Synthesis and oxidation of Cp*Ir^{III} compounds: functionalization of a Cp* methyl group†

Lisa S. Park-Gehrke,[a] John Freudenthal,[b] Werner Kaminsky,[b] Antonio G. DiPasquale[c] and James M. Mayer*[a]

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[Cp*IrCl$_2$]$_2$ (**1**) and new Cp*Ir^{III}(L–L)X complexes (L–L = N–O or C–N chelating ligands; X = Cl, I, Me) have been prepared and their reactivity with two-electron chemical oxidants explored. Reaction of **1** with PhI(OAc)$_2$ in wet solvents yields a new chloro-bridged dimer in which each of the Cp* ligands has been singly acetoxylated to form [Cp^{OAc}Ir^{III}Cl$_2$]$_2$ (**2**) (Cp^{OAc} = η^5-C$_5$Me$_4$CH$_2$OAc). Complex **2** and related carboxy- and alkoxy-functionalized Cp^{OR} complexes can also be prepared from **1** plus (PhIO)$_n$ and ROH. [Cp^{OAc}Ir^{III}Cl$_2$]$_2$ (**2**) and the methoxy analogue [Cp^{OMe}Ir^{III}Cl$_2$]$_2$ (**3**) have been structurally characterized. Treatment of [Cp*IrCl$_2$]$_2$ (**1**) with 2-phenylpyridine yields Cp*Ir^{III}(ppy)Cl (**4Cl**) (ppy = cyclometallated 2-phenylpyridyl) which is readily converted to its iodide and methyl analogues Cp*Ir^{III}(ppy)I (**4I**) and Cp*Ir^{III}(ppy)Me (**4Me**). Cp*Ir^{III} complexes were also prepared with N–O chelating ligands derived from anthranilic acid (2-aminobenzoic acid) and α-aminoisobutyric acid (H$_2$NCMe$_2$COOH), ligands chosen to be relatively oxidation resistant. These complexes and **1** were reacted with potential two-electron oxidants including PhI(OAc)$_2$, hexachlorocyclohexadienone (C$_6$Cl$_6$O), *N*-fluoro-2,4,6-trimethylpyridinium (Me$_3$pyF$^+$), [Me$_3$O]BF$_4$ and MeOTf (OTf = triflate, CF$_3$SO$_3$). Iridium(V) complexes were not observed or implicated in these reactions, despite the similarity of the potential products to known Cp*Ir^{V} species. The carbon electrophiles [Me$_3$O]BF$_4$ and MeOTf appear to react preferentially at the N–O ligands, to give methyl esters in some cases. Overall, the results indicate that Cp* is not inert under oxidizing conditions and is therefore not a good supporting ligand for oxidizing organometallic complexes.

Introduction

Oxidation reactions and oxidizing compounds have historically been among the least developed areas of organometallic chemistry. Recent years have seen advances in organometallic ruthenium(IV),[1] palladium(IV),[2] and platinum(IV)[3] chemistry and some mildly oxidizing species have been prepared. Iridium(V) compounds have the potential to be stronger oxidants, but this oxidation state remains mostly unexplored. The relatively few known Ir^{V} compounds predominantly have cyclopentadienyl, hydrocarbyl and hydride ligands, including Cp*IrMe$_4$,[4] Cp*IrMe$_3$X and Cp*IrMe$_3$(L)$^+$ (X$^-$ = Cl$^-$, OTf$^-$ [CF$_3$SO$_3^-$], L = PR$_3$, *etc.*),[5] [CpIrH$_3$(PMe$_3$)]$^+$,[6] (mes)$_3$Ir(O),[7] Cp^{0}IrH$_3$SiEt$_3$,[8] (^{i}PrBDI)IrH$_4$,[9] and others[10] [Cp = C$_5$H$_5$, Cp* = C$_5$Me$_5$, Cp^0 = (2-methoxyethyl)cyclopentadienyl, mes = 2,4,6-trimethylphenyl, ^{i}PrBDI = ArNC(Me)CH(Me)CNAr, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$]. The Ir^{III}/Ir^{V} redox couple has also been implicated in a number of catalytic reactions.[11]

The known isolated organometallic Ir^{V} complexes, while reactive and often not very stable, do not appear to be strong oxidants. In contrast, high oxidation state iridium systems with non-organometallic ligands are very strongly oxidizing. For example, hexachloroiridate(IV), Ir^{IV}Cl$_6^{2-}$, has $E°$ = 0.67 V *vs.* SHE in MeCN[12] and Ir^{V} is not accessible with chloride ligation. This dichotomy arises because replacement of a Cl ligand for an alkyl or aryl group typically shifts the redox potential down by *ca.* 0.3 V per ligand, based on related Re and Os complexes.[13] Thus, variation in the ligands should have a substantial effect on the redox character and reactivity of Ir^{V} complexes. Another strategy for stabilizing high oxidation states is the use of ligands that can be deprotonated upon oxidation, as in aquo/hydroxo/oxo and amine/amide/imido complexes of ruthenium and osmium.[14] The osmium aniline/anilide complexes TpOsCl$_2$(NH$_x$Ph) are a particularly dramatic example, as the Os^{III}/Os^{IV} redox potential shifts from +0.48 to −1.05 V (*vs.* Cp$_2$Fe$^{+/0}$ in MeCN) upon deprotonation.[15]

The studies reported herein are part of a program to use these approaches to develop the chemistry of the Ir^{III}/Ir^{V} redox couple and, more generally, to develop the chemistry of oxidizing organometallic compounds. We describe the reactivity of new and known Ir^{III} complexes with two-electron chemical oxidants such as those in Chart 1. These reagents are all formally sources of electrophiles X$^+$ (Cl$^+$, OAc$^+$, F$^+$, or Me$^+$) which could add to an Ir^{III} centre to form [Ir^{V}–X]$^+$ complexes. While this work was in progress, Periana *et al.* reported related reactions of Ir^{III} compounds with strong oxidants.[16] Our studies have used the

[a]*Department of Chemistry, Campus Box 351700, University of Washington, Seattle, WA 98195, US. E-mail: mayer@chem.washington.edu; Fax: 1 206 685 8665; Tel: 1 206 543 2083*
[b]*University of Washington X-ray Crystallographic Facility, Seattle, WA 98195, US*
[c]*20A Lewis Hall, X-ray Crystallographic Facility, College of Chemistry, University of California, Berkeley, CA 94720, US. E-mail: adipasqu@berkeley.edu; Tel: 1 510 642 7336*

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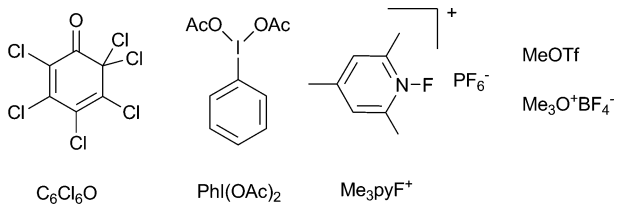


Chart 1

Cp* ligand that appears in many of the known Ir^V complexes. We have also used cyclometallated 2-phenylpyridine (ppyH) and chelating amide ligands (Chart 2), to explore how different types of ligands influence the reactivity of Ir^{III} in an oxidizing environment. Cyclometallated 2-arylpyridine ligands are strong donors and their iridium complexes are of much current interest due to their photophysical properties.[17] Complexes of this ligand are also involved in palladium oxidation catalysis.[18] The N-O chelating ligands that have been used, derivatives of anthranilic acid (*o*-$H_2NC_6H_4CO_2H$, anthrH-NH_2) and N-tosyl-*o*-aminoisobutyric acid ($TsNHCMe_2CO_2H$, $TAIBAH_2$), should be fairly oxidation resistant due to the absence of C–H bonds α to the nitrogen donor.[19] Anthranilic acid is an unusual β-amino acid that can coordinate as the singly, doubly, or triply deprotonated ligand.[20] $TAIBAH_2$ is related to α-amino acid ligands that make interesting

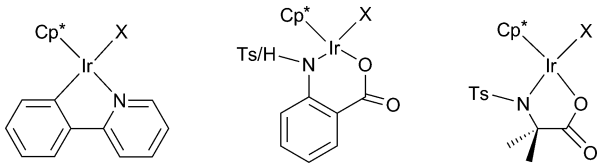


Chart 2

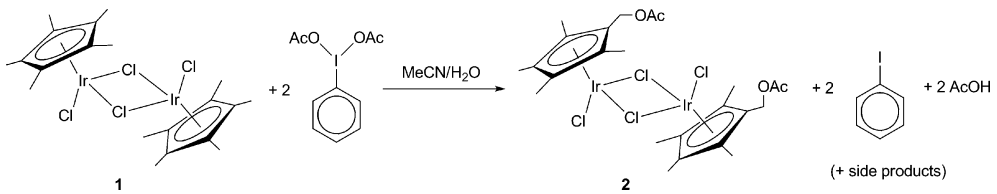
five and six coordinate Cp^*Ir^{III} complexes.[21] The Cp* ligand was chosen for this study because it has been widely used as a supporting ligand, both in Ir^V compounds and reactions that have implicated Ir^V intermediates.[4–6,10b,e,f,11b,c,h,i] We find, however, that under oxidizing conditions the Cp* ligand is not an inert bystander but can be oxidized.

Results

1. Oxidation of $[Cp^*IrCl_2]_2$ to $[Cp^{OR}IrCl_2]_2$

As part of our survey of oxidation reactions of Cp^*Ir^{III} complexes, the well-known $[Cp^*IrCl_2]_2$ dimer (**1**)[22] was reacted with the hypervalent iodine reagent $PhI(OAc)_2$ in wet MeCN (eqn (1)). $PhI(OAc)_2$ is being increasingly used in organometallic oxidations, for instance in the palladium reactions developed by Sanford *et al.*[23] Over a day at room temperature, or during 2 hours at 50 °C, reactions of **1** and $PhI(OAc)_2$ convert to one main product, **2**, and a few side products, according to ^1H NMR spectra. The single crystal X-ray structure of **2** (Fig. 1, Table 1) shows an iridium chloro-bridged dimer very similar to **1**,[24] except that one methyl group on each Cp* ligand has been oxidized to a CH_2OAc group: $[(\eta^5\text{-}C_5Me_4CH_2OAc)IrCl_2]_2$ ($[Cp^{OAc}IrCl_2]_2$, **2**). The metrical data for this structure are discussed below.

The ^1H NMR spectrum of **2** in CD_3CN shows a characteristic four signals with constant relative integrations of 6:6:3:2, consistent with the solid state structure: two pairs of $Cp^*\text{-}CH_3$ groups (each 6H, δ1.73, 1.66 ppm), the OAc group (3H, δ2.01 ppm), and the acetoxylated CH_2 downfield at δ4.67 ppm. This ^1H NMR spectrum is similar to that reported by Maitlis and co-workers for the related Cp^{OAc}-ruthenium complex $[(C_5Me_4CH_2OAc)Ru(CO)_2Cl]$.[25] ESI mass spectra of **2** show a primary peak at 421.1 *m*/*z*, which corresponds to $Cp^{OAc}IrCl^+$.



(1)

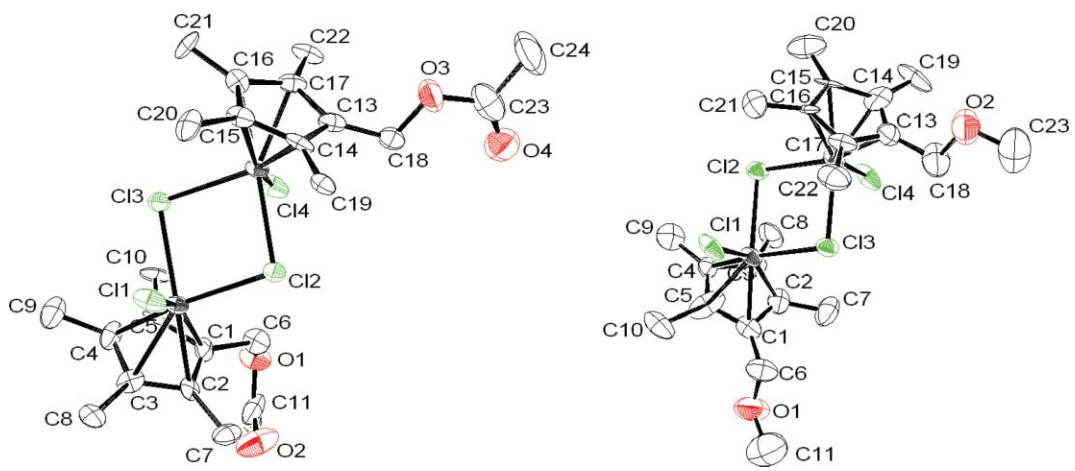


Fig. 1 ORTEPs of **2**·**PhI** and **3**·**PhI** (PhI and hydrogen atoms omitted for clarity) with thermal ellipsoids drawn at the 50% probability level.

Table 1 Selected bond distances (Å) for comparison of $[Cp^{OAc}IrCl_2]_2$ (**2**) and $[Cp^{OMe}IrCl_2]_2$ (**3**) with $[Cp^*IrCl_2]_2$ (**1**) and other η^5-$C_5Me_4CH_2R)Ir^{III}$ complexes

	$[Cp^*IrCl_2]_2$ (**1**)[a]	$[Cp^{OAc}IrCl_2]_2$ (**2**)	$[Cp^{OMe}IrCl_2]_2$ (**3**)	$[Cp^{PPh3}IrCl(PPh_3)_2]^+$ [b]	$Cp^{CO2H}IrMe(CO)Cl$[c]
Ir–C1	2.121(12)	2.120(13)	2.117(13)	2.226(10)	2.291(15)
Ir–C2	2.118(16)	2.123(13)	2.138(12)	2.278(10)	2.277(15)
Ir–C3	2.121(11)	2.134(14)	2.150(12)	2.289(10)	2.225(17)
Ir–C4	2.155(12)	2.127(13)	2.095(12)	2.258(10)	2.260(20)
Ir–C5	2.145(14)	2.140(12)	2.021(18)	2.245(10)	2.191(17)
Avg Ir–C	2.132(16)	2.129(8)	2.112(8)	2.259(25)	2.249(40)
$C–C_{func}$		1.468(19)	1.485(18)	1.479(15)	1.539(54)
Avg C–C	1.531(15)	1.499(9)	1.543(67)	1.495(11)	1.526(26)

[a] Ref. 24. [b] Ref. 26. [c] Ref. 27.

The maximum conversion of **1** to **2** in reaction 1 is about 60% by NMR and a number of minor products are also formed. Yellow reaction mixtures rapidly turn a dark brown colour which lightens to a golden hue upon heating or if left standing for hours. Heating also causes some decomposition of the $PhI(OAc)_2$, both in the presence and absence of iridium complexes. Even with the addition of 8 equivalents of $PhI(OAc)_2$, some **1** remains; addition of further aliquots of oxidant leads to reaction with both **1** and **2**. The further reaction between **2** and $PhI(OAc)_2$ appears to lead to oxidation of additional Cp*-Me groups, as far as we can tell from the complex ^{1}H NMR spectra that result.

The balanced reaction to form **2** from **1** and $PhI(OAc)_2$ (eqn (1)) gives two equiv of acetic acid, which is quantitatively observed by ^{1}H NMR. While water is not stoichiometrically needed, under anhydrous conditions there is virtually no reaction between **1** and $PhI(OAc)_2$.

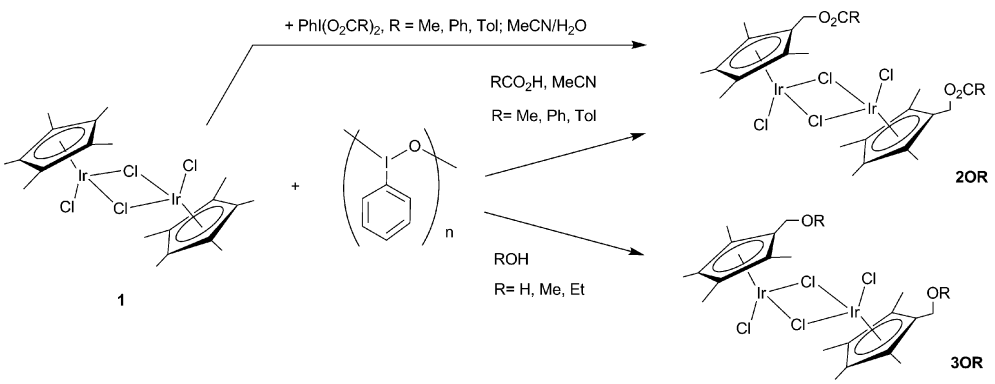
Complex **2** is formed well in wet (undried) bench-top MeCN, or in MeCN to which significant water has been added. This suggests that a hydrolysis product of $PhI(OAc)_2$, a hydroxyl derivative or a $(PhIO)_n$ oligomer (eqn (2)), is the actual reactive oxidant.[28]

$$PhI(OAc)_2 + H_2O \rightleftharpoons {}^1/_n\,(PhIO)_n + 2\ AcOH \qquad (2)$$

Monitoring reaction 1 over time by ^{1}H NMR shows that $PhI(OAc)_2$ is consumed faster than **2** appears, implicating an intermediate iodine species. In support of this, **2** is also formed from **1** plus independently prepared iodosylbenzene $[(PhIO)_n]$ and excess AcOH in wet MeCN (Scheme 1). This reaction is, however, very slow—not complete after a month at 22 °C—perhaps due to poor solubility of the isolated iodosylbenzene polymer in acetonitrile.

Complex **1** also reacts with iodosylbenzene-dibenzoate and -di-*p*-toluate, $PhI(O_2CPh)_2$ and $PhI(O_2CTol)_2$, in wet MeCN. The primary products appear to be aryl analogues of **2**, $[Cp^{O2CPh}IrCl_2]_2$ and $[Cp^{O2CTol}IrCl_2]_2$, although the modest yields and inseparable side products have precluded their isolation. $[Cp^{O2CPh}IrCl_2]_2$ and $[Cp^{O2CTol}IrCl_2]_2$ are also formed from **1** + $(PhIO)_n$ + $ArCO_2H$ at 50 °C (Scheme 1). The Cp^{O2CAr} iridium dimers are identified by the characteristic 6:6:2 signal pattern in the ^{1}H NMR and the correct integral ratio with the carboxylate groups. Their ESI mass spectra show prominent peaks for the respective $Cp^{O2CAr}IrCl^+$ fragment, at *m*/*z* 483.1 for $[Cp^{O2CPh}IrCl_2]_2$ and *m*/*z* 497.1 for $[Cp^{O2CTol}IrCl_2]_2$. The $PhI(O_2CAr)_2$ reactions are much slower than those with $PhI(OAc)_2$, requiring 7 days at 50 °C in MeCN, apparently due to poor solubility of the iodine reagents.

The Cp* functionalization is not limited to carboxylate groups: heating $[Cp^*IrCl_2]_2$ (**1**) and $(PhIO)_n$ at 50 °C in methanol yields the related methoxy-functionalized dimer, $[Cp^{OMe}IrCl_2]_2$ (**3**; Scheme 1). The ^{1}H NMR spectrum of **3** in dry CD_2Cl_2 exhibits the now-familiar 6:6:3:2 pattern: Cp-*Me* groups at δ1.58, 1.61; a methoxy group at δ3.36; and the methoxylated methylene group at 4.07 ppm. The ESI/MS spectrum of **3** shows the characteristic fragment for $[Cp^{OMe}IrCl]^+$, 393.2 *m*/*z*. Complex **3** has also been characterized by an X-ray crystal structure (Fig. 1 above). The reaction of **1** plus PhIO in ethanol proceeds similarly



Scheme 1

to $[Cp^{OEt}IrCl_2]_2$, based on ^{1}H NMR and ESI-mass spectra. In the formation of **3** *via* Scheme 1, addition of $(PhIO)_n$ to an orange suspension of **1** in MeOH forms a forest green solution, which then changes to the orange-brown of **3** over a day at room temperature (or rapidly upon heating). ^{1}H NMR spectra of the green solutions shows signals in the Cp*-region for as yet unidentified species, including a material ("**A**") that is seen in many of the oxidations of **1**. As the green solution turns orange, most of the Cp* signals decay leaving primarily **3**, **A**, PhI and **1**. The formation of multiple products means that these reactions, while somewhat general, are not (as yet) attractive synthetic routes to functionalized Cp* compounds.

Complexes **1–3** have similar Ir–C and Ir–Cl bond lengths (Table 1), suggesting that the acetoxy and methoxy groups do not have a significant electronic effect on the metal centre. The C–C bonds between the Cp*-ring and the CH_2OAc or CH_2OMe carbon, on both sides of both molecules, are at most only slightly shorter than the Cp*–Me bond lengths. For Ir(1) in **2**, for instance, the C1–C6 bond of 1.468(19) Å is within 2σ of the 1.499(9) Å average of the (Cp)C–Me bonds. Thus there appears to be little contribution from a fulvene resonance form $[\eta^5\text{-}(MeC)_4C{=}CH_2{}^+OR^-]$.[29]

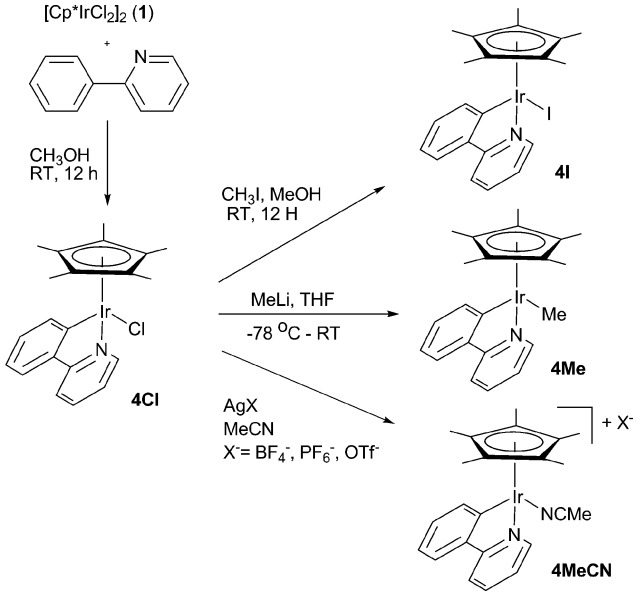
Reacting **1** with $(PhIO)_n$ in wet CD_3CN in the *absence* of any acid or alcohol gives a new species (in addition to **A**). This compound has a similar 6:6:2 pattern of NMR resonances in CD_3CN except that the methylene signal is a doublet (δ4.13 ppm, $^3J_{HH} = 5.5$ Hz), in addition to the two Cp*–Me singlets (δ1.71 and 1.65 ppm). A triplet integrating to 1 H is also observed at δ3.42 ppm ($^3J_{HH} = 5.5$ Hz). These data indicate that a Cp*-methyl group has been oxidized to CH_2OH, with the C*H*$_2$ signal split into a doublet by the O*H* and the O*H* signal likewise split into a triplet by the C*H*$_2$. The splitting disappears when an excess of a proton source (*e.g.*, AcOH) is added to the reaction solution and is not visible when the reaction is carried out in the presence of D_2O. While it is unusual to observe coupling to an O*H* group, Maitlis and co-workers have reported similar 3-bond C*H*–O*H* couplings for hydroxylated Cp* ligands bound to ruthenium.[25,30] ESI mass spectra of the **1** + $(PhIO)_n$ + H_2O/CD_3CN reaction solution show major peak clusters for Cp^*IrCl^+ and for $(C_5Me_4CHO)IrCl^+$; it is not evident why a $Cp^{OH}IrCl^+$ ion analogous to other $[Cp^{OR}IrCl_2]_2$ complexes is not observed. ESI/MS of $[Cp^*IrCl_2]_2$ + $(PhI^{16}O)_n$ + $H_2{}^{18}O$ reaction mixtures show the formation of $(C_5Me_4CH^{18}O)IrCl^+$.

Complex **1** reacts readily with $PhICl_2$ or $PhI(TFA)_2$ (TFA = trifluoroacetate, O_2CCF_3) but by ^{1}H NMR no $[Cp^{Cl}IrCl_2]_2$ is formed and there is at most a trace of $[Cp^{TFA}IrCl_2]_2$. Heating **1** with a slight excess of benzoyl peroxide $[PhC(O)O]_2$ and $PhCO_2H$ in wet CD_3CN at 75 °C gives a small amount of $[Cp^{O2CPh}IrCl_2]_2$, suggesting that functionalization of the Cp*–Me group could proceed by a radical pathway.

Attempts to elucidate the mechanism of oxidation of **1** by $PhI(OR)_2$ or $(PhIO)_n$ + ROH have been complicated by the moderate yields and side products that are observed by ^{1}H NMR. These materials may include dimers with singly or otherwise non-symmetrically functionalized Cp* ligands, or monomeric analogues. One significant product, called **A** above, is initially present in roughly 20–30% yield in all reactions. It has the characteristic 6:6:2 ^{1}H NMR signals (δ1.65, 1.72, and 4.26 ppm) and could possibly be an alkoxide analogue, $[(O\overline{CH_2Me_4})IrCl]_n$, but attempts to isolate it have not been successful.

2. Cp*Ir(ppy)X (4X) complexes

A. Synthesis and characterization. The chemistry of cyclometallated 2-phenylpyridine complexes Cp*Ir(ppy)X (**4X**) has been explored because these compounds should be more electron rich than the dichloride derivative $[Cp^*IrCl_2]_2$ (**1**). Addition of 2-phenylpyridine (ppyH) to methanol solutions of **1** forms orange solid Cp*Ir(ppy)Cl (**4Cl**) in good yield (Scheme 2). While this work was in progress, **4Cl** was described by Djukic *et al.*, who prepared it from **1**, ppyH and NaOAc in CH_2Cl_2, and isolated it by air-free column chromatography at 0 °C.[31] The synthesis of **4Cl** described here (see Experimental section) appears to be simpler, with easier isolation and comparable product yields.



Scheme 2

Addition of excess MeI to **4Cl** in methanol proceeds by Cl-for-I exchange, yielding rust-coloured Cp*Ir(ppy)I (**4I**; Scheme 1). When the reaction is conducted in CD_3OD, CH_3Cl is observed by ^{1}H NMR at δ3.01 ppm (confirmed by comparison with an authentic sample). Treatment of **4Cl** with AgOTf, $AgPF_6$ or $AgBF_4$ in MeCN yields [Cp*Ir(ppy)NCMe]X (**4MeCN**; $X^- = OTf^-$, PF_6^-, or BF_4^-) (Scheme 2), which were characterized by ^{1}H NMR. The red methyl derivative Cp*Ir(ppy)Me (**4Me**) is prepared by reaction of MeLi with **4Cl** in THF (Scheme 2).

^{1}H NMR spectra of **4Cl**, **4I**, **4MeCN**, and **4Me** in CD_2Cl_2 all show a single Cp* resonance (δ1.66 for **4Cl**) and eight sometimes overlapping ppy signals (δ7.04–8.68 for **4Cl**). The assignments for **4Cl** were confirmed by ^{1}H 2D NMR (COSY).[32] Complex **4Me** also has an Ir*Me* signal at δ–0.33 ppm, while **4MeCN** has an IrC*H*$_3$CN signal at δ2.30 ppm. ESI mass spectra of **4Cl**, **4I** and **4Me** show ion clusters at M^+ and prominent $Cp^*Ir(ppy)^+$ peaks ($M^+ - X$). ESI mass spectra of **4MeCN** variants show primarily the ($M^+ - X$) peak.

The X-ray crystal structures of **4Cl** and **4I**† are very similar, both containing isolated molecules with "three-legged piano stool" geometries (Fig. 2). As expected, the Ir–I bond of 2.691(5) in **4I** is almost 0.3 Å longer than the 2.401(3) Ir–Cl bond in **4Cl**. Selected bond lengths and angles for **4I** are listed in Table 2; Table 3 gives the data collection parameters (the data for **4Cl** are given in the

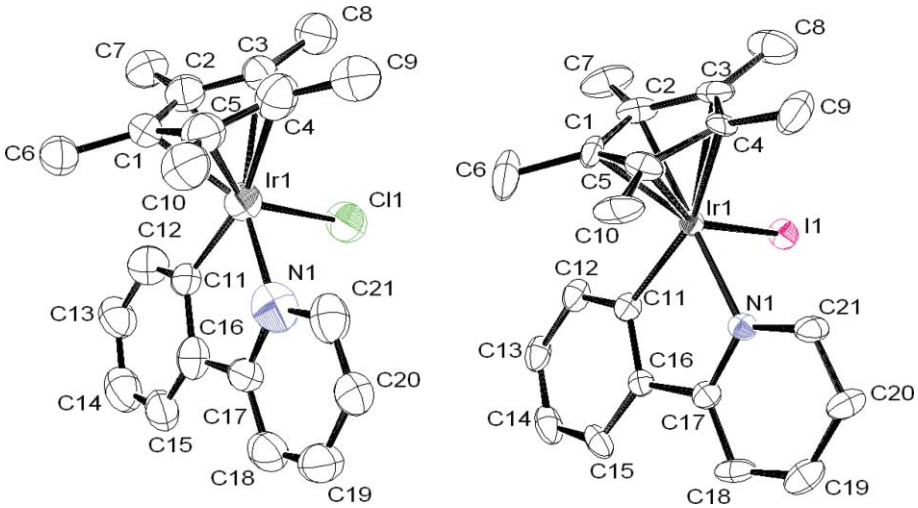


Fig. 2 ORTEPS of Cp*Ir(ppy)Cl (**4Cl**) and Cp*Ir(ppy)I (**4I**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

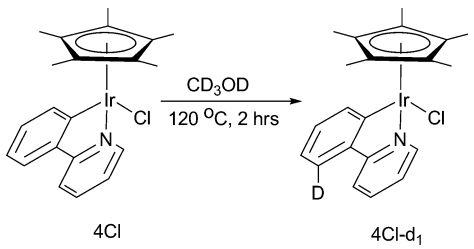
Table 2 Selected bond distances (Å) and angles (°) for Cp*Ir(ppy)I (**4I**), Cp*Ir($H_2NC_6H_4CO_2$)Cl·MeOH (**6·MeOH**) and Cp*Ir($TsNC_6H_4CO_2$)(MeCN)·H_2O (**7·H_2O**)

	4I	6·MeOH	7·H_2O
Ir(1)–C(1)	2.167(7)	2.122(7)	2.130(6)
Ir(1)–C(2)	2.164(8)	2.170(8)	2.153(6)
Ir(1)–C(3)	2.260(8)	2.150(8)	2.150(6)
Ir(1)–C(4)	2.256(6)	2.146(7)	2.143(6)
Ir(1)–C(5)	2.168(7)	2.152(7)	2.148(6)
Ir(1)–I(1)	2.691(5)		
Ir(1)–Cl(1)		2.3875(16)	
Ir(1)–N(1)	2.082(7)	2.133(5)	2.115(5)
Ir(1)–C(11)	2.053(7)		
Ir(1)–O(1)		2.136(5)	2.083(4)
Ir(1)–N(2)			2.062(5)
N(1)–Ir(1)–O(1)	77.7(3)[a]	77.8(2)	82.92(17)
N(1)–Ir(1)—X	89.17(15)[b]	82.60(17)[c]	89.02(18)[d]
I(1)–Ir(1)–C(11)	110.5(3)	83.91(15)[e]	80.05(17)[f]

[a] N(1)–Ir(1)–C(11). [b] N(1)–Ir(1)–I(1). [c] N(1)–Ir(1)–Cl(1). [d] N(1)–Ir(1)–N(2). [e] Cl(1)–Ir(1)–O(1). [f] N(2)–Ir(1)–O(1).

supporting information†). The metrical data for **4Cl** and **4I** are similar to related Ir^{III} complexes, in the 2.15–2.23 Å Ir–C(Cp*) bond lengths[5,33] and in the Ir–C and Ir–N bond lengths to the ppy moiety.[34]

Heating **4Cl** (but not **4I**) in CD_3OD over two hours at 120 °C results in exchange of one hydrogen on the ppy ligand for deuterium. ^{1}H NMR spectra show the gradual disappearance of one ppy resonance and the conversion of one triplet resonance to a doublet signal. The ^{2}H NMR spectrum of the exchanged compound shows a single, sharp signal at δ7.72. Based on assignments of the ^{1}H NMR spectrum of **4Cl** by COSY and NOESY experiments, the exchanged hydrogen is H4 of the ppy phenyl ring (eqn (3)). No other changes occur in the ^{1}H NMR spectrum, and ESI/MS analysis in CD_3OD shows a [M-d_1]-Cl peak for **4Cl**-d_1 (483 m/z), confirming that **4Cl** is unchanged except for exchange of one D for H. This *ortho*-H/D exchange in CD_3OD is very similar to the exchange recently reported by Peris and co-workers for the cyclometallated N-heterocyclic carbene (NHC) complex Cp*Ir^{III}(C–NHC)Cl, where C–NHC = cyclometallated 1-benzyl-3-methylimidazolylidene.[33e] To test for possible catalytic 2-phenylpyridine deuteration, solutions of ppyH in CD_3OD were heated with 5–20 mol% **4Cl** for 1.5 days. ^{1}H NMR spectra indicated deuteration of **4Cl**, but the signals for free ppyH remained unchanged.



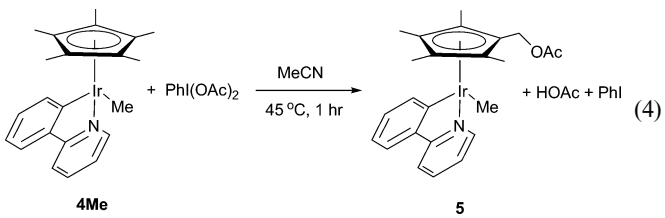
(3)

B. Oxidations of Cp*Ir^{III}(ppy)X (4X). Compounds **4X** were treated with the two-electron chemical oxidants shown above in Chart 1. In a typical experiment, the oxidant was added to Cp*Ir^{III}(ppy)L in 'dry' CD_3CN in a J. Young NMR tube at ambient temperatures, except for reactions between Me_3pyF^+ and **4Cl** or **4I**, which were heated at 100°C because no reactivity was seen at room temperature. All reactions were monitored by ^{1}H NMR.

Heating a solution of **4Me** and $PhI(OAc)_2$ for an hour at 45 °C gives a single new iridium species. Its ^{1}H NMR spectrum shows signals for phenylpyridyl and Ir-*Me* ligands, a 3:3:3:3 pattern in the Cp* region, a –OAc signal at δ1.92 integrating to 3 hydrogens, and a quasi-quartet centred at δ4.65 integrating to 2 hydrogens. These data suggest that a Cp*-methyl functionalized product has been formed, Cp^{OAc}Ir(ppy)Me (**5**) (eqn (4)), similar to the formation of **2**. The ESI/MS of **5** shows peaks at m/z = 554 and 540 which correspond to [Cp^{OAc}Ir(ppy)Me–H]$^+$ and Cp^{OAc}Ir(ppy)$^+$, consistent with this formulation. In contrast to **2** and **3**, the iridium centre of **5** is chiral and therefore the four Cp^{OAc} methyl groups are inequivalent, accounting for the 3:3:3:3 pattern. In addition, the methylene hydrogens are diastereotopic, so the apparent quartet at δ4.65 is actually an AB pattern.

Table 3 Crystal data and structure refinement for $[Cp^{OAc}IrCl_2]_2$·PhI (**2·PhI**) and $[Cp^{OMe}IrCl_2]_2$ (**3·PhI**), Cp*Ir(ppy)I (**4I**), Cp*Ir($H_2NC_6H_4CO_2$)Cl (**6·MeOH**), Cp*Ir($TsNC_6H_4CO_2$)(MeCN)·H_2O (**7·H_2O**)

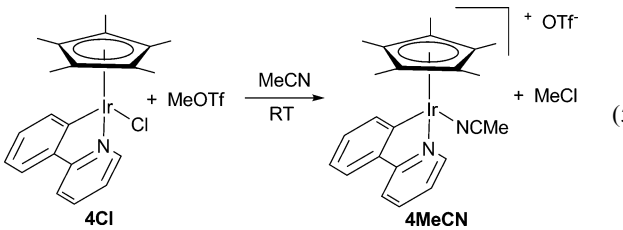
	2·PhI	**3·PhI**	**4I**	**6·MeOH**	**7·H_2O**
Empirical formula	$C_{30}H_{39}Cl_4IIr_2O_4$	$C_{28}H_{39}Cl_4IIr_2O_2$	$C_{21}H_{23}IIrN$	$C_{18}H_{25}ClIrNO_3$	$C_{26}H_{31}IrN_2O_5S$
Formula weight	1116.76	1060.73	608.50	531.04	675.79
Temperature (K)	130(2)	130(2)	130(2)	130(2)	143(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal description/colour	Cut block/yellow	Cut block/orange	Prism/yellow	Needle/yellow	Plate/yellow
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	*P*-1	*P*-1	$P2_1/c$	$P2_12_12_1$	*P*-1
Unit cell dimensions					
a (Å)	8.8660(4)	8.7721(5)	13.7010(4)	7.18200(10)	8.686(3)
b (Å)	13.3300(5)	13.6754(10)	9.0000(3)	15.0380(3)	8.726(3)
c (Å)	16.1160(7)	14.3727(9)	15.8690(5)	16.8710(4)	19.065(6)
α (°)	112.939(2)	105.435(4)	90	90	76.821(4)
β (°)	94.7220(19)	100.301(3)	99.9800(15)	90	87.514(4)
γ (°)	98.9320(17)	99.207(3)	90	90	63.397(3)
V (Å^3)	1711.27(12)	1595.41(18)	1927.18(10)	1822.12(6)	1255.1(7)
Z	2	2	4	4	2
Calculated density (g cm^{-3})	2.167	2.208	2.097	1.936	1.788
Abs coeff (mm^{-1})	9.016	9.659	8.532	7.490	5.442
F(000)	1052	996	1144	1032	688
Crystal size (mm)	0.30 × 0.30 × 0.10	0.20 × 0.10 × 0.10	0.35 × 0.32 × 0.15	0.59 × 0.10 × 0.07	0.08 × 0.04 × 0.02
Reflections for indexing	52	468	1320	1294	1294
θ range for data coll. (deg)	2.35 to 25.56	2.42 to 25.47	2.61 to 28.33	2.41 to 28.36	3.05 to 27.02
Index ranges	$-10 \le h \le 10$	$-10 \le h \le 10$	$-18 \le h \le 18$	$-9 \le h \le 9$	$-11 \le h \le 10$
	$-15 \le k \le 16$	$-16 \le k \le 16$	$-11 \le k \le 11$	$-19 \le k \le 19$	$-10 \le k \le 10$
	$-19 \le l \le 19$	$-17 \le l \le 17$	$-21 \le l \le 21$	$-21 \le l \le 21$	$-22 \le l \le 23$
Reflns collected	11070	10263	8271	6923	11426
Unique reflns	4517 $R_{int} = 0.081$	4343 $R_{int} = 0.047$	4877 $R_{int} = 0.042$	6230 $R_{int} = 0.129$	5708 $R_{int} = 0.087$
Completeness to $\theta = 25.00$	98.9%	97.3%	98.2%	99.9%	98.7%
Refinement method	Full-matrix least-squares on F^2				
Data/restraints/parameters	6230/30/380	5708/0/346	4517/0/222	4343/0/224	4877/0/329
Goodness-of-fit on F^2	$S = 0.979$	$S = 0.926$	$S = 1.004$	$S = 1.049$	$S = 1.058$
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.058$	$R_1 = 0.053$	$R_1 = 0.058$	$R_1 = 0.037$	$R_1 = 0.038$
R indices (all data)	$wR_2 = 0.127$	$wR_2 = 0.112$	$wR_2 = 0.155$	$wR_2 = 0.098$	$wR_2 = 0.076$



(4)

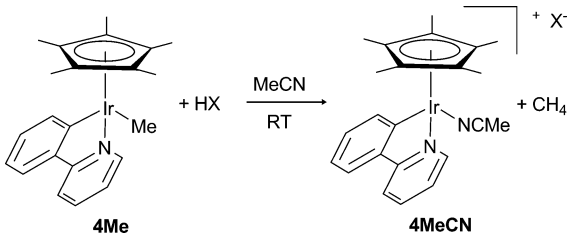
The reaction of Cp*Ir(ppy)Cl (**4Cl**) with $PhI(OAc)_2$ gives a complex mixture of products, but **4Cl** + C_6Cl_6O in methylene chloride may give a Cp*-oxidized material similar to **2**, **3**, and **5**. C_6Cl_6O (Chart 1) is a valuable Cl^+ donor in organic reactions, with pentachlorophenoxide as the leaving group,[35] but to our knowledge it has not been used in transition metal chemistry. A major product of this reaction exhibits a 6:6:2 pattern in the ^1H NMR, with the 2H signal at δ4.30 ppm, which is characteristic of the Cp^{OR} compounds. A new set of ppy signals is also observed. This product unfortunately could not be isolated cleanly, away from the $[Cp^*Ir(ppy)MeCN]^+$ and other products formed. ESI-MS analysis of this solution showed a peak at 516 *m*/*z* (**4Cl**-H^+), which likely corresponds to the functionalized Cp* fragment ion $(\eta^5\text{-}C_5Me_4CH_2Cl)Ir(ppy)^+$, although the fulvene derivative $(C_5Me_4CH_2)Ir(ppy)Cl^+$ cannot be ruled out.

Reactions of the Me^+ donors MeOTf and $[Me_3O]BF_4$ with **4Cl** in acetonitrile yield [Cp*Ir(ppy)NCMe]X (**4MeCN**, X^- = OTf^- or BF_4^-), by comparison of the ^1H NMR signals with independently synthesized material. With **4Cl** + MeOTf, a signal at δ3.01 indicates that CH_3Cl is formed (eqn (5)). Monitoring reaction 4 from –40 °C to 25 °C in an NMR probe showed no chemical change until the spectrometer was at room temperature, and then only product formation was observed with no evidence of an intermediate species.



(5)

The reaction of **4Me** with MeOTf is very slow unless water is present. In wet MeCN, this reaction gives **4MeCN** and CH_4 (eqn (6)). When CD_3OTf is used, only CH_4 is formed (δ0.20), while **4Me** and CH_3OTf in $MeCN/D_2O$ gives CH_3D (δ0.18, $^3J_{HD} = 1.8$ Hz). These results suggest that the methane results from protonation of **4Me**. Consistent with this conclusion, additions of the protic acids NH_4OTf or HOTf to **4Me** also yield methane and **4MeCN**. Me_3pyF^+ (which has been used by Sanford *et al.*[36]) reacts with **4Me** in wet CD_3CN to also give CH_4 and **4MeCN** but it is not reactive with **4Cl** or **4I**.



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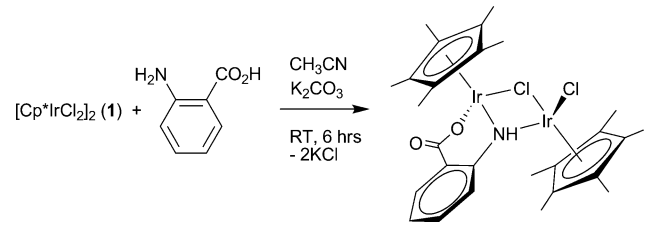

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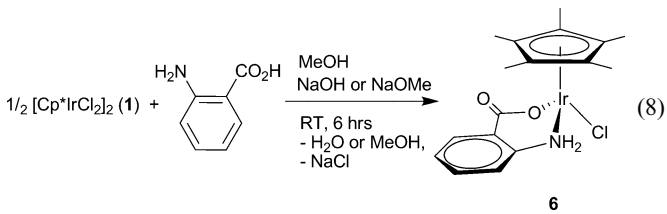


(8)

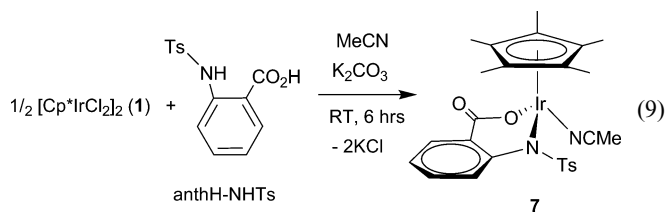
6

3. Ir^{III} complexes with N–O chelates

Three Cp^*Ir^{III} complexes with N–O chelating ligands have been synthesized to test reactivity with the oxidants in Chart 1: $Cp^*Ir(H_2NC_6H_4CO_2)Cl$ (**6**), $Cp^*Ir(TsNC_6H_4CO_2)(MeCN)$ (**7**), and Cp*Ir(TAIBA) (**8**). Grotjahn *et al.* has prepared related $Cp^*Ir^{III}(N–O)$ compounds from $[Cp^*IrCl_2]_2$ (**1**), an amino acid, and K_2CO_3 in N_2-sparged MeCN.[21d,e] These pseudo-five-coordinate Cp*Ir(N–O) complexes contain a doubly deprotonated (N,O) ligand.

With anthranilic acid, $H_2NC_6H_4CO_2H$, we find that Grotjahn's synthetic procedure yields a mixture of products. A few crystals of one of these products were isolated and structurally characterized to reveal an asymmetric dimer with a bridging amido ligand (eqn (7); ESI†). In an alternative approach, **1** was stirred with anthranilic acid and NaOH or NaOMe in methanol, yielding $Cp^*Ir(H_2NC_6H_4CO_2)Cl$ (**6**) as a yellow precipitate (eqn (8)) in 31% yield. ^1H NMR spectra of **6** in CD_2Cl_2 show resonances for one Cp* and one coordinated anthranilate ligand (the NH_2 signal was not observed). Despite the limited stability of **6** in solution, single crystals were grown by slow evaporation of a benzene solution, and the crystal structure shows six-coordinate "piano-stool" **6** (Fig. 3). The anthranilate ligand is mono-deprotonated, with carboxylate group and aniline donors to the iridium. Surprisingly, the anthranilate ring is nearly parallel to the plane of the Cp* ring. In other amino-acid $Cp^*Ir^{III}(N–O)Cl$ complexes, the plane of the ligand contains the metal centre and intersects the plane of the Cp* ring.[37]

To facilitate deprotonation of the amino group and inhibit amide bridging, complexes of tosylated amino acid ligands have been explored. Using *N*-tosyl anthranilic acid and Grotjahn's synthetic method mentioned above,[21] yellow $Cp^*Ir(TsNC_6H_4CO_2)(MeCN)$ (**7**) was isolated in 67% yield (eqn (9)). The yellow colour indicates a pseudo-six-coordinate species, since five-coordinate Cp*Ir(N–O) compounds are typically red.[21e] Complex **7** has been characterized by elemental analysis, ESI/MS ($M^+ - MeCN = 618.1\ m/z$), ^1H NMR, and X-ray crystallography (Fig. 3, right). The NMR resonances for **7** are broad in CD_2Cl_2 but sharp in CD_3CN, where the Cp* and aryl peaks are evident; surprisingly, the signal for the MeCN is not visible (either as free MeCN or coordinated to Ir). Anthranilate and its derivatives thus do not appear to form pseudo five-coordinate Cp*Ir(N-O) complexes as readily as alkylamine-carboxylate ligands.



(9)

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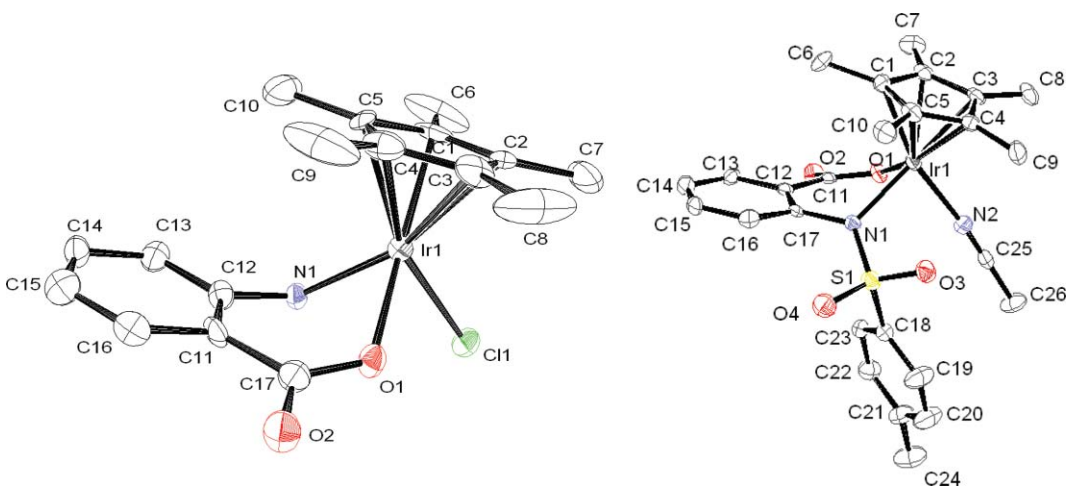
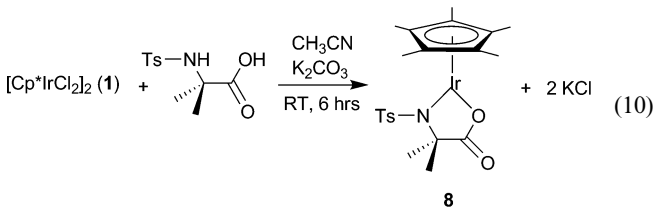


Fig. 3 ORTEPs of the iridium complexes in $Cp^*Ir(H_2NC_6H_4CO_2)Cl{\cdot}MeOH$ (**6·MeOH**) (left) and $Cp^*Ir(TsNC_6H_4CO_2)(MeCN){\cdot}H_2O$ (**7·H₂O**) (right) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity.

Reaction of **1** with N-*p*-toluenesulfonyl-*o*-aminoisobutyric acid ($TsNHCMe_2CO_2H$) and K_2CO_3 forms Cp*Ir(TAIBA) (**8**) (TAIBA = $N(Ts)CMe_2CO_2$) in good yield (eqn (10)). In this case, the red colour of **8** indicates a pseudo-five coordinate complex.[21e] ^1H NMR spectra of **8** in CD_3CN show a Cp* resonance (δ1.52 ppm), methyl and aryl resonances for the tosyl group, and a singlet at δ1.29 ppm integrating to six protons (*vs.* Cp* = 15) for the equivalent TAIBA methyl groups. The equivalence of the two methyl groups also indicates a five-coordinate C_s structure, since these would be inequivalent in a (non-fluxional) three-legged piano-stool complex. Addition of PPh_3 to a red acetonitrile solution of **8** causes a colour change to yellow and the ^1H NMR spectrum of the product shows inequivalent TAIBA methyl groups, both indicating phosphine binding to unsaturated **8** to make a six-coordinate chiral-at-metal adduct.



(10)

8

Addition of $[Me_3O]BF_4$ to Cp*Ir(TAIBA) (**8**) in dry CD_3CN at ambient temperatures initially gives a new Cp*Ir(N–O) product, "[Cp*Ir(TAIBA)]-Me^+," with an ESI mass spectral signal at M^+ = 598 *m*/*z* and a new ^1H NMR methyl resonance at δ3.97 ppm. This low-field chemical shift and the equivalence of the TAIBA methyl groups indicate that "Me^+" has not added to the iridium centre. Over 2 hours, the red solution pales in colour and the intermediate iridium complex decomposes to give the *N*-*p*-tosylamino-isobutyrate methyl ester (TAIBAH–Me). This ester product was identified by ^1H NMR and confirmed by independent synthesis (see Experimental section). Thus it seems likely that the intermediate species has Me^+ added to an oxygen of the TAIBA ligand, forming Cp*Ir(TAIBA-Me), and then slow protonation of the TAIBA nitrogen liberates the methyl ester.

The reactions of MeOTf and $[Me_3O]BF_4$ with **7** and **8** all appear to proceed analogously, with loss of the solution colour and formation of the free methyl ester (the formation of the anthranilate ester has not been confirmed by independent synthesis). Complex **6** reacted with the Me^+ donors in CD_2Cl_2 to form multiple products by ^1H NMR. Reactions between **7** or **8** with the "X^+ donors" C_6Cl_6O or $[Me_3pyF^+]$ in dry CD_3CN form a complex mixtures of products; with C_6Cl_6O the major species are $[Cp^*IrCl_2]_2$ (**1**) and the protonated ligand ($TsNH_2C_6H_4CO_2H$ or $TAIBAH_2$). $PhI(OAc)_2$ is unreactive with **7** or **8** in wet CD_3CN. In sum, the Cp*Ir(N–O)(X) compounds **6–8** are in many cases susceptible to electrophilic attack, which appears to occur preferentially at the amino-acid ligand rather than at the iridium centre.

Discussion

1. Oxidation of the Cp* ligand of $(Cp^*IrCl_2)_2$

The functionalization of the Cp* ligand in $[Cp^*IrCl_2]_2$ by hypervalent iodine reagents was unexpected because Cp* has been a widely valuable supporting ligand, even for somewhat oxidizing compounds such as Cp^*ReO_3,[38] Cp^*RuX_3 (X= Cl, Br, I)[39] and Cp^*IrMe_3X.[4,5] Most studies of Cp*-methyl group activation and functionalization have involved initial deprotonation to give a fulvene which is then susceptible to attack.[40] Nucleophile-induced hydride transfer to Ir has been suggested in the formation of $(\eta^5\text{-}C_5Me_4CH_2PPh_3)Ir(PPh_3)_2H$.[26] We are aware of just a few other examples of activation of a Cp* methyl group under oxidative conditions.[41]

The active oxidant in the $[Cp^*IrCl_2]_2$ (**1**) ligand oxidation appears to be a hydrolysis product of $PhI(OAc)_2$ since water is required. However, isolated $(PhIO)_n$ is much less reactive, perhaps because of its low solubility. The Cp* oxidation by $(PhIO)_n$ in wet MeCN or in ROH forms a $C_5Me_4CH_2OR$ ligand, where the OR group is derived from the carboxylic acid, alcohol, or water present in the solution. This suggests that an intermediate functionalized derivative is generated, which then reacts with ROH to give $[(C_5Me_4CH_2OR)IrCl_2]_2$ ($[Cp^{OR}IrCl_2]_2$: **2**, **3**). Although $[Cp^{OR}IrCl_2]_2$ are readily formed, the stronger oxidant $PhICl_2$ does not appear to convert **1** to $[Cp^{Cl}IrCl_2]_2$. An open coordination site at Ir does not appear to be required since **4Me** is readily functionalized. More detailed mechanistic studies, however, have been stymied by the complexity of the reactions.

Functionalized Cp* derivatives have been isolated starting from **1**, and observed starting from **4Me**. The apparent formation of $Cp^{Cl}Ir(ppy)Cl$ from **4Cl** and the "Cl^+" donor C_6Cl_6O is another example of this oxidative reactivity. There are also hints of similar chemistry in a number of the other reactions explored here, from observations of 6:6:2 patterns with downfield methylene signals in the ^1H NMR spectra of reaction mixtures. These observations indicate that Cp* is not a good supporting ligand for oxidations of Ir^{III} to Ir^V, and more generally for use in oxidation chemistry.

2. Addition of electrophiles to Ir(III) complexes

An initial motivation of this study was to generate Ir^V complexes by reacting Ir^{III} compounds with electrophiles, the sources of Me^+, Cl^+, F^+, or AcO^+ in Chart 1. While a range of reactivity has been observed, in no case is there good evidence for an Ir^V product or transient intermediate.

Electrophiles appear to react preferentially at the ligand rather than adding to the iridium centre. For instance, NMR spectra indicate that $[Me_3O]BF_4$ delivers Me^+ to a carboxylate oxygen of Cp*Ir(TAIBA) (**8**), forming the methyl ester. This is despite the tosylamide ligand being a significant π donor[21d,e] and **8** having an apparent open coordination site for Me^+ addition to the iridium. Addition to the ligand appears to be a major pathway for many of the reactions of the amino-acid complexes **6–8** with Me^+ sources.

The most favourable case for electrophile addition to the iridium centre should be the addition of Me^+ to Cp*Ir(ppy)Me (**4Me**). This could have formed "$Cp^*Ir^V(ppy)Me_2^+$", which would have been very similar to known $Cp^*Ir^VMe_3(L)^+$ species, containing a Cp* group, three hydrocarbyl ligands and one neutral donor.[5] However, the only reaction between MeOTf and **4Me** appears to involve trace acid protonating the methyl ligand to give methane. Given this result, the ready formation of MeCl from Cp*Ir(ppy)Cl (**4Cl**) plus MeI, MeOTf or $[Me_3O]BF_4$ most likely proceeds by Me^+ addition directly to the chloride ligand and not *via* reductive elimination from a cationic Ir^V–methyl chloride complex. In general, the iridium(III) complexes appear to have limited nucleophilicity.

The reactions of the **4X** complexes with electrophiles do not form functionalized 2-phenylpyridine products such as 2-(2-chlorophenyl)pyridine or 2-(*o*-tolyl)pyridine (by comparison of the ^{1}H NMR spectra of reaction solutions with literature spectral data[42]). This contrasts with the facile formation of functionalized ppy derivatives upon treatment of Pd^{II}(ppy) complexes with electrophiles.[43] Similarly, MeOAc was not observed from **4Me** and $PhI(OAc)_2$, in contrast to its formation in a related reaction of an Ir^{III}-methyl-triflate complex with $PhI(OAc)_2$, recently reported by Periana *et al*.[16] The Pd^{II}(ppy) reactions appear to proceed *via* reductive elimination from Pd^{IV}(ppy) complexes, and apparently the Ir^{V} analogues are not accessible in these reactions. Oxidation of a Cp* methyl group is more facile than oxidation of either Ir–Me or Ir–aryl linkages.

Conclusions

Treatment of $[Cp^*IrCl_2]_2$ with the hypervalent iodine reagents $PhI(O_2CR)_2$ or $(PhIO)_n + RCO_2H$ in wet MeCN result in oxidation of a Cp*-methyl group to form $[(\eta^5\text{-}C_5Me_4CH_2OC(O)R)IrCl_2]_2$ complexes. In methanol or ethanol solvent (R′OH), the Cp*-ether derivatives $[(\eta^5\text{-}C_5Me_4CH_2OR')IrCl_2]_2$ are formed. These results show that Cp* is not an inert supporting ligand in the chemistry of strongly oxidizing metal complexes. A number of new Cp^*Ir^{III}(L-L)X compounds, with electron-donating chelating ligands, have been reacted with the electrophiles MeOTf, Me_3O^+, C_6Cl_6O, and $PhI(OAc)_2$. None of the reactions form observable Ir^{V} complexes despite precedent for moderately stable Cp^*IrMe_3X compounds. Alkylation of the amide-carboxylate complex Cp*Ir(TAIBA) occurs at the carboxylate group and forms the free ester, rather than adding Me^+ to the open coordination site on the Ir^{III} centre. Cp*Ir(ppy)Cl (**4Cl**; ppy = cyclometallated 2-phenylpyridine) reacts with MeI or MeOTf to give MeCl. The iridium(III) complexes appear to have limited nucleophilicity.

Experimental

General considerations

$IrCl_3{\cdot}nH_2O$ was used as received from Pressure Chemical Company. $[Cp^*IrCl_2]_2$,[6] $PhI(O_2CPh)_2$,[44] $PhI(O_2CTol)_2$,[44] N-*p*-tosyl-*o*-aminobenzoic acid (anthrH-NHTs),[45] *N*-*p*-tosyl-2-aminoisobutyric acid ($TAIBAH_2$),[46] 2-aminoisobutyrate methyl ester,[47] and *N*-*p*-tosyl-2-aminoisobutyrate methyl ester[45] were prepared by following (or in some cases, adapting) literature procedures. All other reagents were used as received from Aldrich. Solvents were used as received from Fisher except for THF which was distilled and stored over Na/Ph_2CO and MeCN, which was purchased in a steel keg (Burdick and Jackson, low-water brand) and piped directly into a glovebox. Deuterated solvents (from Cambridge Isotope Laboratories) were either used as received, or dried and stored under nitrogen: CD_2Cl_2 over CaH_2, THF-d_8 over Na/Ph_2CO, and CD_3CN over P_2O_5 then CaH_2. Reactions were performed open to ambient atmosphere unless otherwise noted. ^{1}H NMR spectra were recorded on Bruker AV-500 or DRX-499 spectrometers at 298 K, with chemical shifts (in ppm) referenced to residual solvent peaks and coupling constants reported in Hz. ESI/MS were recorded on a Bruker Esquire LC-Ion Trap instrument. UV-Vis spectra were recorded on Agilent 8453 and spectral data are reported in the form of λ_{max} nm (extinction coefficient, M^{-1} cm^{-1}). Elemental analyses were performed by Atlantic Microlabs, Inc. (Norcross, GA).

$[Cp^{OAc}IrCl_2]_2$ (2). A solution of $[Cp^*IrCl_2]_2$ (94 mg, 0.118 mmol) and $PhI(OAc)_2$ (281.5 mg, 1.27 mmol) in wet acetonitrile (5 mL) was stirred overnight at 50 °C. Solvent and PhI were removed by vacuum from the light brown solution and the precipitate was washed with 3 mL H_2O and 5 mL Et_2O to give 55.1 mg of light brown **2** of moderate purity (51%). Attempts at bulk recrystallization of **2** and obtaining analytically pure material have not been successful. In one case, crystals were obtained by slow evaporation of a CD_3CN solution. ^{1}H NMR (CD_3CN, 298 K): 1.67 (s, 6H); 1.73 (s, 6H); 2.01 (s, 3H), 4.67 (s, 2H). ^{13}C NMR (CD_3CN, 298 K): 94.37, 88.04, 58.27, 20.79, 9.27, 9.01 (one signal was too weak to see). ESI/MS: 420 ($Cp^{OAc}IrCl^+$). UV/vis: 230 (15937), 280 (4686).

$[Cp^{OMe}IrCl_2]_2$ (3). A solution of $[Cp^*IrCl_2]_2$ (27 mg, 34 mmol) and PhIO (28.5 mg, 130 mmol) in MeOH (5 mL) was stirred overnight at 50 °C. Four more equivalents of PhIO were added and the solution was stirred at 50 °C for an additional 10 min. The solvent and PhI were removed *in vacuo* and the precipitate was washed with 2 mL H_2O and 3 mL Et_2O to give 12 mg of light brown **7** of moderate purity (42%). ^{1}H NMR (CD_2Cl_2, 298 K): 1.57 (s, 6H); 1.61 (s, 6H); 3.37 (s, 3H), 4.06 (s, 2H). ESI/MS: 393 ($Cp^{OMe}IrCl^+$).

$[Cp^{O2CPh}IrCl_2]_2$ and $[Cp^{O2CTol}IrCl_2]_2$. A J. Young sealable NMR tube was charged with **1** (4 mg, 5 μmol), $PhI(O_2CPh)_2$ (7 mg, 16 μmol) [or $PhI(O_2CTol)_2$ (7 mg, 15 mmol)] and 0.75 mL of wet (non-dried, benchtop-stored) MeCN and heated for 7 d at 50 °C. ^{1}H NMR for $[Cp^{O2CPh}IrCl_2]_2$ (CD_3CN, 298 K): 1.66 (s, 6H); 1.80 (s, 6H); 4.94 (s, 2H); 6.95 (ddd, 1H, $^3J_{HH}$ = 8.0 Hz); 7.43 (d, 2H, $^3J_{HH}$ = 8.0 Hz); 8.19 (d, 2H, $^3J_{HH}$ = 7.5 Hz). ^{1}H NMR for $[Cp^{O2CTol}IrCl_2]_2$ (CD_3CN, 298 K): 1.66 (s, 6H); 1.79 (s, 6H); 4.92 (s, 2H); 6.79 (d, 2H, $^3J_{HH}$ = 7.5 Hz); 7.25 (d, 2H, $^3J_{HH}$ = 7.5 Hz). ESI/MS: ($Cp^{O2CPh}IrCl^+$), 483; ($Cp^{O2CTol}IrCl^+$), 497.

Cp*Ir(ppy)Cl (4Cl). A solution of $[Cp^*IrCl_2]_2$ (236 mg, 0.456 mmol) and excess 2-phenylpyridine (0.3 mL, 2.40 mmol) in MeOH (10 mL) was stirred overnight. The solution was concentrated to ~2 mL by rotary evaporation and filtered. The 'creamsicle orange' precipitate was washed with 10 mL H_2O and 2 × 10 mL benzene, and remaining ppyH was sublimed off of crude **4Cl** to yield 269 mg (87%). ^{1}H NMR (CD_2Cl_2): 1.66 (s, 15H, Cp*); 7.04 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 7.13 (t, 1H, $^3J_{HH}$ = 7.0 Hz), 7.18 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 7.69–7.72 (m, 2H, $^3J_{HH}$ = 8.0 Hz), 7.78 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 7.84 (d, 1H, $^3J_{HH}$ = 8.5 Hz), 8.68 (d, 1H, $^3J_{HH}$ = 5.5 Hz). ESI/MS: 517 (M^+), 482 (M-Cl)$^+$. UV/vis: 240 (12500), 252 (12000), 300 (6300), 360 (2600). Anal. Calcd (found) for $C_{21}H_{23}NClIr$: C, 48.78 (48.81); H, 4.48 (4.53); N, 2.71 (2.70).

Cp*Ir(ppy)I (4I). MeI (1.0 mL, 18 mmol) was added to a solution of Cp*Ir(ppy)Cl (**4Cl**) (25.6 mg, 0.050 mmol) in 3 mL MeOH. The solution was stirred overnight and a brick-red solid precipitated. The solvent was removed using a rotary evaporator, leaving 27.7 mg of product (92%). ^{1}H NMR (CD_2Cl_2): 1.75 (s, 15H, Cp*); 6.98 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 7.05 (t, 1H, $^3J_{HH}$ = 7.0 Hz), 7.16 (t, 1H, $^3J_{HH}$ = 7.0 Hz), 7.66 (t, 1H, $^3J_{HH}$ = 7.0 Hz), 7.67–7.71 (m, 2H, $^3J_{HH}$ = 7.5 Hz), 7.82 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 8.69 (d, 1H,

$^3J_{HH}$ = 5.5 Hz). ESI/MS: 609 (M^+), 482 ($M - I)^+$. UV/vis: 245 (9900), 295 (5100), 360 (2600).

Cp*Ir(ppy)Me (4Me). MeLi (1.6 M in Et_2O, 240 μL, 3.8 × 10^{-4} mmol, 4 equiv) was added to a solution of Cp*Ir(ppy)Cl (**4Cl**) (50.5 mg, 0.097 mmol) in 20 mL THF at −78 °C. The yellow solution was allowed to come to room temperature, at which time the solution colour changed to deep red. The solution was filtered through a plug of weakly acidic Al_2O_3. The solvent and other volatiles were removed from the filtrate by rotary evaporation and then under high vacuum, yielding 30.5 mg of dark orange-red **4Me** (63%).^{1}H NMR (CD_2Cl_2): −0.38 (s, 3H, IrMe); 1.73 (s, 15H, Cp*); 6.87 (t, 1H, $^3J_{HH}$ = 7.0 Hz), 6.96 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 7.04 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 7.52–7.57 (m, 2H, $^3J_{HH}$ = 7.0 Hz), 7.72 (d, 1H, $^3J_{HH}$ = 7.5 Hz), 7.82 (d, 1H, $^3J_{HH}$ = 8.5 Hz), 8.49 (d, 1H, $^3J_{HH}$ = 5.5 Hz). ESI/MS: 496 (M^+). Anal. Calcd (found) for **(4Me)·2THF**, $C_{30}H_{42}NO_2Ir$: C, 56.22 (56.76); H, 6.61 (6.37); N, 2.19 (2.38) (THF was visible in NMR spectra of this material).

[Cp*Ir(ppy)NCMe]PF$_6$ (4MeCN). $AgPF_6$ (22.0 mg, 1.6 mmol) was added to an orange solution of **4Cl** (14.1 mg, 0.27 mmol) in 5 mL MeCN. After stirring for thirty seconds, the resulting light yellow solution was filtered through a glass wool/celite pipette filter. The solvent was removed from the filtrate by rotovap and the residue was taken up in minimal CH_2Cl_2 and filtered again, to ensure that no salts remained. The solvent was removed from the filtrate and the yellow residue was stirred with 1 mL Et_2O to form a fine yellow powder, which was isolated by filtration, yielding 14.0 mg 76% **4MeCN**. ^{1}H NMR (CD_2Cl_2): 1.70 (s, 15H, Cp*); 2.30 (s, 3H, CH_3CN), 7.20 (t, 1H, $^3J_{HH}$ = 7.0 Hz), 7.27–7.33 (m, 2H, $^3J_{HH}$ = 5.5 Hz, 6.5 Hz), 7.74–7.78 (m, 2H, $^3J_{HH}$ = 8.5 Hz, 10.0 Hz), 7.90–7.97 (m, 2H, $^3J_{HH}$ = 7.5 Hz), 8.49 (d, 1H, $^3J_{HH}$ = 5.0 Hz).

Cp^{OAc}Ir(ppy)Me (5). $PhI(OAc)_2$ (2.8 mg, 8.7 μmol) was added to a 0.6 mL CD_3CN solution of Cp*Ir(ppy)Me (3.7 mg, 7.5 μmol), which was heated in a J. Young NMR tube at 45 °C for one hour.^{1}H NMR (CD_3CN, 298 K): −0.29 (s, 3H, IrMe); 1.75 (s, 3H); 1.77 (s, 3H); 1.79 (s, 3H); 1.81 (s, 3H); 1.92 (s, 3H); 4.65 (dd, 2H, $^3J_{HH}$ = 10.5, 12.5 Hz); 6.97 (t, 1H, $^3J_{HH}$ = 7.0 Hz), 6.98 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 7.02 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 7.52–7.57 (m, 2H, $^3J_{HH}$ = 7.0 Hz), 7.65 (d, 1H, $^3J_{HH}$ = 7.5 Hz), 7.91 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 8.53 (d, 1H, $^3J_{HH}$ = 6.0 Hz). ESI/MS: 554 (M − H)$^+$, 540 (M − $CH_3COO^-)^+$.

Cp*Ir($H_2NC_6H_4CO_2$)Cl (6). $[Cp^*IrCl_2]_2$ (28.6 mg, 36 μmol), anthranilic acid (9.8 mg, 71 μmol, 2 equiv) and NaOMe (3.8 mg, 70 μmol, 2 equiv) were mixed in 2 mL of 3:1 CH_2Cl_2/MeOH. Alternatively, NaOMe was generated *in situ* by addition of NaOH to the methanol solution. The solution was stirred for five minutes and white solids precipitated from the mixture. The solvent was removed by rotary evaporation and CH_2Cl_2 was added to the residue. Filtration of the yellow solution removed the white solids, and then addition of pentane gave yellow **3** (11.5 mg, 31%).^{1}H NMR (CD_3OD, 298 K): 1.34 (s, 15H); 7.21 (m, C_6H_4, 2H); 7.43 (C_6H_4, 1H, $^3J_{HH}$ = 7.5 Hz), 7.88 (d, C_6H_4, 1H, $^3J_{HH}$ = 7.5 Hz). ESI/MS: 499 (M^+).

Cp*Ir($TsNC_6H_4CO_2$)(MeCN) (7). To a 20 mL acetonitrile solution of $[Cp^*IrCl_2]_2$ (92.3 mg, 1.16 mmol) was added 2 equiv $TsNHC_6H_4CO_2H$ (60.0 mg, 2.3 mmol) and 4 equiv K_2CO_3 (61.6 mg, 4.5 mmol). The solution was stirred for 6 h, resulting in a yellow solution with white solids. The solvent was removed by rotary evaporation, the residue was taken up in CH_2Cl_2. Filtration to remove the white solids and addition of pentanes precipitated yellow **4** (102.5 mg, 67%).^{1}H NMR (CD_3CN, 298 K): 1.40 (s, 15H); 2.29 (s, 3H); 6.86 (d, 1H, $^3J_{HH}$ = 8.5 Hz); 7.13–7.17 (m, 3H); 7.48 (d, 2H, $^3J_{HH}$ = 8.5 Hz); 7.63 (d, 1H, $^3J_{HH}$ = 7.0 Hz); 7.88 (d, 1H, $^3J_{HH}$ = 8.5 Hz); the CH_3CN signal was not observed. Anal. Calcd (found) for **4·2H$_2$O**, $C_{26}H_{34}IrN_2O_6S$: C, 44.94 (44.20); H, 4.93 (4.43); N, 4.03 (3.97).

Cp*Ir(TAIBA) (8). To a 5 mL acetonitrile solution of $[Cp^*IrCl_2]_2$ (36.7 mg, 46.1 μmol) was added 2 equiv $TAIBAH_2$ (23.9 mg, 92.9 μmol) and 4 equiv K_2CO_3 (25.7 mg, 186.2 μmol). The solution was stirred for 6 hours. White solid (KCl) was filtered from the dark red solution and then solvent was removed from the filtrate by rotary evaporation. The red precipitate was further dried *in vacuo* to give 45 mg (84%) yield. ^{1}H NMR (CD_3CN, 298 K): 1.29 (s, 6H); 1.63 (s, 15H); 2.39 (s, 3H); 7.31 (d, 2H, $^3J_{HH}$ = 8.0 Hz); 7.74 (d, 2H, $^3J_{HH}$ = 8.0 Hz). ESI/MS: 584 (M + H)$^+$. UV/vis: 288 (6700), 395 (2200), 520 (500). Anal. Calcd (found) for $C_{21}H_{28}IrNO_4S$: C, 43.28 (42.92); H, 4.84 (4.90); N, 2.40 (2.38).

***N*-*p*-tosylaminoisobutyrate methyl ester.** A solution of aminoisobutyrate methyl ester[47] (106 mg, 390 μmol) and Et_3N (0.165 mL, 1.2 mmol, 3 equiv) in 15 mL of 2:1 H_2O/THF was cooled to 0 °C in an ice bath and *p*-toluenesulfonyl chloride added (74.4 mg, 390 μmol, 1 equiv). The solution was warmed to 20 °C and stirred for 3 hrs. The solution was reduced in volume to 10 mL by rotovap, and white solids precipitated from the remaining solution. The solid was dissolved in CH_2Cl_2, treated with $MgSO_4$ which was then filtered off, and solvent was removed to yield 21 mg *N*-*p*-tosylaminoisobutyrate methyl ester (13%). ^{1}H NMR ($CDCl_3$, 298 K): 1.410 (s, 6H); 2.394 (s, 3H, Ph-CH_3); 3.63 (s, 3H, O-CH_3); 7.26 (d, 2H, $^3J_{HH}$ = 8.5 Hz); 7.73 (d, 2H, $^3J_{HH}$ = 8.5 Hz).

Crystal structure determinations for 2, 3, 4Cl, 4I, 6, and 7†. Crystals of yellow **2·PhI** and **3·PhI** were grown by slow evaporation of MeCN (**2**) and MeOH (**3**) reaction solutions. Crystals of orange **4Cl**, yellow **4I**, and yellow **6** were grown by slow evaporation of benzene (**4Cl**), CD_3OD (**4I**), or CH_2Cl_2 (**6**) solutions at room temperature. Crystals of yellow **7** were grown by vapour diffusion of Et_2O into an MeCN solution. A yellow block of **6** was cut to 0.30 × 0.30 × 0.10 mm orange and a block of **4Cl** was cut down to 0.26 × 0.25 × 0.24 mm. All crystals but **7** were mounted on glass fibres with oil; **7** was mounted on a Cryoloop. The crystal-to-detector distance was 30 mm (60 mm for **7**) and exposure time was 30 sec (**4Cl**), 20 sec (**4I**, **6**), 45 sec (**3**) or 60 sec (**7**, **2**) per degree. The scan width was 2.0° (**2**, **3**, **4Cl**), 1.9° (**6**), 1.5° (**4I**), or 0.3° sec (**7**). The final cell parameters and specific collection parameters are given in Table 1. **4Cl** and **4I** crystallize in space group $P2_1/c$ (No. 14), **6** crystallizes in $P2_12_12_1$ (No. 19) and **7**, **2** and **3** crystallize in *P*-1 (No. 2). In each case but **7**, the data were integrated and scaled using hkl-SCALEPACK; **7** was integrated by Bruker SAINT and was scaled by SADABS software. hkl-SCALEPACK applies a multiplicative correction factor (S) to the observed intensities (I) and has the following form: $S = \exp(2B(\sin q/\lambda)^2)/\text{scale}$. S is calculated from the scale and the B factor is determined for each frame and is then applied to I to give the corrected intensity (I_{corr}). Solution by direct methods (SIR92) produced a complete heavy atom phasing model

consistent with the proposed structure. All hydrogen atoms were located using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Crystals of **4Cl** had a tendency to twin, and the crystal analyzed was of somewhat poor quality. Complex **6** co-crystallized with a molecule of MeOH, which hydrogen-bonds to O1. The proton on N1 (complex **6**) hydrogen-bonds to a different Me*O*H. The Cp* moiety exhibits considerable oscillatory motion, causing large thermal ellipsoids of Cp*-*Me*.

Note added in proof

After this paper was submitted, the crystal structure of **4Cl** was reported by Davies *et al.*,[48] who used the same synthetic procedure as Djukic *et al.*[31]

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