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

Gemma L. Moxham, Simon K. Brayshaw and Andrew S. Weller*

Received 15th February 2007, Accepted 13th March 2007
First published as an Advance Article on the web 26th March 2007
DOI: 10.1039/b702399e

Reaction of $[Ir(PPh_3)_2(COD)][BAr^F{}_4]$ with H_2 in dichloroethane solution results in $[Ir(PPh_3)_2(H)_2(ClCH_2CH_2Cl)][BAr^F{}_4]$, which has been fully characterised by X-ray crystallography, NMR spectroscopy and ESI-MS. Its activity towards alkene hydrogenation has been compared with analogous CH_2Cl_2 complexes.

Cationic late transition metal complexes partnered with weakly coordinating anions such as $[BAr^F{}_4]^-$ $\{Ar^F = C_6H_3(CF_3)_2\}$ play an important part in the landscape of catalysis,[1] providing systems that are useful for a number of important reactions such as hydrogenation,[2] cyclisations[3] and cycloaddition reactions.[4] As well as depending on the weakly coordinating properties of the anion, the success of such systems also lies in the choice of solvent. Strongly coordinating solvents (such as acetonitrile or THF) can attenuate activity as they preferentially bind over substrates, while the charged nature of the catalysts means that a solvent of a suitably high dielectric constant has to be used.[2a,g] Thus weakly coordinating chlorinated solvents such as CH_2Cl_2 and $ClCH_2CH_2Cl$ are most often used in these systems. Even though solvent bound complexes are often implicated in catalytic cycles definitive characterisation of such species is often difficult, a consequence of the weak binding of solvent ligands to metal centres. Although well characterised transition metal complexes CH_2Cl_2 are known;[5] surprisingly, to our knowledge, no transition metal complexes of $ClCH_2CH_2Cl$ (DCE) have been definitively characterised although silver(I),[6] Tl(I)[7] and Cs(I)[8] complexes have been reported.

Given that DCE is a common solvent for catalysis by late transition metals, often as a substitute for CH_2Cl_2 where a higher temperature is required (such as in hydrogenation,[9] oxidation[10] and hydroacylation[11]) the characterisation of a complex interacting with this solvent would be useful. Herein we report the synthesis and full characterisation of such a complex, $[Ir(PPh_3)_2(H)_2(ClCH_2CH_2Cl)][BAr^F{}_4]$ including a solid-state structure (Fig. 1).

The complex $[Ir(PPh_3)_2(H)_2(ClCH_2CH_2Cl)][BAr^F{}_4]$, **1**, was synthesised by hydrogenation of $[Ir(PPh_3)_2(COD)][BAr^F{}_4]$ in dichloroethane solution and has been fully characterised by X-ray crystallography‡, NMR spectroscopy and ESI-MS.§ In the solid state, complex **1** has a six coordinate, octahedral, iridium centre with the P–Ir–P angle of 165.577(15)° comparable to 166.5(2)° in the analogous complex $[(PPh_3)_2IrH_2(C_6H_4I_2)]^+$.[12] The dichloroethane is bound to the iridium centre *via* both chlorine atoms with Ir–Cl distances of 2.5289(5) and 2.5329(5) Å. These are shorter than the Ir–Cl bond length of 2.816 Å for the complex $[(PNP)IrH(C_6H_4Cl)]^+$ (where PNP = 2,6-bis-(di-*tert*-butyl phosphino methyl)pyridine and in which the chloro is *ortho* to the Ir–C bond),[13] possibly due to less ring strain in complex **1**. It is, however, comparable to the Rh–Cl bond length of 2.488(1) Å in the compound $[Cp^*(PMe_3)RhMe(CH_2Cl_2)][BAr^F{}_4]$.[5d]

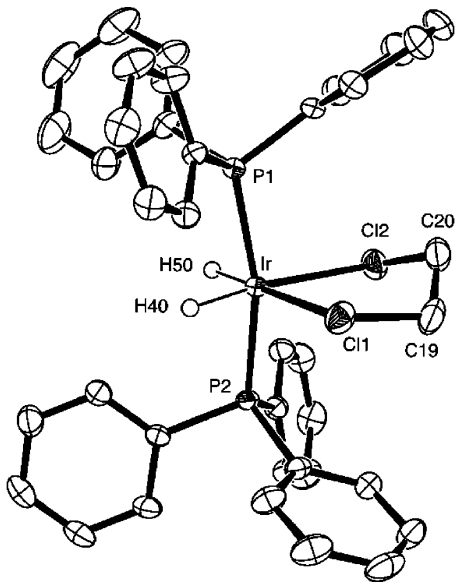


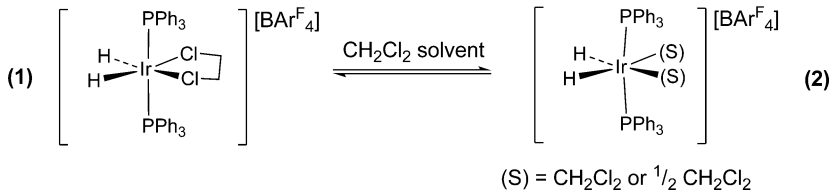
Fig. 1 Solid-state structure of $[Ir(PPh_3)_2H_2(ClCH_2CH_2Cl)][BAr^F{}_4]$ (anion and selected hydrogen atoms omitted for clarity). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Ir–P 2.3136(4), 2.3145(4), Ir–H 1.43(2), 1.49(2), Ir–Cl 2.5289(5), 2.5329(5), H–Ir–H 87.2(12), P–Ir–P 165.577(15), Cl–Ir–Cl 81.437(17).

Complex **1** in DCE solution at 298 K shows a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 19.1 ppm. In the ^1H NMR spectrum a hydride resonance is observed at δ −23.84 ppm as a triplet [J(PH) 15 Hz]. There is no observed change to the NMR spectra on cooling the sample to 240 K. Similar compounds of the formula $[(PPh_3)_2IrH_2(C_6H_4X_2)]^+$,[12] where X = Cl, Br or I, show that the hydride chemical shift varies according to the identity of the *trans* halogen. For comparison, in the dichlorobenzene complex the hydride chemical shift is δ −20.8 ppm compared to δ −16.5 ppm for the diiodobenzene complex.

When crystals of **1** are dissolved in CD_2Cl_2 solution at 298 K the observed ^1H NMR spectrum suggests that a fluxional process or equilibrium is taking place as the hydride resonance is broadened considerably and shifted upfield to δ −25.08 ppm. There is a broad signal observed at δ 3.23 ppm corresponding to DCE. In the $^{31}P\{^1H\}$ NMR spectrum the phosphorus resonance is now observed at δ 21.4 ppm and is also broad. On cooling to 270 K in the ^1H NMR spectrum the hydride resonance splits into two

Department of Chemistry, University of Bath, Bath, UK. E-mail: a.s.weller@bath.ac.uk

† Electronic supplementary information (ESI) available: Full experimental and spectroscopic data for compound (**1**). See DOI: 10.1039/b702399e



Scheme 1 Temperature dependant equilibrium between complexes **1** and **2** in CH_2Cl_2 solution.

broad peaks as does the DCE resonance. Further cooling to 220 K resolves the two hydrides into triplet resonances at δ −23.12 and −25.29 ppm [J(PH) 15 Hz] in approximately a 12 : 1 ratio. The signal for the DCE methylene protons resolves into two sharp singlets at this temperature which we assign to free and metal-bound DCE. The $^{31}P\{^1H\}$ NMR spectrum also shows two peaks at δ 23.2 and 19.7 ppm in the same ratio. We assign the major compound in solution at low temperature as the DCE complex (**1**) (Scheme 1). The minor compound in solution is assigned as the CH_2Cl_2 complex $[(PPh_3)_2IrH_2(CH_2Cl_2)_n][BAr^F{}_4]$, **2**, previously observed on hydrogenation of $[Ir(PPh_3)_2(COD)][BAr^F{}_4]$ in CD_2Cl_2[14] (n = 1 or 2, see ESI† also). The relative integrals for both compounds change reversibly with temperature indicating a dynamic equilibrium.

In order to determine the relative binding strengths to the $\{Ir(PPh_3)_2H_2\}^+$ fragment of CH_2Cl_2 *versus* DCE the relative ratios of complexes **1** and **2** were measured over the temperature range 250–210 K. A van't Hoff plot (Fig. 2) was constructed, from which ΔH° = +18.5 ± 1.5 kJ mol^{-1}, ΔS° = +8.6 ± 6.7 J K^{-1} mol^{-1} and $\Delta G^\circ(298)$ = +16.0 ± 3.5 kJ mol^{-1} were derived.[15] The positive value for ΔH° indicates that complex **1** is enthalpically favoured over complex **2**, *i.e.* DCE binds more strongly than DCM. ΔS° is positive but small, as might be expected.

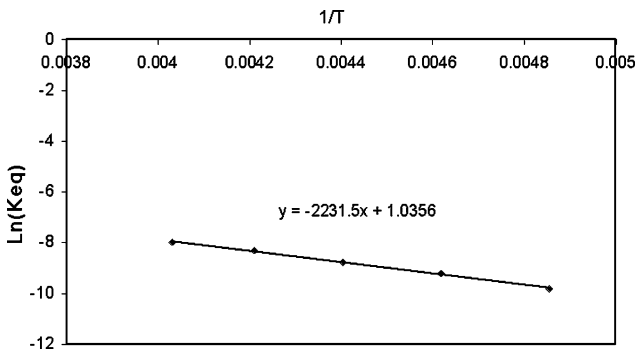


Fig. 2 Van't Hoff plot for the equilibrium between **1** and **2**.

Complex **1** is more stable to decomposition than complex **2**. Previous attempts to crystallise complex **2** from CH_2Cl_2 solvent have resulted in the isolation of the hydride-bridged dimer $[(PPh_3)_2HIrH_3IrH(PPh_3)_2][BAr^F{}_4]$[14] whereas crystals of complex **1** were obtained from a solution of the complex in DCE, suggesting the complex is significantly more stable in this solvent. There has also been no evidence for dimer formation from the NMR studies on **1** undertaken in CH_2Cl_2. With this in mind it was of interest to see if complex **1** was an active hydrogenation catalyst[16] and if so how its activity compared to complex **2**, which has the weaker bound CD_2Cl_2 molecule. The substrate used was methylcyclohex-1-ene.

As shown in Fig. 3 complex **1** is active towards methylcyclohexene hydrogenation, but very much slower than complex **2**. This indicates that the DCE binds too strongly with the cationic iridium centre to allow the catalysis to take place at an appreciable rate. This is similar to the effect previously observed by partnering the $[(PPh_3)_2IrH_2]^+$ cation with the [*closo*-$CB_{11}H_6I_6]^-$ anion.[14] In this case it is the anion which binds too strongly to the iridium for catalysis to occur rather than the solvent.

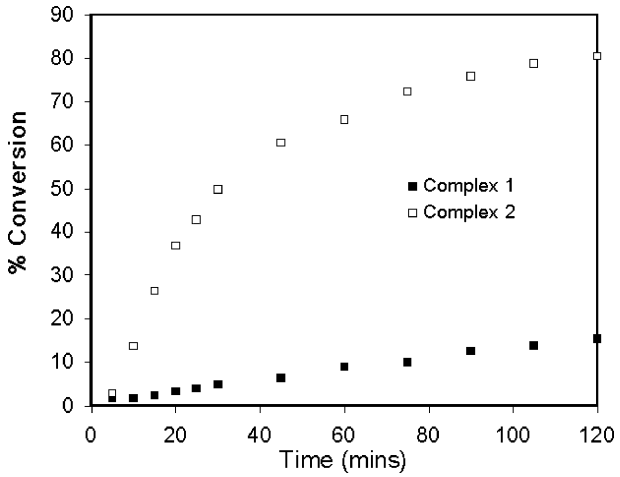


Fig. 3 Relative rates of hydrogenation of methylcylcohex-1-ene using $[Ir(PPh_3)_2(COD)][BAr^F{}_4]$ precatalyst in CH_2Cl_2 (complex **2**) and DCE (complex **1**) solutions. Conversions measured by GC. See ESI† for conditions.

In conclusion, we have presented a well characterised complex of dichloroethane and have also demonstrated that this solvent forms stronger adducts with a cationic transition metal fragment than does CH_2Cl_2. This has a negative impact on the catalytic rate in the hydrogenation of a hindered olefin, but this is counterbalanced with the improved resistance to decomposition. This further underlines the inverse correlation that can often exist between catalytic activity and catalyst robustness and makes dichloroethane a sensible choice of solvent over CH_2Cl_2 when activity is less a concern than catalyst longevity.

Notes and references

‡ Crystallographic data for complex **1**. Intensity data were collected at 150 K on a Nonius Kappa CCD, using graphite monochromated MoKα radiation (λ = 0.71073 Å). $C_{70}H_{48}BCl_2F_{24}IrP_2$, M = 1680.93, triclinic, space group $P\bar{1}$ (no. 2), Z = 2, a = 14.2336(1), b = 14.2460(1), c = 17.5082(1) Å, α = 95.9592(4), β = 99.1182(4), γ = 100.7170(4)°, V = 3411.50(4) Å^3, μ = 2.190 mm^{-1}, T_{min}/T_{max} = 0.84, $2\theta_{max}$ = 70.0°, 96 150 reflections

collected, 29 864 unique [R(int) = 0.0514]. wR_2 0.0687 (all data). R_1 = 0.0335 ($I > 2\sigma(I)$). CCDC reference number 636296. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702399e The hydrogen atoms H40 and H50 were located and freely refined.

§ Spectroscopic data for complex **1.** ^{1}H NMR (δ *$C_2H_4Cl_2$ 298 K*) 7.67–6.85 (m, 42H, ArH), −23.84 (t, J(PH) 15 Hz, 2H, IrH). ^{31}P{^{1}H} (δ/ppm $C_2H_4Cl_2$ 298 K) 19.1 (s). ^{1}H NMR (δ *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{^{1}H} (δ/ppm CD_2Cl_2 298 K) 21.4 (br s). ^{1}H NMR (δ *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{^{1}H} (δ CD_2Cl_2 270 K) 22.8 (br s, (**2**)) 19.2 (br s, (**1**)). ^{1}H 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 triplet coupling not resolved, 0.3H, IrH (**2**)). ^{31}P{^{1}H} (δ *CD_2Cl_2 250 K*) 23.1 (br s, (**2**)) 19.3 (br s, (**1**)). ^{1}H NMR (δ *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{^{1}H} (δ CD_2Cl_2 220 K) 23.2 (br s, (**2**)) 19.7 (br s, (**1**)). ESI-MS (CH_2Cl_2) m/z 817.1 (exp) 817.1 (calc.).

1 (*a*) A. Macchioni, *Chem. Rev.*, 2005, **105**, 2039; (*b*) I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066.

2 (*a*) R. H. Crabtree, P. C. Demou, D. Eden, J. M. Mihelcic, C. A. Parnell, J. M. Quirk and G. E. Morris, *J. Am. Chem. Soc.*, 1982, **104**, 6994; (*b*) A. Lightfoot, P. Schnider and A. Pfaltz, *Angew. Chem., Int. Ed.*, 1998, **37**, 2897; (*c*) J. M. Buriak, J. C. Klein, D. G. Herrington and J. A. Osborn, *Chem.–Eur. J.*, 2000, **6**, 139; (*d*) D. R. Hou, J. Reibenspies, T. J. Colacot and K. Burgess, *Chem.–Eur. J.*, 2001, **7**, 5391; (*e*) A. Rifat, N. J. Patmore, M. F. Mahon and A. S. Weller, *Organometallics*, 2002, **21**, 2856; (*f*) J. van den Broeke, E. de Wolf, B. J. Deelman and G. van Koten, *Adv. Synth. Catal.*, 2003, **345**, 625; (*g*) S. P. Smidt, N. Zimmermann, M. Studer and A. Pfaltz, *Chem.–Eur. J.*, 2004, **10**, 4685; (*h*) X. Cui and K. Burgess, *Chem. Rev.*, 2005, **105**, 3272.

3 S. Gilbertson and G. S. Hoge, *Tetrahedron Lett.*, 1998, **39**, 2075.

4 (*a*) E. P. Kundig, C. M. Saudan and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 1220; (*b*) E. P. Kundig, C. M. Saudan and F. Viton, *Adv. Synth. Catal.*, 2001, **343**, 51; (*c*) N. J. Patmore, C. Hague, J. H. Cotgreave, M. F. Mahon, C. G. Frost and A. S. Weller, *Chem.–Eur. J.*, 2002, **8**, 2088; (*d*) P. G. A. Kumar, P. S. Pregosin, M. Vallet, G. Bernardinelli, R. F. Jazzar, F. Viton and E. P. Kundig, *Organometallics*, 2004, **23**, 5410; (*e*) D. A. Evans, S. J. Miller, T. Lectka and P. von Matt, *J. Am. Chem. Soc.*, 1999, **121**, 7559; (*f*) J. W. Faller and P. P. Fontaine, *Organometallics*, 2005, **24**, 4132.

5 (*a*) M. D. Butts, B. L. Scott and G. J. Kubas, *J. Am. Chem. Soc.*, 1996, **118**, 11831; (*b*) D. J. Huang, J. C. Huffman, J. C. Bollinger, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1997, **119**, 7398; (*c*) J. Huhmann-Vincent, B. L. Scott and G. J. Kubas, *Inorg. Chem.*, 1999, **38**, 115; (*d*) F. L. Taw, H. Mellows, P. S. White, F. J. Hollander, R. G. Bergman, M. Brookhart and D. M. Heinekey, *J. Am. Chem. Soc.*, 2002, **124**, 5100; (*e*) J. Zhang, K. A. Barakat, T. R. Cundari, T. B. Gunnoe, P. D. Boyle, J. L. Petersen and C. S. Day, *Inorg. Chem.*, 2005, **44**, 8379; (*f*) J. R. Krumper, M. Gerisch, J. M. Suh, R. G. Bergman and T. D. Tilley, *J. Org. Chem.*, 2003, **68**, 9705; (*g*) F. A. Cotton, C. A. Murillo, S.-E. Stiriba, X. Wang and R. Yu, *Inorg. Chem.*, 2005, **44**, 8223.

6 (*a*) I. Krossing, *Chem.–Eur. J.*, 2001, **7**, 490; (*b*) M. R. Colsman, T. D. Newbound, L. J. Marshall, M. D. Noirot, M. M. Miller, G. P. Wulfsberg, J. S. Frye, O. P. Anderson and S. H. Strauss, *J. Am. Chem. Soc.*, 1990, **112**, 2359.

7 P. K. Hurlburt, O. P. Anderson and S. H. Strauss, *Can. J. Chem.*, 1992, **70**, 726.

8 T. G. Levitskaia, J. C. Bryan, R. A. Sachleben, J. D. Lamb and B. A. Moyer, *J. Am. Chem. Soc.*, 2000, **122**, 554.

9 (*a*) C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M. A. Esteruelas and L. A. Oro, *Organometallics*, 1992, **11**, 138; (*b*) V. Herrera, A. Fuentes, M. Rosales, R. A. Sanchez-Delgado, C. Bianchini, A. Meli and F. Vizza, *Organometallics*, 1997, **16**, 2465.

10 R. Neumann and A. M. Khenkin, *Inorg. Chem.*, 1995, **34**, 5753.

11 (*a*) M. Tanaka, M. Imai, Y. Yamamoto, K. Tanaka, M. Shimowatari, S. Nagumo, N. Kawahara and H. Suemune, *Org. Lett.*, 2003, **5**, 1365; (*b*) M. C. Willis, S. J. McNally and P. J. Beswick, *Angew. Chem., Int. Ed.*, 2004, **43**, 340; (*c*) M. Imai, M. Tanaka, K. Tanaka, Y. Yamamoto, N. Imai-Ogata, M. Shimowatari, S. Nagumo, N. Kawahara and H. Suemune, *J. Org. Chem.*, 2004, **69**, 1144.

12 R. H. Crabtree, J. W. Faller, M. F. Mellea and J. M. Quirk, *Organometallics*, 1982, **1**, 1361.

13 E. Ben-Ari, M. Gandelman, H. Rozenberg, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2003, **125**, 4714.

14 G. L. Moxham, T. M. Douglas, S. K. Brayshaw, G. Kociok-Köhn, J. P. Lowe and A. S. Weller, *Dalton Trans.*, 2006, **46**, 5492.

15 These figures arise from the assumption that one CH_2Cl_2 is bound. If there are two bound then ΔH° +18.5 ± 1.5 kJ mol^{-1}, ΔS° = −14.3 ± 6.6 J K^{-1} mol^{-1} and $\Delta G^\circ(298)$ = +22.8 ± 2.1 kJ mol^{-1}. The conclusions about the qualitative relative strength of binding of DCE over CH_2Cl_2 remain the same.

16 R. H. Crabtree, *Acc. Chem. Res.*, 1979, **12**, 331.