The binding of small nitrogen-containing heterocycles to neutral and cationic (pentamethylcyclopentadienyl)Ir(III) complexes and the X-ray crystal structure of an unexpected diaquo complex, [(Cp*)IrCl(H$_2$O)$_2$][PF$_6$]

Swamy Bodige, Leigh Christopher Porter *

Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968, USA

Abstract

Cleavage of the chloro-bridged [Cp*IrCl$_2$]$_2$ dimer by halide abstraction using [NH$_4$][PF$_6$] leads to the formation of the [Cp*IrCl]$^+$ cation which reacts with 2-picoline, 2,6-lutidine, and 2-methylquinoline to form stable N-bound complexes of the type [Cp*Ir(L)$_2$Cl]$^+$. Halide abstraction using AgBF$_4$ results in complete removal of all halides from the dimer to produce the [(Cp*)Ir]$^{2+}$ dication. Both N and π-bound complexes can be obtained, depending on the nature of the nitrogen-containing heterocycle. Direct reaction of the [(Cp*)IrCl$_2$]$_2$ dimer with 2,6-lutidine results in cleavage of the dimer to form a Cp*Ir(L)Cl$_2$ complex containing one N-bound 2,6-lutidine ligand. An iridium complex having the formula [(Cp*)IrCl(H$_2$O)$_2$][PF$_6$] was obtained fortuitously during the course of attempts to grow crystals of the cationic 2-picoline complex. The presence of two molecules of water in the coordination sphere of the Ir(III) ion was verified crystallographically. The complex crystallizes in the orthorhombic *Pnma* space group with $a = 20.260(7)$ Å, $b = 8.700(2)$ Å, $c = 9.656(3)$ Å, and $V = 1702.0(9)$ Å^3. Convergence to conventional R values of $R = 0.0417$ and $R_W = 0.0560$ with a goodness-of-fit of 0.72 was obtained for 110 variable parameters and 1205 reflections with $I > 0\sigma(I)$.

Keywords: Pentamethylcyclopentadienyl; Iridium derivatives; Nitrogen heterocycles; Aquo complexes

1. Introduction

Hydrodenitrification (HDN) is a hydrotreating process in which nitrogen is removed from various nitrogen-containing organics during the refinement of crude petroleum feedstocks. It constitutes one of the single most important industrial application of catalyst materials with a world-wide consumption of catalyst materials in excess of 50 000 tons annually [1]. Despite both the economic and environmental importance of the HDN process, little is known regarding many crucial aspects of the hydrodenitification process. Key features that are not well-defined include (a) how the various nitrogen-containing heterocycles bind to the surface of the catalyst; and (b) how the mode of binding correlates with the hydrogenation of the aromatic ring and subsequent C–N bond cleavage. Ideally the HDN process would involve regioselective hydrogenation of the ring containing the nitrogen atom followed immediately by C–N bond cleavage. However, under actual conditions it is found that a broad spectrum of products is obtained, many of which are extensively hydrogenated. Since the heterocycle can bind to surface of the heterogeneous catalyst in a number of ways, it is likely that the mode of binding is pivotal to the hydrogenation step and subsequent cleavage of the C–N bond.

To learn more about the possible mechanisms associated with the HDN process, we sought to explore the binding of various nitrogen-containing complexes to small-well-characterized transition metal systems. We were especially interested in defining the preferred modes of ligand binding in the platinum group metals, since these elements are predicted to have a particularly high activity with respect to both hydrodenitrifica-

---

* Corresponding author.

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Ir(1)	4134(1)	2500	3940(1)	26(1)
Cl(1)	5150(2)	2500	5261(4)	41(1)
P(1)	6061(3)	2500	10(4)	52(2)
F(1)	5947(6)	2500	−1592(11)	82(5)
F(2)	5315(8)	2500	146(22)	190(13)
F(3)	6064(9)	2500	1654(12)	118(7)
F(4)	6762(8)	2500	−122(28)	271(21)
F(5)	6024(8)	757(12)	8(11)	191(8)
O(1)	4651(4)	804(10)	2710(8)	61(3)
C(1)	3122(7)	2500	3344(14)	33(4)
C(2)	3237(4)	1156(12)	4202(10)	38(3)
C(3)	3478(5)	1649(12)	5519(11)	44(3)
C(4)	2845(8)	2500	1887(18)	67(7)
C(5)	3134(6)	−450(13)	3762(13)	64(5)
C(6)	3650(6)	660(16)	6735(12)	71(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

tion and hydrodesulfurization (HDS) reactions as well [2]. Ruthenium and rhodium have been used extensively, particularly with respect to studies involving η^1-N to η^6-π rearrangements, hydrogenations, and transalklylations [3–17]. Iridium, on the other hand, has not received much attention, even though reactivity patterns suggest that it may even be better than rhodium with respect to hydrogenation and C–N bond cleavage reactions.

In this paper we present the results of our work involving the interaction of small nitrogen-containing heterocycles with Ir(III) and describe the X-ray crystal structure of an unexpected water-soluble Ir(III) product obtained fortuitously during the course of our investigations.

2. Results and discussion

The chloro-bridged $[Cp^*Ir(Cl)_2]_2$ dimer is a versatile starting material for the preparation of monomeric (Cp^*)Ir(III) complexes. In our investigations we found that the dimer could be cleaved in methanol using either $[NH_4][PF_6]$ or $AgBF_4$ to produce cationic and dicationic species, respectively. Direct addition of 2,6-lutidine also resulted in cleavage of the dimer, in this case, producing a neutral complex containing two halides and one molecule of 2,6-lutidine.

The elemental analyses for several of the complexes prepared in this investigation reveal discrepancies beyond the range that we would normally consider reasonable for very clean products. Attempts were made to ensure that the compounds were rigorously purified before being sent for analysis, and from a careful inspection of the NMR data we do not find any evi-

dence for the presence of mixtures or impurities. In several instances the experimentally determined C and H values were found to be lower than expected and may reflect the presence of small amounts of AgCl present in the sample. Alternatively, it may be that incomplete combustion of these complexes constitutes a problem owing to the formation of refractory carbides.

Attempts to grow crystals suitable for X-ray diffraction were unsuccessful, however, a considerable amount of information can be obtained from an inspection of the ^{1}H and ^{13}C data for these complexes. A number of studies involving both N-bound and π-bound nitrogen-containing heterocycles have established that upfield shifts are seen the in ^{13}C NMR spectra of N-bound complexes, with slight downfield shifts also present in the ^{1}H NMR spectra relative to the free ligand [11]. In contrast, upfield shifts typically on the order of 20–40 ppm are seen in the ^{13}C NMR spectra of complexes containing π-bound heterocycles. Slight downfield shifts are also witnessed for the hydrogen atoms attached to the coordinated carbons, however, the extent to which they are shifted relative to the free arene is not as dramatic.

When the $[Cp^*IrCl]^+$ cation was allowed to react with excess 2-picoline, 2,6-lutidine, or 2-methylquinoline, the carbon atoms associated with the N-containing heterocycles were observed shifted downfield on the order of 5 ppm or less. Slight downfield shifts (up to 1 ppm) were also seen in the ^{1}H NMR spectra of all three of these complexes. This pattern of chemical shifts is consistent with a mode of bonding in which the N atom is involved in σ-bond formation to the transi-

Table 2

Selected bond lengths (Å) and angles (°)

Ir(1)–Cl(1)	2.423(4)	Ir(1)–O(1)	2.165(8)
Ir(1)–C(1)	2.129(13)	Ir(1)–C(2)	2.176(9)
Ir(1)–C(3)	2.154(10)	Ir(1)–O(1A)	2.165(8)
Ir(1)–C(2A)	2.176(9)	Ir(1)–C(3A)	2.154(10)
P(1)–F(1)	1.564(11)	P(1)–F(2)	1.516(16)
P(1)–F(3)	1.587(13)	P(1)–F(4)	1.425(17)
P(1)–F(5)	1.518(10)	P(1)–F(5A)	1.518(10)
C(1)–C(2)	1.452(13)	C(1)–C(4)	1.515(22)
C(1)–C(2A)	1.452(13)	C(2)–C(3)	1.429(14)
C(2)–C(5)	1.475(16)	C(3)–C(6)	1.496(16)
C(3)–C(3A)	1.481(21)		
Cl(1)–Ir(1)–O(1)	83.0(2)	O(1)–Ir(1)–O(1A)	85.9(4)
F(1)–P(1)–F(2)	86.5(9)	F(1)–P(1)–F(3)	171.7(9)
F(2)–P(1)–F(3)	85.3(11)	F(1)–P(1)–F(4)	93.4(12)
F(2)–P(1)–F(4)	180.0(16)	F(3)–P(1)–F(4)	94.9(13)
F(1)–P(1)–F(5)	89.5(4)	F(2)–P(1)–F(5)	87.2(6)
F(3)–P(1)–F(5)	90.1(4)	F(4)–P(1)–F(5)	92.8(6)
F(5)–P(1)–F(5A)	174.4(13)	C(2)–C(1)–C(4)	126.1(6)
C(2)–C(1)–C(2A)	107.3(12)	C(4)–C(1)–C(2A)	126.1(6)
C(1)–C(2)–C(3)	108.7(9)	C(1)–C(2)–C(5)	125.2(9)
C(3)–C(2)–C(5)	126.1(10)	C(2)–C(3)–C(6)	127.3(10)
C(2)–C(3)–C(3A)	107.5(6)	C(6)–C(3)–C(3A)	125.1(7)

tion metal center [11]. Elemental analysis of all these complexes indicated a 1 : 2 metal : ligand stoichiometry providing these systems with the nominal stoichiometry [Cp*Ir(Cl)L₂]⁺ (L = 2-picoline, 2,6-lutidine, 2-methylquinoline) and one PF₆⁻ counterion.

Compared with the [Cp*IrCl]⁺ cation, a nearly identical ¹³C and ¹H spectrum was obtained when 2,6-lutidine was reacted with the [Cp*Ir]²⁺ dication obtained using AgBF₄ in place of [NH₄][PF₆]. However, an elemental analysis of the product indicated the presence of three molecules of 2,6-lutidine consistent with a complex having the formula [(Cp*Ir(2,6-lutidine)₃][BF₄]₂. When the dicationic Ir(III) complex was reacted with either N-methyl- or 2,5-dimethylpyrrole, however, quite different products were obtained. Pronounced upfield shifts were seen in the ¹³C spectra of both products, typically on the order of 20–40 ppm. A proton NMR spectrum of the complex also revealed upfield shifts (ca. 1 ppm) relative to the free ligand, both of which are strongly indicative of the presence of π-bound complexes. An eighteen electron configuration for the complex can be realized if the pyrrole ligands are acting as six electron donors using the π-electrons of the ring to bind to the Ir(III) center, and this is consistent with the observed chemical shift data.

Direct reaction of the [Cp*Ir(Cl)₂]₂ with 2,6-lutidine was also carried out. However, in this case the NMR data and elemental analysis indicated that a neutral complex having the formula [Cp*Ir(Cl)₂(2,6-lutidine)] was obtained. A summary of these reactions is presented in Fig. 1.

All of the products formed were isolated as reasonably air-stable solids. However, in no instances were we able to isolate single well-formed crystals suitable for
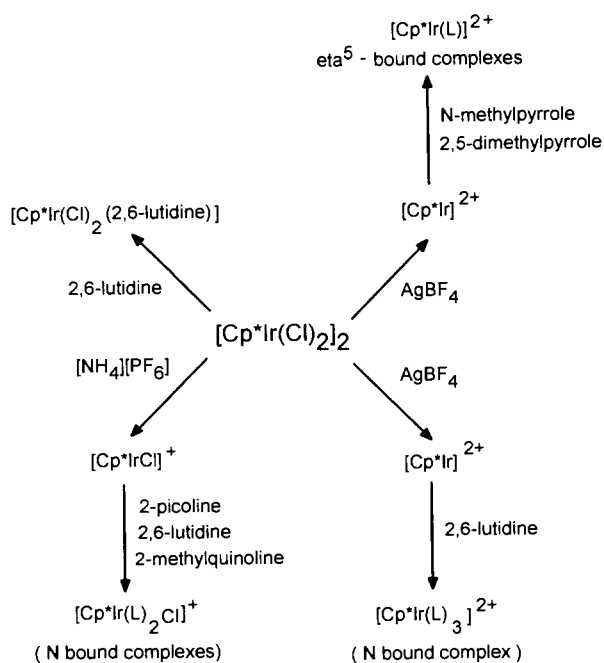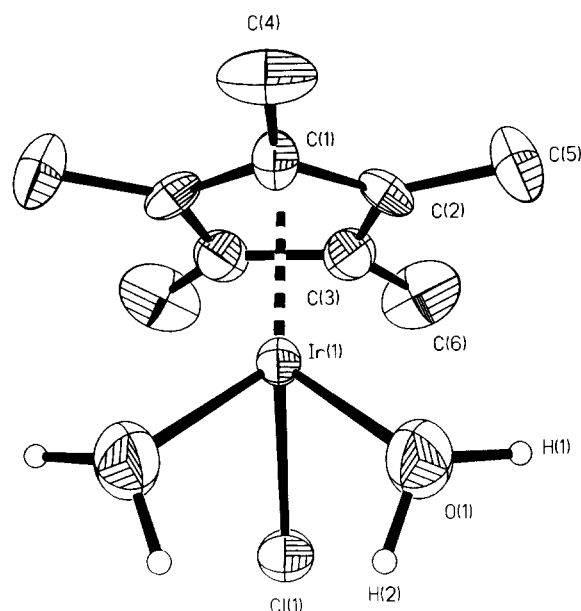

Fig. 2. View of the structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. The PF₆⁻ counterion is not shown and H-atoms have been omitted for clarity.

an X-ray crystal structure determination (see below). In solution the complexes tend to be less stable, and in the presence of adventitious molecules of water or other oxygen-containing solvents, the complexes tend to undergo ligand substitution reactions. As we were to discover, recrystallization of the [Cp*IrCl(2-picoline)₂] complex from a methanol-diethyl ether solution resulted in the formation of the unexpected di(aquo) complex, the structure of which is described in paragraph that follows.

2.1. Description of the structure of [(Cp*)IrCl-(H₂O)₂][PF₆]

This complex was isolated fortuitously from a methanol-diethyl ether solution following reaction of the [Cp*Ir(Cl)⁺] cation with 2-picoline. The structure consists of a π-bound Cp* ring, one chloride ligand, and two molecules of water (Fig. 2). Fractional atomic coordinates given in Table 1 and pertinent bond lengths and angles are summarized in Table 2. The (Cp*Ir(Cl)(H₂O)₂]⁺ cation lies on a special position of m symmetry and the PF₆⁻ counterion sits on a site of inversion. The complex therefore possesses a mirror plane of symmetry and belongs to the C_s point group. The Ir atom is located 1.888 Å from the centroid defined by the five atoms of the Cp* ring and the mirror plane bisects C(1) and the bond that joins C(3) and C(3A). The I–Cl bond measures 2.423(4) Å and bonds to the oxygen atoms of the water molecules are 2.165(8) Å in length. The water molecules in this complex adopt a pyramidal conformation and the O atom is displaced by 0.4384 Å from the plane defined

Fig. 1. Schematic illustration of all reactions.

by the two H atoms and the transition metal to which it is coordinated. From an inspection of the packing diagram for the complex, we find that the unit cell is comprised of molecules that are extensively cross-linked by an intricate network of hydrogen bonds involving these ligand groups. Since the presence of water molecules in organometallic complexes is not common, this molecule constitutes a rare example of a mononuclear aquo $[(Cp^*)Ir(Cl)(H_2O)_2]^{1+}$ complex. The only other organometallic Ir(III) aquo complex of which we are aware is an Ir(III) complex containing one coordinated molecule of water [17]. Our product is air-stable and exhibits fair solubility in water. Its reaction chemistry, however, has not yet been explored and will constitute the focus of additional investigations.

3. Experimental details

All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or an inert atmosphere glove box. Methanol was distilled over Mg metal and halogenated solvents were dried over P_2O_5. 2-picoline, 2,6-lutidine, 2-methylquinoline, N-methylpyrrole and 2,5-dimethylpyrrole were purchased from the Aldrich Chemical Company, Inc., and used as received. Iridium(III)chloride hydrate was obtained from the Johnson-Matthey company. NMR spectra were recorded in CD_3NO_2 on a Bruker AM-250 spectrometer and referenced to TMS, and crystallographic data were collected on Siemens R3m/V diffractometer. Elemental analyses were performed by either Texas Analytical Laboratories, Inc. or Atlantic Nicholas, Inc.

3.1. Preparation of complexes

3.1.1. Preparation of di-μ-chloro-bis[chloro(η⁵-pentamethylcyclopentadienyl)Ir(III)]

The chloro-bridged dimer, di-μ-chloro-bis[chloro-(η⁵-pentamethylcyclopentadienyl)Ir(III)], was prepared according to the literature procedure and used without any additional purification [18].

3.1.2. Preparation of [(η⁵-pentamethylcyclopentadienyl)bis(η¹-2-picoline)IrCl][PF₆]

To a Schlenk flask containing 80 mg (0.10 mmol) of Ir(III) dimer in 15 ml of methanol was added NH_4PF_6 (65 mg, 0.4 mmol) and 2-picoline (0.15 ml, 1.54 mmol). An immediate reaction took place giving a dark orange solution. The solution was allowed to reflux for 6 h whereupon it was cooled and the solution transferred to a clean Schlenk flask via a cannula, one end of which was covered with filter paper. The solvent was removed under reduced pressure and the resulting orange residue was extracted into dichloromethane followed by removal of the solvent under reduced

pressure. The residue was washed with a 5.0 ml portion of diethyl ether, then dried in vacuo resulting in the isolation of 103 mg of an orange powder in 74% yield with decomposition observed beginning at 273°C.

Anal. $[C_{30}H_{33}N_2ClIr][PF_6]$ Calc.: C 45.36%, H 4.18%; Found: C 43.28%, H 4.02%. ^1H NMR Cp*: 1.60, 1.73 (s, 15H); 2-picoline: 2.75 (s, 6H), 7.65 (t, 2H, $J = 6.50$ Hz), 7.70 (d, 2H, $J = 7.50$ Hz), 8.22 (t, 2H, $J = 7.70$ Hz), 8.60 (d, 2H, $J = 5.20$ Hz). ^{13}C NMR Cp*: 8.70, 8.95, 87.35; 2-picoline: 2.75, 124.59, 127.87, 144.29, 145.10, 154.46.

3.1.3. Preparation of [(η⁵-pentamethylcyclopentadienyl)bis(η¹-2-methylquinoline)IrCl][PF₆]

The same procedure as above was used in the preparation of this complex. 80 mg (0.10 mmol) of Ir(III) dimer in methanol was allowed to react with 65 mg (0.04 mmol) of NH_4PF_6 and 0.25 ml (265 mg, 1.85 mmol) of 2-methylquinoline. After 6 h 94 mg of a yellow compound that decomposed at 241°C was isolated in 69% yield.

Anal. $[C_{22}H_{29}N_2ClIr][PF_6]$ Calc.: C 38.06%, H 4.21%; Found: C 37.53%, H 4.45%.^1H NMR Cp*: 2.00 (s, 15H); 2-methyllquinoline: 3.09 (s, 6H), 7.65 (d, 2H, $J = 8.08$ Hz), 7.70 (t, 2H, $J = 7.60$ Hz), 7.88)t, 2H, $J = 8.08$ Hz), 8.02 (d, 2H, 8.03 Hz), 8.68 (d, 2H, $J = 8.5$ Hz), 8.75 (d, 2H, $J = 8.50$ Hz). ^{13}C NMR Cp*:11.07, 94.02; 2-methylquinoline: 21.48, 122.37, 122.89, 126.77, 128.02, 128.48, 132.68, 133.11 143.38, 157.18

3.1.4. Preparation of [(η⁵-pentamethylcyclopentadienyl)(η¹-2,6-lutidine)IrCl][PF₆]

80 mg (0.11 mmol) of the iridium(III) dimer was allowed to react with NH_4PF_6 (65 mg, 0.4 mmol) and 2,6-lutidine (0.15 ml, 1.3 mmol) in 10.0 ml of methanol. After 6 h the reaction was stopped and the solution transferred to a fresh Schlenk flask. Removal of the solvent under reduced pressure resulted in the formation of an orange powder which was extracted into a 5.0 ml aliquot of chloroform and isolated by solvent removal under reduced pressure. The product was then washed with 5.0 ml diethyl ether and dried in vacuo to give 90 mg of an orange powder in 62% yield with decomposition observed beginning at 232°C.

Anal. $[C_{24}H_{33}N_2ClIr][PF_6]$ Calc.: C 39.91%, H 4.60%; Found: C 37.53%, H 4.45%. ^1H NMR Cp*: 1.87 (s, 15H); 2,6-lutidine: 2.80 (s, 12H), 7.68 (d, 4H, $J = 7.80$ Hz), 8.35 (t, 2H, $J = 7.80$ Hz). ^{13}C NMR Cp* : 8.66, 8.86, 87.06; 2,6-lutidine: 19.98, 125.84, 147.38, 154.96.

3.1.5. Preparation of [(η⁵-pentamethylcyclopentadienyl)tris(η¹-2,6-lutidine)Ir][BF₄]₂

In this reaction and those that follow, a silver salt $(AgBF_4)$ was used instead of $[NH_4][PF_6]$. To a Schlenk flask containing 80 mg (0.10 mmol) of the iridium (III) dimer in acetone was added $AgBF_4$ (78 mg, 0.40 mmol).

The reaction mixture was stirred at room temperature for 15 min and the yellow solution fraction was separated by filtration from the AgCl precipitate and transferred to a clean Schlenk flask. To this solution was then added 0.10 ml of 2,6-lutidine (0.86 mmol) and the reaction mixture was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure, and the residue that remained was washed with diethyl ether and extracted into chloroform. Removal of the chloroform under reduced pressure resulted in the isolation of 130 mg of a clean yellow solid in 84% yield which began to decompose at 236°C.

Anal. [$C_{36}H_{42}N_3Ir$][BF_4]$_2$ Calc.: C 47.70%, H 5.42%; Found: C 45.10%, H 5.12%. ^{1}H NMR Cp*: 1.53 (s, 15H); 2,6-lutidine:2.71 (s, 12H), 7.47 (d, 4H, $J = 8.00$ Hz), 8.12 (t, 2H, $J = 8.01$ Hz). ^{13}C NMR Cp*:9.14, 80.79; 2,6-lutidine: 20.77, 124.08, 144.38, 154.42.

3.1.6. Preparation of [(η^5-pentamethylcyclopenta-dienyl)(η^5-1-methylpyrrole)Ir][BF_4]$_2$

80 mg (0.10 mmol) of the chloro-bridged Ir(III) dimer was allowed to react with AgBF$_4$ (78 mg, 0.40 mmol) in 10.0 ml of acetone. The reaction mixture was allowed to stir at room temperature for 15 min, after which the solution fraction was transferred to a second Schlenk flask. To this solution was added N-methylpyrrole (0.018 ml, 0.20 mmol) dissolved in 5.0 ml of acetone. The reaction mixture was stirred at room temperature for 4 h under N$_2$ which resulted in the formation of a precipitate that was isolated by filtration, washed with 5.0 ml of CH$_2$Cl$_2$, followed by an additional 5.0 ml aliquot of diethyl ether. The product, in the form of an air-stable yellow powder was dried in vacuo then recrystallized from a nitromethane-diethyl ether solution to give well-formed light yellow crystals. The overall yield was 88 mg of product (77%) that decomposed at 316°C.

Anal. [$C_{15}H_{23}NIr$][BF_4]$_2$ Calc.: C 31.70%, H 3.90%; Found: C 30.78%, H 3.75% ^{1}H NMR Cp*: 2.34 (s, 15H); N-methylpyrrole: 4.00 (s, 3H), 6.78 (s, 2H), 7.87 (s, 2H). ^{13}C NMR Cp*: 8.02, 88.34; N-methylpyrrole: 40.24, 100.75, 100.95.

3.1.7. Preparation of [(η^5-pentamethylcyclopenta-dienyl)(η^5-2,5-dimethylpyrrole)Ir][BF_4]

78 mg, (0.40 mmol) AgBF$_4$ and 80 mg (0.10 mmol) of the chloro-bridged Ir(III) dimer were stirred together in acetone for 15 min. The AgCl precipitate was removed by filtration, and to the resulting solution was added 0.10 ml (0.98 mmol) of 2,5-dimethylpyrrole. The reaction mixture was allowed to stir at room temperature under an atmosphere of N$_2$ for 6 h producing a brown solution. The solvent was removed under reduced pressure and the resulting product was washed with 5.0 ml of CH$_2$Cl$_2$, followed by 5.0 ml of diethyl ether. The product was dried in vacuo yielding 92 mg

of an air-stable light-yellow product in 79% yield that was found to decompose when heated beginning at 275°C.

Anal. [$C_{16}H_{24}NIr$][BF_4]$_2$ Calc.: C 33.01%, H 4.15%; Found: C 32.06%, H 4.13%. ^{1}H NMR Cp*: 2.14 (s, 15H); 2,5-dimethylmethylpyrrole: 2.35 (s, 6H), 5.85 (s, 2H). ^{13}C NMR Cp*: 9.72, 96.48; 2,5-dimethylpyrrole: 12.98, 86.67, 108.82.

3.1.8. Preparation of [(η^5-pentamethylcyclopenta-dienyl)bis(η^1-2,6-lutidine)IrCl$_2$]

2,6-lutidine (0.15 ml 1.3 mmol) was added directly to 80 mg (0.10 mmol) of the chlorobridged iridium dimer in 10.0 of methanol. A immediate reaction took place following to give a brown colored solution. The reaction mixture was allowed to reflux for a period of six hours, after which the solvent was removed under reduced pressure. The brown residue was washed with 5.0 ml a 5.0 ml aliquot of diethyl ether, extracted into chloroform, then dried under vacuum. From this reaction was isolated 90 mg of a light brown powder in 87% yield that decomposed ca. 175°C.

Anal. [$C_{17}H_{24}N_2Cl_2Ir$] Calc.: C 40.39%, H 4.78%; Found: C 38.44%, H 4.78%. ^{1}H NMR Cp*: 1.87 (s, 15H); 2,6-lutidine: 2.69 (s, 12H), 7.27 (d, 4H, $J = 9.00$ Hz), 7.96 (t, 2H, $J = 9.00$ Hz). ^{13}C NMR Cp*: 9.05, 94.06; 2,6-lutidine: 20.44, 124.09, 144.39, 154.15.

3.2. X-ray crystal structure determination

3.2.1. Crystal data

$C_{10}H_{19}ClF_6O_2IrP$, $M = 543.9$, orthorhombic, space group $Pnma$, $a = 20.260(7)$ Å, $b = 8.700(2)$ Å, $c = 9.656(3)$ Å, $V = 1702.0(9)$ Å^3. $D_{(calc)} = 2.122$ Mg m^{-3}, $Z = 4$, $\mu = 8.122$ mm^{-1}, λ(Mo Kα) = 0.71073 Å, $F(000) = 1032$, $T = 298$ K.

3.2.2. Data collection

Crystals suitable for crystallographic work were obtained upon recrystallization from a methanol-diethyl ether solution. A regularly shaped pale-yellow crystal having approximate dimensions 0.36 × 0.10 × 0.60 mm^3 was selected and mounted on the end of a glass fiber in a random orientation. Orthorhombic symmetry was suggested on the basis of the interaxial angles and axial rotation photographs. Refined cell parameters were determined from the setting angles of 22 reflections with 15° < 2θ < 30°. Data collection was carried out at ambient temperature using the ω-scanning technique in bisecting geometry on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation. Scan rate variable, 3–15° min^{-1}; scan range, 1.2° in ω. Three standards measured every 97 data showed only minor variations in intensity (< 3.0%) over the period of data collection. A total of 1369 reflections (+h, +k, +l; $h_{max} = 21$, $k_{max} = 9$, $l_{max} = 10$) with 3.5° < 2θ < 45° were obtained and corrected for

Lorentz and polarization effects. Absorption corrections were applied empirically on the basis of azimuthal scans of seven strong reflections spanning a range of 2θ values. Equivalent reflections were merged leading to 1207 unique reflections with $R_{int} = 1.56\%$.

3.2.3. Crystal structure solution and refinement

A view of the structure is shown in Fig. 2. The SHELXTL-PC collection of crystallographic software was used to solve and refine the structure [19]. The $Pna2_1$ and $Pnma$ space groups were considered but could not be distinguished solely on the basis of an examination of the systematically absent reflections or intensity statistics. Initial structure solution was carried out in the acentric $Pna2_1$ space group then changed to the centrosymmetric $Pnma$ space group when it became clear that the molecule possessed a mirror plane of symmetry namely in the $Pnma$ space group. The remainder of the atoms in the structure were located using standard difference-Fourier techniques. All non-hydrogen atoms were refined anisotropically using scattering factors that included terms for anomalous dispersion [20]. For the Cp* ring, hydrogen atoms were included in idealized positions with fixed isotropic $U = 0.08$ Å^2. No attempt was made to locate specifically any of the methyl hydrogens, especially in light of the fact that H-atoms of the methyl groups are frequently subject to some degree of rotational disorder. Surprisingly, however, we were able to locate and refine the positions of the H-atoms associated with the two coordinated molecules of water molecules as the structure refinement progressed. Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0042(F^2)]$. The maximum shift/$\sigma$ for the final cycle was 0.000 with minimum and maximum residual electron densities of -1.26 e Å^{-3} and $+1.29$ e Å^{-3} in the vicinity of the PF_6^- anion. Two intense low-angle reflection (2 0 0 and 0 2 0) appeared to suffer from some form of extinction and were therefore omitted during the final stages of refinement. Convergence to conventional R value of $R = 0.0417$ and $R_W = 0.0560$ with a goodness-of-fit of 0.72 was obtained for 110 variable parameters and 1205 reflections with $I > 0\sigma$ (I). A list of observed and calculated structure factor amplitudes is available from one of the authors (I.C.F.) upon request.

References and notes

[1] For recent reviews of concerning the HND process see (a) R.M. Laine, Catal. Rev. Sci. Eng., 25 (1983) 1459; (b) H. Schultz, M. Shon and N.M. Rahman Studies in Surface Science and Catalysis, Vol. 27, Elsevier: Amsterdam, 1986, in L. Ceverny (ed.), 201.
[2] S. Harris and R.R. Chianelli, J. Catal., 86 (1984) 400.
[3] A. Eisenstadt C.M. Giandomico, M.F. Frederic and R. Laine, Organometallics, 4 (1985) 2033.
[4] R.H. Fish, A.D. Thormodsen and G.A. Cremer, J. Am. Chem. Soc., 104 (1982) 5234.
[5] R.H. Fish, J.L. Tan and A.D. Thormodsen, J. Org. Chem., 49 (1984) 4500.
[6] R.H. Fish, J.L Tan and A. Thormodsen, Organometallics, 4 (1985) 1743.
[7] R.H. Fish, H.-S Kim, J.E. Babbin and R.A. Adams, Organometallics, 7 (1988) 2250.
[8] R.H. Fish, H.-S Kim, R.A. Fong, Organometallics, 8 (1989) 1375.
[9] R.H. Fish, H.-S Kim, R.A. Fong, Organometallics, 10 (1991) 1375.
[10] R.H. Fish, E. Baralt S.J. Smith, Organometallics, 10 (1991) 54.
[11] R.H. Fish, H.-S. Kim and R.H. Fong, Organometallics, 10 (1991) 770.
[12] R.H. Fish, R.H. Fong, A. Tran and E. Baral, Organometallics, 10 (1991) 1209.
[13] R.H. Fish, E. Baralt, H.-S Kim, Organometallics, 10 (1991) 1965.
[14] R.A. Sanchez-Delgado and E. Gonzalez, J. Chem. Soc., Dalton Trans., (1989) 1431.
[15] B. Chaudret and F.A. Jalon, J. Chem. Soc., Chem. Commun., (1988) 711.
[16] Y. Shvo, D.W. Thomas and R.M. Laine, J. Am. Chem. Soc., 103 (1981) 2461.
[17] X.-L. Luo, G.K. Schulte & R.H. Crabtree, Inorg. Chem., 29 (1990) 682.
[18] C. White, A. Yates & D.M. Maitlis, Inorg. Synth., 29 (1990) 230.
[19] Sheldrick, G.M. SHELXTL-PC An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, Univ. of Gottingen, 1990.
[20] International Tables for X-ray Crystallography, Vol. IV, Kynoch Birmingham Present distributor D. Reidel, Dordrecht, 1974.