $PiPr_3$ (25 μL, 0.13 mmol) and in an NMR tube was irradiated at 10 °C for 1 h with a 500-W Hg lamp (Oriel). The solution was then chromatographed on Al_2O_3 (neutral, activity grade V) with hexane. With benzene a yellow fraction was eluted which was brought to dryness in vacuo. The pale yellow air-stable residue was washed with pentane and dried; yield 73 mg (88%); mp 118 °C. Anal. Calcd for $C_{25}H_{53}IrO_2P_2$: C, 46.93; H, 8.35. Found: C, 46.60; H, 8.58. IR (KBr): ν(IrH) 2237, ν(acac) 1590 and 1515 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 8.51 (dd, *J*(HH) = 18.0 and 10.4 Hz, $IrCH{=}CH_2$), 6.03 (dd, *J*(HH) = 10.4 and 3.6 Hz, one H of $IrCH{=}CH_2$, trans to Ir), 5.19 (s, C*H* of acac), 5.12 (dd,

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J(HH) = 18.0 and 3.6 Hz, one H of IrCH=C*H*$_2$, cis to Ir), 2.52 (m, PC*H*CH$_3$), 1.76 and 1.58 (both s, C*H*$_3$ of acac), 1.26 and 1.25 (both dvt, *N* = 15.0, *J*(HH) = 7.2 Hz, PCHC*H*$_3$), −24.97 (t, *J*(PH) = 16.4 Hz, IrH). ^{13}C NMR (100.6 MHz, C_6D_6): δ 186.02 and 183.74 (both s, *C*O of acac), 129.74 (t, *J*(PC) = 8.9 Hz, Ir*C*H=CH$_2$), 117.11 (t, *J*(PC) = 2.8 Hz, IrCH=*C*H$_2$), 102.12 (s, *C*H of acac), 28.83 and 28.14 (both s, *C*H$_3$ of acac), 22.80 (vt, *N* = 24.9 Hz, P*C*HCH$_3$), 18.98 and 18.94 (both s, PCH*C*H$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ 21.41 (s; d in off-resonance).

Preparation of [IrH(CH=CH$_2$)(acac)(py)(P*i*Pr$_3$)] (5). A solution of 2 (60 mg, 0.13 mmol) in 0.2 mL of C_6D_6 was treated with excess pyridine (0.2 mL) and in an NMR tube was irradiated at 10 °C for 4 h with a 500-W Hg lamp (Oriel). The solvent was removed in vacuo, and the oily residue was dissolved in 5 mL of hexane. The solvent was again removed, and this procedure was repeated three times to distill off all the pyridine. A yellow, highly viscous oil was obtained; yield 62 mg (86%). IR (THF): ν(IrH) 2198, ν(acac) 1584 and 1514 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 8.8, 6.8, and 6.4 (all m, NC$_5$H$_5$), 8.72 (dd, *J*(HH) = 17.5 and 10.2 Hz, IrC*H*=CH$_2$), 6.33 (dd, *J*(HH) = 10.2 and 3.8 Hz, one H of IrCH=C*H*$_2$, trans to Ir), 5.54 (dd, *J*(HH) = 17.5 and 3.8 Hz, one H of IrCH=C*H*$_2$, cis to Ir), 5.00 (s, C*H* of acac), 2.40 (m, PC*H*CH$_3$), 1.77 and 1.65 (both s, C*H*$_3$ of acac), 1.39 and 1.26 (both dd, *J*(PH) = 12.8, *J*(HH) = 7.2 Hz, PCHC*H*$_3$), −25.23 (d, *J*(PH) = 23.2 Hz, IrH). ^{13}C NMR (100.6 MHz, C_6D_6): δ 184.90 and 184.60 (both s, *C*O of acac), 152.75 and 135.84 (both s, NC$_5$H$_5$), 130.77 (d, *J*(PC) = 9.1 Hz, Ir*C*H=CH$_2$), 123.61 (d, *J*(PC) = 2.7 Hz, NC$_5$H$_5$), 120.36 (s, IrCH=*C*H$_2$), 100.92 (s, *C*H of acac), 29.05 and 28.67 (both s, *C*H$_3$ of acac), 24.08 (d, *J*(PC) = 30.9 Hz, P*C*HCH$_3$), 18.99 and 18.60 (both s, PCH*C*H$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ 18.83 (s; d in off-resonace).

Preparation of [IrH$_2$(acac)(P*i*Pr$_3$)$_2$] (6). A solution of 2 (68 mg, 0.14 mmol) in 10 mL of hexane was treated at −78 °C with P*i*Pr$_3$ (27 μL, 0.14 mmol), and then a slow stream of H$_2$ was passed through the solution for 5 min. The reaction mixture was warmed under H$_2$ to room temperature, and after it was stirred for 1 h, the solvent was removed. The oily residue was dissolved in 2 mL of hexane, and the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V). With benzene/THF (1:1) a yellow fraction was eluted which after removal of the solvent gave yellow air-stable crystals; yield 64 mg (74%); mp 51 °C. Anal. Calcd for $C_{23}H_{51}IrO_2P_2$: C, 45.01; H, 8.37. Found: C, 45.02; H, 8.64. ^{1}H NMR (400 MHz, C_6D_6): δ 5.20 (s, C*H* of acac), 2.17 (m, PC*H*CH$_3$), 1.72 (s, C*H*$_3$ of acac), 1.24 (dvt, *N* = 13.3, *J*(HH) = 7.1 Hz, PCHC*H*$_3$), −27.94 (t, *J*(PH) = 16.8 Hz, IrH$_2$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 184.21 (s, *C*O of acac), 100.95 (s, *C*H of acac), 28.52 (s, *C*H$_3$ of acac), 25.77 (vt, *N* = 26.0 Hz, P*C*HCH$_3$), 19.98 (s, PCH*C*H$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ 39.78 (s; t in off-resonance).

Preparation of [IrH$_2$(acac)(py)(P*i*Pr$_3$)] (7). This compound was prepared analogously as described for 6, using 2 (68 mg, 0.14 mmol), pyridine (113 μL, 0.14 mmol), and H$_2$. Yellow air-stable crystals were isolated: yield 51 mg (69%); mp 75 °C. Anal. Calcd for $C_{19}H_{35}IrNO_2P$: C, 42.84; H, 6.62; N, 2.63. Found: C, 42.56; H, 6.92; N, 2.39. ^{1}H NMR (400 MHz, C_6D_6): δ 8.9, 6.7, and 6.3 (all m, NC$_5$H$_5$), 5.10 (s, C*H* of acac), 2.15 (m, PC*H*CH$_3$), 1.78 (s, C*H*$_3$ of acac), 1.31 (dd, *J*(PH) = 13.1, *J*(HH) = 7.1 Hz, PCHC*H*$_3$), −27.04 (d, *J*(PH) = 23.2 Hz, IrH$_2$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 184.17 (s, *C*O of acac), 153.96 and 135.45 (both s, NC$_5$H$_5$), 123.86 (d, *J*(PC) = 2.7 Hz, NC$_5$H$_5$), 100.32 (s, *C*H of acac), 28.97 (s, *C*H$_3$ of acac), 26.01 (d, *J*(PC) = 31.5 Hz, P*C*HCH$_3$), 19.93 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 30.82 (s; t in off-resonace).

Crystal Structure Analysis of 4. Single crystals were grown from hexane. Crystal data (from 23 reflections, $12° < \theta < 14°$): monoclinic space group $P2_1/c$ (No. 14); a = 10.690(5) Å, b = 12.882(3) Å, c = 21.66(1) Å, β = 90.95(2)°, V = 2983(2) Å^3, Z = 4, d_{calcd} = 1.424 g cm^{-3}, μ(Mo Kα) = 45.8 cm^{-1}; crystal size 0.2 × 0.15 × 0.1 mm; Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirkon filter (factor 15.41); T = 295 K; ω/θ-scan, max 2θ = 46°; 4181 reflections measured, 3916 independent reflections, 2504 regarded as being observed [$F_o > 3\sigma(F_o)$]. Intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction (Ψ-scan method), was applied (minimum transmission 53.98%). The structure was solved by direct methods (SHELXS-86). Atomic coordinates and anisotropic thermal parameters of the nonhydrogen atoms were refined by full-matrix least-squares (unit weights, SHELX-76), the position of the metal-bound hydrogen, was calculated with the programm HYDEX[8] but not refined, and positions of other hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å); R = 0.043, R_w = 0.050; reflex/parameter ratio 9.24; residual electron density <0.54 e Å^{-3}.

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Supplementary Material Available: Tables of crystal data, bond lengths and angles, positional and thermal parameters, and least-squares planes and a molecular structure drawing for 4 (11 pages). Ordering information is given on any current masthead page.

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