Supporting Information for

[Ir(PPh_3)$_2$(H)$_2$($ClCH_2CH_2Cl$)][$BAr^F{}_4$]: A well characterised transition metal dichloroethane complex

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Experimental

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk-line and glove-box techniques. Glassware was oven dried at 130°C overnight and flamed under vacuum prior to use. CH_2Cl_2 and pentane were dried over activated alumina, copper and molecular sieves using an MBraun solvent purification system. CD_2Cl_2 and $ClCH_2CH_2Cl$ were distilled under vacuum from CaH_2 and stored over 3Å molecular sieves. Microanalyses were performed by Elemental Microanalysis Limited. Gas chromatography was performed using a Perkin-Elmer GC, helium carrier gas (14psi) injection volume 0.2 μl, oven temperature 40 °C and a flame ionisation detector. Data were analysed using the TurboChrom software package.

NMR spectroscopy

^{1}H and ^{31}P{^{1}H} spectra were recorded on Bruker Avance 400 MHz and Bruker Avance 500 MHz spectrometers. Residual protio solvent was used as reference for ^{1}H NMR spectra. ^{31}P{^{1}H} spectra were referenced against 85% H_3PO_4 (external). Chemical shifts are quoted in ppm. Coupling constants are quoted in Hz.

X-Ray Crystallography

Hemispheres of intensity data were collected at 150K on a Nonius Kappa CCD, using graphite monochromated MoKα radiation (λ = 0.71073 Å). Data were processed using the supplied Nonius software. Structure solution, followed by full matrix least squares refinement on F^2 (all data) was performed using SHELX97 [1] under the WINGX 1.70 [2] package, after using SORTAV [3] for absorption correction. In the structure of **1** some disorder of the CF_3 groups in the anion was evident. For **1** the Iridium bound hydrogen atoms were located and reliably refined.

CCDC- 636296 contains additional supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Starting materials

The starting materials $Na[BAr^F_4]$,[4] $[Ir(COD)Cl]_2$,[5] and $[Ir(PPh_3)_2(COD)][BAr^F_4]$[6] were prepared by published literature methods or variations thereof.

Synthesis of $[Ir(PPh_3)_2(H)_2\text{-}\eta^2\text{-}(ClCH_2CH_2Cl)][BAr^F_4]$ (1)

A solution of $[(PPh_3)_2Ir(COD)][BAr^F_4]$ (20mg, 1.18 x 10^{-5} moles) in dichloroethane was freeze-thaw degassed and back-filled with H_2. On warming to room temperature there was a colour change from red to colourless. X-ray quality crystals of **1** were obtained by diffusion of pentane into a solution of the compound in dichloroethane. Yield 12mg, 60%. Microanalysis: $[(PPh_3)_2IrH_2(C_2H_4Cl_2)][BAr^F_4]$ $C_{70}H_{48}BCl_2F_{24}IrP_2$ requires C 50.02%, H 2.88%. Found C 50.21%, H 2.91%.

^1H NMR (δ/ppm $C_2H_4Cl_2$ 298 K) 7.67-6.85 (m, 42H, ArH), -23.84 (t, J(PH) 15 Hz, 2H, IrH). $^{31}P\{^1H\}$ (δ/ppm $C_2H_4Cl_2$ 298 K) 19.1 (s).

*NMR spectra in CD_2Cl_2 (a mixture of **(1)** and **(2)**):*

^1H NMR (δ/ppm CD_2Cl_2 298 K) 7.74-6.88 (m, 42H, ArH), 3.23 (br s, 4H, $C_2H_4Cl_2$), -25.08 (br s, 2H, IrH). $^{31}P\{^1H\}$ (δ/ppm CD_2Cl_2 298 K) 21.4 (br s). ^1H NMR (δ/ppm CD_2Cl_2 270 K selected) 3.71 (br s, 1.8H, free $C_2H_4Cl_2$), 2.27 (br s, 2.1H, bound $C_2H_4Cl_2$), -23.47 (br s, 0.7H, IrH, **1**), -25.69 (br s, 0.5H, IrH, **2**). $^{31}P\{^1H\}$ (δ/ppm CD_2Cl_2 270 K) 22.8 (br s, **2**) 19.2 (br s, **1**). ^1H NMR (δ/ppm CD_2Cl_2 250 K selected) 3.75 (s, 1.2H, free $C_2H_4Cl_2$), 2.05 (2.3H, bound $C_2H_4Cl_2$), -23.29 (t, J(PH) 15 Hz, 1.1H, IrH, **1**), -25.53 (br s, 0.3H, IrH, **2**). $^{31}P\{^1H\}$ (δ/ppm CD_2Cl_2 250 K) 23.1 (br s, **2**) 19.3 (br s, **1**). ^1H NMR (δ/ppm CD_2Cl_2 220 K selected) 3.85 (s, 0.7H, free $C_2H_4Cl_2$), 1.98 (s, 2.8H, bound $C_2H_4Cl_2$), -23.12 (t, J(PH) 15 Hz, 1.3H, IrH, **1**), -25.29 (t, J(PH) 15 Hz, 0.1H, IrH, **2**). $^{31}P\{^1H\}$ (δ/ppm CD_2Cl_2 220 K) 23.2 (br s, **2**) 19.7 (br s, **1**).

Characterisation of $[Ir(PPh_3)_2(H)_2(ClCH_2Cl)_n][BAr^F_4]$ (2) (n = 1 or 2)

Given that dichloromethane is a weakly coordinating solvent it was unclear whether **(2)** was a solvent compound or a complex containing an agostic interaction. To determine this, compound **(1)** was dissolved in a non-coordinating solvent, 3-fluorotoluene. Only resonances attributable to **(1)** were observed. Addition of 0.20 ml CD_2Cl_2 to the solution of **(1)** in 3-fluorotoluene resulted in the appearance of new signals in approximately 10% intensity that corresponded to those previously reported for **(2)**.[7] This unequivocally confirms that **(2)** is a CD_2Cl_2 complex. It does not, however, allow the distinction to be made between one or two bound CD_2Cl_2 ligands. Given that all of the crystallographically characterised CH_2Cl_2 complexes have shown only one CH_2Cl_2 ligand,[8] we suggest a formulation of $[Ir(PPh_3)_2(H)_2(ClCH_2Cl)][BAr^F{}_4]$ for **(2)**.

(1) in 3-fluorotoluene

^{1}H NMR (δ/ppm $CH_3C_6H_4F$ 298 K selected) -23.68 (t, *J*(PH) 15 Hz, IrH). $^{31}P\{^1H\}$ (δ/ppm $CH_3C_6H_4F$ 298 K) 19.1 (s). ^{1}H NMR (δ/ppm $CH_3C_6H_4F$ 250 K selected) -23.28 (t, *J*(PH) 15 Hz, IrH). $^{31}P\{^1H\}$ (δ/ppm $CH_3C_6H_4F$ 250 K) 19.2 (s).

(1) and **(2)** in 3-fluorotoluene and CD_2Cl_2

^{1}H NMR (δ/ppm $CH_3C_6H_4F$ and CD_2Cl_2 250 K selected) -22.92 (br t, IrH, **1**) -25.20 (br, IrH, **2**). $^{31}P\{^1H\}$ (δ/ppm $CH_3C_6H_4F$ and CD_2Cl_2 250 K) 19.6 (s, **1**) 23.5 (s, **2**).

Methylcyclohexene hydrogenations

In a Schlenk tube 5mg (2.96×10^{-6} moles) of $[(PPh_3)_2Ir(cod)][BAr^F{}_4]$ was dissolved in 5 cm^3 CH_2Cl_2 or $C_2H_4Cl_2$. 100 equivalents of methylcyclohexane was added. The solution was freeze-thaw degassed and back filled with hydrogen. The solution was left stirring under 1 atmosphere of hydrogen at 22°C and samples were taken at 5 minute intervals for 30 minutes and then 15 minute intervals for a further 90 minutes. The samples were quenched with dppe and analysed using Gas chromatography.

References

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