Iridium hydride complexes with P,C,P pincer ligands based on ferrocene and ruthenocene

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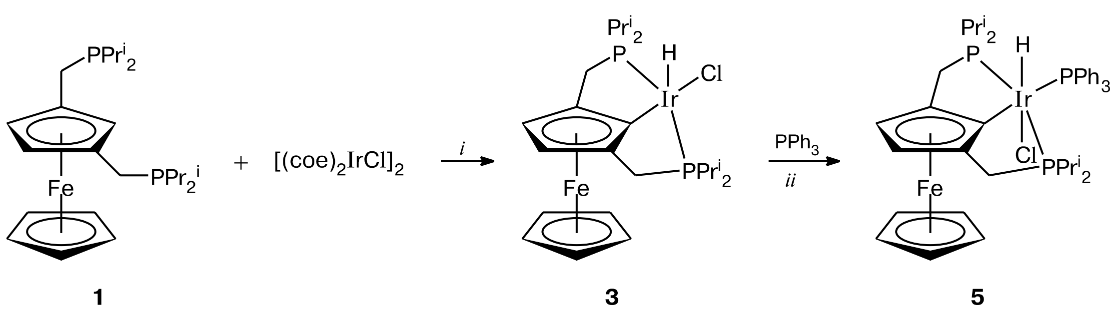
Earlier,[1] we have synthesized the binuclear *cis*-$RhCl_2(CO)[\{2,5-(Pr^i_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ complex with a new P,C,P pincer ligand based on ferrocene and established its structure by X-ray diffraction analysis. In the present study, we prepared iridium complexes with ferrocene- and ruthenocene-based P,C,P ligands. The iridium hydride complexes were synthesized by the reactions of $\{1,3-(Pr^i_2PCH_2)_2C_5H_3\}Fe(C_5H_5)$ (**1**) or $\{1,3-(Bu^t_2PCH_2)_2C_5H_3\}Ru(C_5H_5)$ (**2**) with $[(coe)_2IrCl]_2$ (coe is cyclooctene) in benzene (80 °C) or toluene (90 °C), respectively. The resulting complexes were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and mass spectrometry.

The reaction of diphosphine **1** with $[(coe)_2IrCl]_2$ afforded four hydride complexes, whose ratio varied depending on the temperature and reaction time. The content of some of them, for instance, of complexes **3** and **4**, in a mixture of hydrides can reach ~70%. Complexes **3** and **4** were isolated by extraction of the residue with *n*-hexane after evaporation of the solvent. These complexes give triplets in the hydride region of the ^1H NMR spectrum (C_6D_6, 23 °C) at δ −29.65 ($^2J_{H,P}$ = 14.5 Hz) and −26.14 ($^2J_{H,P}$ = 13.7 Hz) and singlets in the $^{31}P\{^1H\}$ NMR spectrum at δ 69.23 and 51.59, respectively. The ^1H NMR spectra of complexes **3** and **4** indicate that the ferrocene unit underwent cyclometallation. These results provide evidence that complex **3** has the structure of chlorohydrido{2,5-bis(di-*iso*-propylphosphinomethyl)ferrocen-1-yl}iridium(III), $IrH(Cl)[\{2,5-(Pr^i_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$, in which the iridium atom is in a tetragonal-pyramidal environment and the hydride ligand is in the apical position (Scheme 1). Earlier, the structurally similar pincer complexes $RhH(Cl)\{2,6-(Bu^t_2PCH_2)_2C_6H_3\}$ [2,3] and $IrH(Cl)\{2,6-(Bu^t_2PCH_2)_2-4-(NO_2)C_6H_2\}$ [4] have been synthesized and characterized by X-ray diffraction analysis. In the spectrum of the latter complex, a resonance of the hydride ligand was observed at δ −41.86 ($J_{H,P}$ = 12.27 Hz) in the region characteristic of P,C,P complexes with the di-*tert*-butylphosphine groups (related complexes based on diphosphine **2** are described below).

Unsaturated iridium complex **3** reacted with triphenylphosphine in benzene at room temperature to give the octahedral 18-electron complex, *viz*., chlorohydridotriphenylphosphino{2,5-bis(di-*iso*-propylphosphinomethyl)ferrocen-1-yl}iridium(III), $IrH(Cl)(PPh_3)[\{2,5-(Pr^i_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**5**), in quantitative yield (Scheme 1). In the ^1H NMR spectrum, the hydride ligand

Scheme 1



1 **3** **5**

i. 80 °C, 3 h, C_6H_6. *ii*. C_6H_6, 23 °C.

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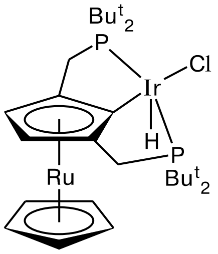
is observed at δ –22.45 (dt, $^2J_{\mathrm{H,PPh_3}}$ = 10.0 Hz, $^2J_{\mathrm{H,PPr^i_2}}$ = 14.0 Hz) and the splitting constants $^2J_{\mathrm{H,P}}$ indicate that the hydride ligand is in the *cis* position with respect to each of three P atoms.

Compared to diphosphine **1** containing the isopropyl groups at the phosphorus atoms, diphosphine **2** bearing the bulkier *tert*-butyl groups reacted with $[(\mathrm{coe})_2\mathrm{IrCl}]_2$ more selectively to form two hydride complexes, *viz.*, the *endo* (**6**) and *exo* isomers (**7**) of chlorohydrido{2,5-bis(di-*tert*-butylphosphinomethyl)ruthenocen-1-yl}iridium(III), $\mathrm{IrH(Cl)[\{2,5\text{-}(Bu^t_2PCH_2)_2C_5H_2\}Ru(C_5H_5)]}$.



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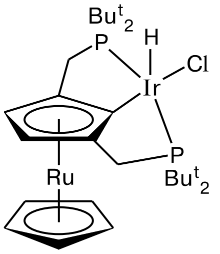

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The content of the sterically more strained *endo* isomer gradually decreased due to its conversion into the *exo* isomer. After heating for 3 h, the **6** : **7** ratio was ~1 : 2 (this mixture contained also the starting diphosphine **2**). After heating at 90 °C for 9 h, the ratio between complexes **6** and **7** was ~1 : 5. In the ^{31}P{^{1}H} NMR spectrum, complexes **6** and **7** give singlets at δ 79.42 and 86.47, respectively. The hydride signals of these complexes are observed in the ^{1}H NMR spectrum as triplets at δ –43.58 ($^2J_{\mathrm{H,P}}$ = 12.8 Hz) and –38.19 ($^2J_{\mathrm{H,P}}$ = 13.8 Hz), respectively.

The resulting iridium complexes with P,C,P ligands based on metallocenes are precursors of the corresponding iridium tetra- and dihydride complexes.

The ^{1}H and ^{31}P NMR spectra were recorded in $\mathrm{C_6D_6}$ on a Bruker AMX-400 instrument (400.13 and 161.98 MHz, respectively). The mass spectra were obtained on a Finnigan LCQ instrument. All operations associated with the synthesis and isolation of the complexes were carried out under argon.

Chlorohydrido{2,5-bis(di-*iso*-propylphosphinomethyl)ferrocen-1-yl}iridium(III) (3). A solution of $[(\mathrm{coe})_2\mathrm{IrCl}]_2$ (156 mg, 0.175 mmol) in anhydrous benzene (20 mL) was added to a solution of diphosphine $\mathrm{\{1,3\text{-}(Pr^i_2PCH_2)_2C_5H_3\}Fe(C_5H_5)}$ (156 mg, 0.354 mmol) in anhydrous benzene (15 mL). The reaction mixture was stirred at ~20 °C for 10 min. Then the temperature of the solution was gradually increased to 80 °C during 1 h. The mixture was stirred at this temperature for 3 h and filtered on a glass filter. The benzene was removed *in vacuo* and the residue was extracted with anhydrous *n*-hexane. Complex **3** was prepared in a yield of 162 mg (68.9%). ^{31}P NMR: δ 69.23 (s). ^{1}H NMR, δ:* –29.65 (t, 1 H, Ir$\underline{\mathrm{H}}$, $J_{\mathrm{H,P}}$ = 14.5 Hz); 4.16 (s, 5 H, $\mathrm{C_5H_5}$); 4.49 (s, $\mathrm{C_5H_2}$). MS, *m/z* (%): 674.1 (29) [M$^+$], 673.1 (31) [M$^+$ – H], 672 (100) [M$^+$ – 2 H].

Chlorohydridotriphenylphosphino{2,5-bis(di-*iso*-propylphosphinomethyl)ferrocen-1-yl}iridium(III) (5). The reaction was performed in an NMR tube. Triphenylphosphine (58 mg, 0.22 mmol) was added to a solution of complex **3** (30 mg, 0.044 mmol) in $\mathrm{C_6D_6}$. The dark-red solution immediately turned colorless. The ^{1}H and ^{31}P NMR spectra are indicative of the complete conversion of complex **3** into **5**. ^{31}P NMR, δ: –10.47 (t, 2 P, $\mathrm{PPr^i_2}$, $^2J_{\mathrm{P,P}}$ = 12.0 Hz); 34.17 (d, 1 P, $\mathrm{PPh_3}$, $^2J_{\mathrm{P,P}}$ = 12.0 Hz).

The reaction of diphosphine **2** with $[(\mathrm{coe})_2\mathrm{IrCI}\}_2$ taken in a molar ratio of 2 : 1 was carried out in toluene at 90 °C for 9 h.

***endo*-Chlorohydrido{2,5-bis(di-*tert*-butylphosphinomethyl)ruthenocen-1-yl}iridium(III) (6).** ^{31}P NMR: δ 79.42 (s). ^{1}H NMR:* δ –43.58 (t, IrH, $^2J_{\mathrm{H,P}}$ = 12.8 Hz).

***exo*-Chlorohydrido{2,5-bis(di-*tert*-butylphosphinomethyl)ruthenocen-1-yl}iridium(III) (7).** ^{31}P NMR: δ 86.47 (s). ^{1}H NMR:* δ –38.19 (t, IrH, $^2J_{\mathrm{H,P}}$ = 13.8 Hz).

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* The relevant signals are given.

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