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Synthesis of Cp* Iridium and Rhodium Complexes Containing Bidentate sp^2-N-Donor Ligands and Counter-Anions $[Cp^*MCl_3]^-$

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Keywords: Iridium(III) / Rhodium(III) / N-donor ligands / Cyclopentadienyl ligands

Complexes of the type $[Cp^*MCl(N–N)][X]$ (M = Rh and Ir) have been synthesised, where N–N is a series of bidentate ligands with sp^2 N-donors: bis(pyrazol-1-yl)methane (bpm), bis(1-methylimidazol-2-yl)methane (bim), bis(3,5-dimethylpyrazol-1-yl)methane (dmbpm), bis(1-methylimidazol-2-yl) ketone (bik), bis(2,4,6-trimethylphenylimino)acenapthene (mesBIAN), 2,4,6-trimethylphenylimino-(1-methyl-2-imidazolyl)methane (mesim–mim), and X = Cl^-, BF_4^- and the unusual anion $[Cp^*MCl_3]^-$. All of these complexes were synthesised by treatment of $[Cp^*MCl_2]_2$ with 2 equivalents of ligand and were isolated as air stable solids. The solid-state structures of $[Cp^*MCl(bpm)][Cp^*MCl_3]$ (M = Rh and Ir) and $[Cp^*IrCl(bim)][Cp^*IrCl_3]$ have been determined by single-crystal X-ray diffraction analysis. All of the structures of the bimetallic species displayed a "piano stool" configuration about the both the anionic and cationic metal centre. The solid-state structures of the monometallic iridium species $[Cp^*IrCl(N–N)][BF_4]$, where N–N = bim, mesBIAN, and mesim-mim, were also determined using single-crystal X-ray diffraction analysis.
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Introduction

Complexes containing rhodium(I) and iridium(I) metal centres have found wide application in homogeneous catalysis. Reactions catalysed by these complexes include the hydrosilylation of imines,[1,2] the hydroamination and hydroalkoxylation of alkynes,[3–9] the hydroamination and hydroaminomethylation of olefins,[10,11] and the Pauson–Khand reaction.[12,13] Increasingly, metal complexes containing Ir^{III} and Rh^{III} metal centres are being investigated as catalysts for a variety of transformations. Unlike Ir^I and Rh^I catalysts, Ir^{III} and Rh^{III} complexes can not promote reactions which require the initial oxidative addition of a substrate. However, Ir^{III} and Rh^{III} metal centres are reactive and have the potential to catalyse a range of other transformations not reliant on oxidative addition. Work by Bergmann et al. with the complexes $Cp^*(PMe_3)Ir(CH_3)(OTf)$, and $Tp^{Me2}(PMe_3)Ir(CH_3)(OTf)$ illustrated the ability of Ir^{III} complexes to effect C–H activation.[14,15] Recent work by Crabtree et al. has utilised an Ir^{III} hydride complex to catalyse the intramolecular hydroamination and hydroalkoxylation of alkynes.[16] $[Cp^*IrCl_2]_2$ is effective as a catalyst for the hydroborylation of styryl sulfonamides,[17] the *N*-alkylation of amines with alcohols[18] and also the transfer hydrogenation of ketones[19] and quinolines.[20] Rh^{III} complexes are known to be effective in catalysing carbon–carbon bond formation,[21] and $[Cp^*RhCl_2]_2$ has been shown to effect transfer dehydrochlorination of aryl chlorides.[22]

1,2,3,4,5-Pentamethylcyclopentadienyl (Cp*) is ubiquitous as a ligand in organometallic complexes. Many complexes incorporating this ligand are important as active catalysts, largely due to the electron-rich nature of the Cp* group and also the ability of Cp* to completely block one face of the complex, imparting steric bulk and structural rigidity. Ir^{III} and Rh^{III} complexes incorporating both the Cp* ligand and bidentate sp^2-nitrogen donor ligands have been synthesised previously.[23–31] In particular, the complex $[Cp^*Ir(bipy)(H_2O)]SO_4$ (bipy = 2,2′-bipyridine) was found to be active as a catalyst for the hydration of phenylacetylene in water,[32] and the complex $[Cp^*Rh(i\text{Pr-pymox})]^{2+}$ (pymox = pyridyloxazoline) was found to promote the enantioselective Diels–Alder reaction of methacrolein with cyclopentadiene.[27]

In the course of the study of both Ir^{III} and Rh^{III} complexes as potential catalysts we have synthesised a series of 1,2,3,4,5-pentamethylcyclopentadienyl complexes incorporating bidentate N donor ligands. Here, we report the synthesis and characterisation of Rh/Ir^{III} complexes of the type $[Cp^*MCl(N–N)][X]$ (M = Rh and Ir), where N–N is a series of bidentate ligands with sp^2 N-donors: bis(pyrazol-1-yl)-methane (bpm), bis(1-methylimidazol-2-yl)methane (bim), bis(3,5-dimethylpyrazol-1-yl)methane (dmbpm), bis(1-methylimidazol-2-yl) ketone (bik), bis(2,4,6-trimethylphenylimino)acenapthene (mesBIAN), 2,4,6-trimethylphenylimino-(1-methyl-2-imidazolyl)methane (mesim–mim), and X = Cl^-, BF_4^- and the unusual anion $[Cp^*MCl_3]^-$ (Fig-

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ure 1). The solid-state structures of the complexes **1c**, **2b**, **2c**, **3c**, **7b** and **8b** have been determined by single-crystal X-ray diffraction analysis. The complexes **1c**, **2c** incorporate the novel anion $[Cp^*IrCl_3]^-$, and complex **3c** incorporates the rare anion $[Cp^*RhCl_3]^-$.

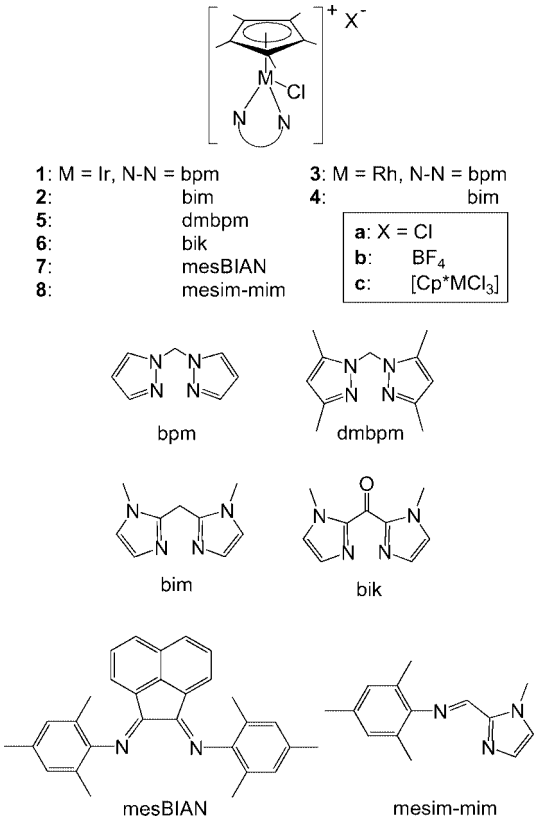
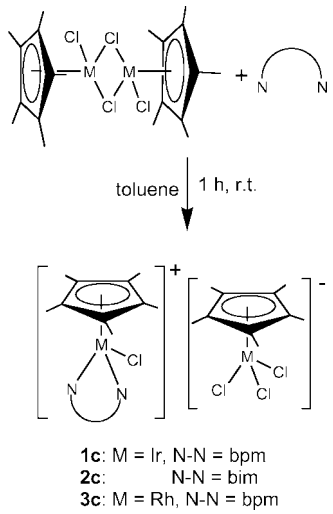


Figure 1. The general structure of complexes **1a**–**8b** and **1a**–**3c** where N–N = bpm = bis(pyrazol-1-yl)methane; bim = bis(1-methylimidazol-2-yl)methane; dmbpm = bis(3,5-dimethylpyrazol-1-yl)-methane; bik = bis(1-methylimidazol-2-yl) ketone; mesBIAN = bis(2,4,6-trimethylphenylimino)acenapthene; mesim–mim = (2,4,6-trimethylphenyl)imino-(1-methylimidazol-2-yl)methane.

Results and Discussion

Synthesis of Complexes [Cp*MCl(N–N)][Cp*MCl$_3$] 1c, 2c, and 3c

Toluene suspensions of the metal precursors $[Cp^*IrCl_2]_2$ and $[Cp^*RhCl_2]_2$ were treated with two molar equivalents of the bidentate nitrogen donor ligands bpm and bim (Scheme 1) to generate the ion pairs $[Cp^*IrCl(bpm)][Cp^*IrCl_3]$ (**1c**), $[Cp^*IrCl(bim)][Cp^*IrCl_3]$ (**2c**), and $[Cp^*RhCl(bpm)][Cp^*RhCl_3]$ (**3c**) (Scheme 1). Using the same approach, **2c** was obtained in low yield as the minor product, with $[Cp^*IrCl(bim)]Cl$ (**2a**) being formed as the major product. Complexes **1c**, **2c**, and **3c** were thermally and air stable over extended periods. The sterically hindered ligand mesBIAN failed to bind to $[IrCp^*Cl_2]_2$.



Scheme 1.

The ^1H NMR spectra of complexes **1c**–**3c** showed the presence of two molar equivalents of bound Cp* per mol of ligand. ^1H NOESY NMR spectrum confirmed that for each of the complexes **1c**–**3c** the sharper singlet occurring slightly downfield at δ = 1.66, 1.61 and 1.69 ppm, respectively, was due to the CH_3 protons of the Cp* moiety bound to the cationic fragment (Table 1). The ^1H NMR spectra also show that the two bridging methylene backbone protons of the N–N ligands, H_a and H_b, are in magnetically distinct environments for each of the complexes **1c**, **2c** and **3c**. For all of the complexes, the resonances due to H_a and H_b occur as doublets. The assignment of these resonances was established using ^1H NOESY NMR, and the resonances due to H_a were consistently shifted significantly downfield relative to the resonances due to H_b (Table 1).

Table 1. Selected chemical shifts for complexes **1c**–**3c**.

Compound	δ (ppm)			
	H_a	H_b	Cp* in cation	Cp* in anion
$[Cp^*Ir(bpm)Cl][Cp^*IrCl_3]$ (**1c**)	8.35	5.67	1.66 (s)	1.58 (br. s)
$[Cp^*Ir(bim)Cl][Cp^*IrCl_3]$ (**2c**)	5.01	4.73	1.61 (s)	1.54 (br. s)
$[Cp^*Rh(bpm)Cl][Cp^*RhCl_3]$ (**3c**)	8.07	5.84	1.69 (s)	1.61 (br. s)

The complexes **1c** and **2c** contain the novel anion $[Cp^*IrCl_3]^-$. Complex **3c** contains the analogous anion $[Cp^*RhCl_3]^-$ which has been reported recently by Severin et al.[33] as the anion in the ruthenium complex $[Cp^*Ru(C_6H_6)][Cp^*RhCl_3]$.[33] The $[Cp^*RhCl_3]^-$ anion has also been observed in equilibrium in solution with the hydrazine-bridged dimer $[(Cp^*RhCl_2)_2(\mu\text{-}NH_2NHMe)]$ by Maitlis et al.[34]

The relative binding strengths of the N-donor ligands correlates to the nature of the products formed on reaction with the dimeric Ir/Rh starting materials. The strongly coordinating bim ligand brings about the complete dissociation of the metal precursor dimer ($[Cp^*IrCl_2]_2$) and primarily formation of the product monomer, [Cp*IrCl-

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(bim)]$^+$Cl, **2a**. The more weakly coordinating bpm ligand leads to the formation of bimetallic ion pairs, [Cp*MCl(bpm)][Cp*MCl_3] **1c** and **3c**. The mesBIAN ligand is unable to bind to Ir with sufficient strength to split the iridium precursor dimer, due to both the weaker binding ability of the imine N-donors and the large steric bulk imparted by the mesityl groups. The complexes **1c**–**3c**, which contain bimetallic pairs, are of interest from the perspective of coordination chemistry. For the purposes of catalysis, the fact that molecules **1c**–**3c** contain two metal centres makes them inefficient in terms of the proportion of metal involved, as only the cationic fragment of the metal complex is catalytically active. To increase the efficiency of the synthesis with respect to the quantity of metal used, the complexes incorporating the alternate counterion BF_4^- were synthesised.

Solid-State Structures of 1c, 2c and 3c

The solid-state structures of **1c**, **2c** and **3c** with thermal ellipsoids at the 50% probability level are shown in Figure 2. Selected bond lengths and angles for **1c**, **2c** and **3c** are presented in Table 2 and crystal structure and refinement data are given in Table 5.

The cationic fragments of **1c**, **2c** and **3c** have very similar structures. The metal centres of **1c**, **2c** and **3c** exist in the piano-stool conformation with the six-membered metallocycle formed by coordination of the bidentate ligands to the metal centres in each case existing in the boat configuration. The N–M–N angles for **1c**, **2c** and **3c** are between 83.8(2)° and 85.25(9)°, which is significantly larger than the values for related [IrCp*Cl(N–N)][X] complexes reported in the literature, where the N–N ligand defines a five-membered metallocycle (values of between 75.6 and 77.5° have been reported previously).[32,23,27,31] The N–M–N bite angles are, however, similar to those reported for other Ir complexes containing the bim and bpm ligand (values of 85.9° and 86.8°).[35,36] N–M–Cl angles of between 85.06(15)° and 88.56(7)° for **1c**, **2c** and **3c** are consistent with literature values of between 83.1° and 91.9° for similar complexes.[32,23,27] The M–N distances in each of the complexes are also comparable to those previously reported in the literature with M–N(pyrazole) distances of 2.107(4) and 2.114(2) Å for **1c** and **3c** respectively and a slightly shorter Ir–N(imidazole) distance of 2.089(5) Å for **2c**. Literature values range from 2.028 and 2.230 Å depending on the nature of the N-donor ligand.[15,23,24,26]

In all of the solid-state structures for **1c**–**3c**, the anions [Cp*MCl_3]$^-$ have the same piano-stool geometry described by the three chloride atoms and the η^5-Cp* ligand around the iridium(III) or rhodium(III) metal centres. The piano-stool geometry is frequently reported for Cp* iridium(III) or rhodium(III) complexes.[24,26,37] The equivalent conformation was also previously observed for the anion of the complex [Cp*Ru(C_6H_6)][Cp*$RhCl_3$].[33] The M–Cl bond lengths reported for this complex were between 2.409 and 2.434 Å, which are comparable to the M–Cl bond lengths of between 2.4100(16) and 2.4335(7) Å for the anions of complexes **1c**–**3c**.

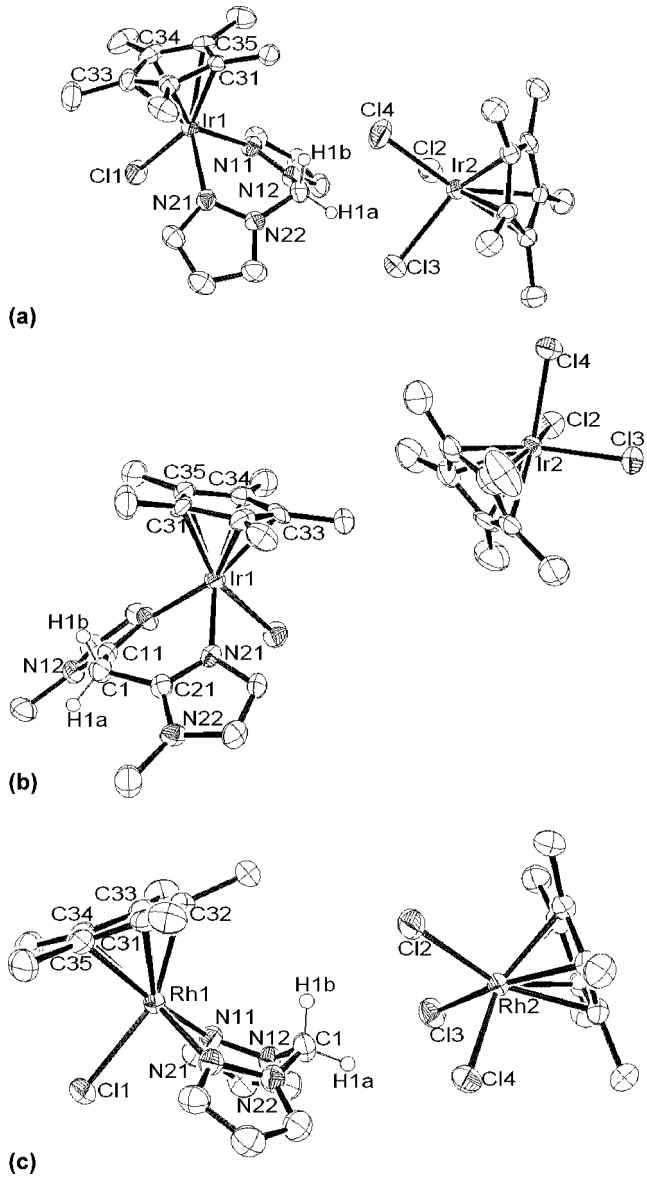

Figure 2. ORTEP depiction of (a) [Cp*IrCl(bpm)][Cp*$IrCl_3$] (**1c**); (b) [Cp*IrCl(bim)][Cp*$IrCl_3$] (**2c**); and (c) [Cp*RhCl(bpm)]-[Cp*$RhCl_3$] (**3c**) at 50% thermal ellipsoids for the non-hydrogen atoms.

Synthesis of Complexes [Cp*MCl(N–N)][BF_4] 1b, 2b, 3b, 4b, 5b, 6b, 7b and 8b

Treatment of toluene suspensions of [MCp^*Cl_2]$_2$ with two molar equivalents of a bidentate nitrogen donor ligand (N–N) and two molar equivalents of $NaBF_4$ in MeOH at room temperature resulted in the formation of the complexes [Cp*IrCl(N–N)]BF_4, [N–N = bpm (**1b**), bim (**2b**) and dmbpm (**5b**), bik (**6b**), mesBIAN (**7b**) and mesim-mim (**8b**)] and [Cp*RhCl(N–N)]BF_4, [N–N = bpm (**3b**), bim (**4b**)] in good to moderate yields (Scheme 2). Selected ^{1}H NMR

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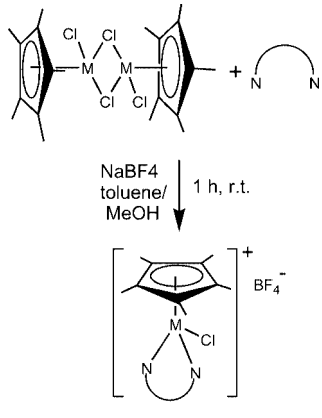
Table 2. Selected bond lengths [Å] and bond angles [°][a] for the inner coordination sphere of **1c**, **2c** and **3c**.

1c		**2c**		**3c**	
Atomic distance [Å]					
Ir(1)–N(11)	2.107(4)	Ir(1)–N(11)	2.089(5)	Rh(1)–N(11)	2.114(2)
Ir(1)–N(21)	2.105(4)	Ir(1)–N(21)	2.090(5)	Rh(1)–N(21)	2.113(2)
Ir(1)–Cl(1)	2.4076(16)	Ir(1)–Cl(1)	2.4012(18)	Rh(1)–Cl(1)	2.4174(8)
Ir(1)–C(31)	2.170(5)	Ir(1)–C(31)	2.143(6)	Rh(1)–C(31)	2.170(3)
Ir(1)–C(32)	2.176(4)	Ir(1)–C(32)	2.158(6)	Rh(1)–C(32)	2.161(3)
Ir(1)–C(33)	2.144(5)	Ir(1)–C(33)	2.149(6)	Rh(1)–C(33)	2.170(3)
Ir(1)–C(34)	2.152(5)	Ir(1)–C(34)	2.156(6)	Rh(1)–C(34)	2.147(3)
Ir(1)–C(35)	2.169(5)	Ir(1)–C(35)	2.160(6)	Rh(1)–C(35)	2.142(3)
Ir(2)–Cl(2)	2.4130(13)	Ir(2)–Cl(2)	2.4163(19)	Rh(2)–Cl(2)	2.4090(8)
Ir(2)–Cl(3)	2.4322(13)	Ir(2)–Cl(3)	2.4100(16)	Rh(2)–Cl(3)	2.4126(7)
Ir(2)–Cl(4)	2.4111(17)	Ir(2)–Cl(4)	2.4158(18)	Rh(2)–Cl(4)	2.4335(7)
Bond angle [°]					
N(21)–Ir(1)–N(11)	83.95(17)	N(11)–Ir(1)–N(21)	83.8(2)	N(21)–Rh(1)–N(11)	85.25(9)
N(11)–Ir(1)–Cl(1)	87.09(12)	N(11)–Ir(1)–Cl(1)	85.06(15)	N(11)–Rh(1)–Cl(1)	88.56(7)
N(21)–Ir(1)–Cl(1)	86.77(12)	N(21)–Ir(1)–Cl(1)	85.67(15)	N(21)–Rh(1)–Cl(1)	88.41(7)
N(22)–C(1)–N(12)	109.5(4)	C(11)–C(1)–C(21)	109.6(6)	N(22)–C(1)–N(12)	109.8(2)
N(11)–N(12)–C(1)	119.8(4)	N(11)–C(11)–C(1)	125.0(5)	N(11)–N(12)–C(1)	120.1(2)
N(21)–N(22)–C(1)	120.5(4)	N(12)–C(11)–C(1)	125.6(6)	N(21)–N(22)–C(1)	120.5(2)
N(12)–N(11)–Ir(1)	123.7(3)	C(11)–N(11)–Ir(1)	124.9(4)	N(12)–N(11)–Rh(1)	122.88(17)
N(22)–N(21)–Ir(1)	123.3(3)	C(21)–N(21)–Ir(1)	125.3(4)	N(22)–N(21)–Rh(1)	122.87(17)

[a] Estimated standard deviation in the least significant figure are given in parentheses.

chemical shifts for these complexes are presented in Table 3. As already observed for the complexes **1c**–**3c**, the two methylene protons (H_a and H_b) of the bridging carbon atoms of the bidentate ligands of the complexes **1b**–**5b** exist in very different magnetic environments, with the ^1H NMR chemical shifts for H_a protons being significantly deshielded. The ^1H chemical shift of the resonance due to the -CH_3 groups of the Cp* ligand of complex **7b** (at δ = 1.27 ppm) is shifted significantly relative to that of the corresponding resonances of the other iridium complexes in this series (complexes **1b**–**5b**), which lie between 1.53 and 1.59 ppm, most likely a result of ring current effects due to the mesityl substituents on the mesim-mim ligand.



1b: M = Ir, N-N = bpm
2b: bim
5b: dmbpm
6b: bik
7b: mesBIAN
8b: mesim-im
3b: M = Rh, N-N = bpm
4b: bim

Scheme 2.

Table 3. Selected chemical shifts for complexes **1b**–**8b**.

Compound	δ (ppm) H_a	H_b	Cp*
[Cp*Ir(bpm)Cl]BF_4 (**1b**)	7.03	5.68	1.56 (br. s)
[Cp*Ir(bim)Cl]BF_4 (**2b**)	4.52	4.14	1.59 (s)
[Cp*Rh(bpm)Cl]BF_4 (**3b**)	7.28	6.00	1.71 (br. s)
[Cp*Rh(bim)Cl]BF_4 (**4b**)	4.47	4.16	1.60 (s)
[Cp*Ir(dmbpm)Cl]BF_4 (**5b**)	6.48	5.67	1.56 (s)
[Cp*Ir(bik)Cl]BF_4 (**6b**)	–	–	1.53 (s)
[Cp*Ir(mesBIAN)Cl]BF_4 (**7b**)	–	–	1.27 (s)
[Cp*Ir(mesim-mim)Cl]BF_4 (**8b**)	–	–	1.49 (s)

The [Cp*IrCl(N–N)]BF_4 complex **7b** (N–N = mesBIAN) was made in good yield, however, the synthesis of the corresponding rhodium complex was unsuccessful. This was attributed to the steric bulk of the mesityl groups on this ligand, which may hinder binding of the ligand to the rhodium metal centre.

The interconversion of the bimetallic ion pair **1c** to **1b**, the analogous BF_4^- salt, was investigated. A toluene solution of **1c**, 1 equivalent of bpm and 1 equivalent of $NaBF_4$ with a small amount of MeOH was stirred at room temperature. **1b** was isolated from the reaction mixture as the only product and its identity was confirmed using ^1H and ^{13}C NMR spectroscopy. The addition of MeOH to the reaction is necessary for the conversion of $[IrCp^*Cl_3]^-$ and anion exchange to occur as both BF_4^- and Cl^- are poorly solubilised by toluene.

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Solid-State Structures of 2b, 7b and 8b

Crystals suitable for X-ray structure determination were obtained for **2b**, **7b** and **8b** and ORTEP depictions of their solid-state structures are depicted in Figure 3. Selected bond lengths and angles for **2b**, **7b** and **8b** are presented in Table 4, and crystal structure and refinement data are given in Table 6.

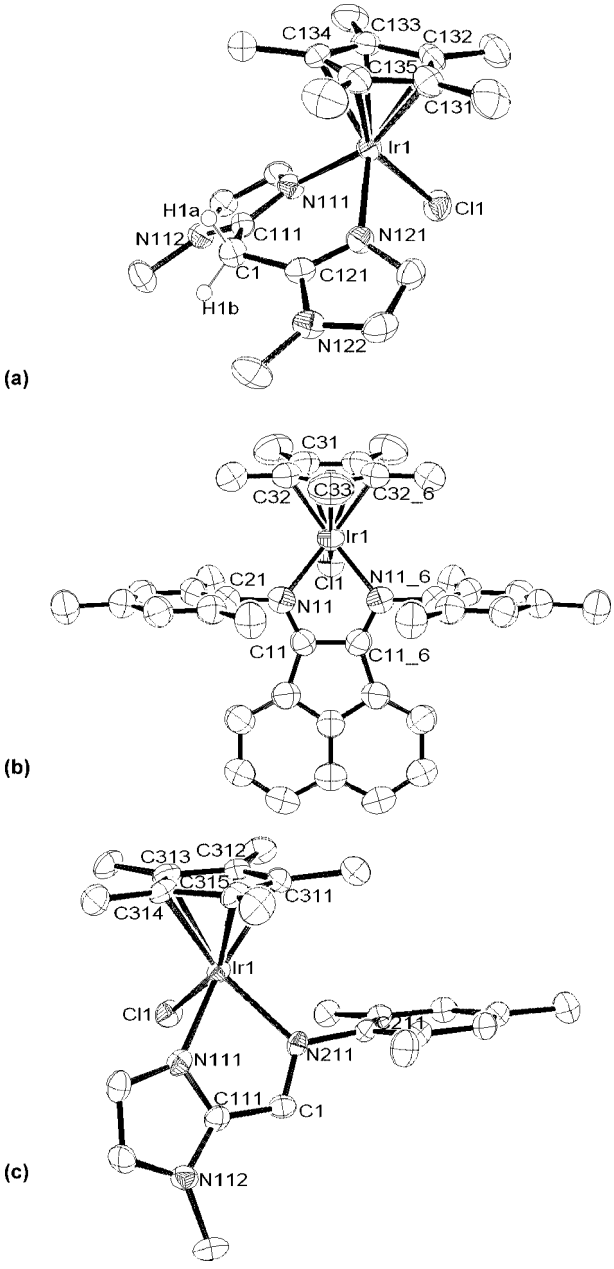

Figure 3. ORTEP depiction of (a) $[Cp^*IrCl(bim)]^+$ (**2b**); (b) $[Cp^*IrCl(mesBIAN)]^+$ (**7b**) and (c) $[Cp^*IrCl(mesim\text{-}mim)]^+$ (**8b**) at 50% thermal ellipsoids for the non-hydrogen atoms.

The solid-state structure of **2b** is very similar to that of **2c** with comparable N–Ir–N bite angles of 83.51(11)° and 83.8(2)°, respectively, and Ir–N bond lengths of 2.095(3) and 2.101(3) Å for **2b** and 2.089(5) and 2.090(5) Å for **2c**. The two Ir–N bond lengths of **7b** are 2.122(5) Å. The Ir–N bond lengths for complex **8b** are 2.100(5) and 2.121(4) Å for the Ir–N(imidazole) and Ir–N(imine) bonds, respectively. These are comparable to the Ir–N(imidazole) and Ir–N(imine) bond lengths in complexes **2b** and **7b**, respectively. All of the Ir–N bond lengths are comparable to the distances found in the literature for similar complexes (values between 2.076 and 2.128 Å).[23,24,26]

The length of the Ir–Cp* bond was dependent on the nature of the cation as well as the nature of the ligand. The Cp*–Ir bond lengths are slightly larger on average for the BF_4^- salt **2b** (2.144–2.181 Å), compared with the equivalent bond lengths in the bimetallic ion pair **2c** (2.143–2.160 Å). The Cp*–Ir bond length in the solid-state structure of **7b** is significantly longer than in **2b** and **2c** (2.171–2.193 Å) due to the high degree of steric hindrance caused by the bulky mesBIAN ligand. The Cp*–Ir bond lengths for complex **8b** (2.158–2.189 Å) containing the hybrid mesitylimine-imidazole ligand are midway between those of complexes **2b** containing the imidazolium ligand, and **7b** which contains the bulky mesBIAN ligand. The Cp*–Ir bond lengths for all of these complexes are within the range previously described in the literature (2.110–2.195 Å).[23,24]

Conclusions

Complexes of the type [Cp*MCl(N–N)][X] were synthesised (M = Rh/Ir^{III}), with a series of bidentate N-donor ligands. Where N–N was bpm or bim and there was no alternate counterion present, bimetallic complexes formed containing the counterion X = $[Cp^*MCl_3]^-$. In the case of the sterically hindered N-donor ligands, these bimetallic complexes did not form. In the presence of the counterion BF_4^-, the complexes where X = BF_4^- were synthesised successfully.

The three dimensional solid-state structures of the cationic fragments of the bimetallic complexes **1c**, **2c** and **3c** were all very similar. Changing the counterion from the $[Cp^*MCl_3]^-$ fragment to the smaller BF_4^- anion, did not significantly change the structure of the cationic fragment. The chemical shift of the resonance due to the -CH_3 protons of the Cp* of the Ir complex containing the mesBIAN ligand $[Cp^*IrCl(mesBIAN)]BF_4$ (**7b**) was significantly shifted upfield relative to the same resonance of the remaining Ir complexes, and this was attributed to the presence of the aromatic rings of the mesBIAN ligand.

The catalytic activity of the complexes reported in this paper is currently under investigation and will be reported in a future paper.

Experimental Section

General Procedures: All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques or in a nitrogen- or argon-filled drybox. All solvents were distilled under argon. *n*-Hexane, *n*-pentane and toluene were distilled from sodium benzophenone ketyl. Dichloromethane was dis-

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Table 4. Selected bond lengths [Å] and bond angles [°][a] for the inner coordination sphere of **2b**, **7b** and **8b**.

2b Atomic distance [Å]		**7b**		**8b**	
Ir(1)–N(111)	2.095(3)	Ir(1)–N(11)	2.122(5)	Ir(1)–N(111)	2.100(5)
Ir(1)–N(121)	2.101(3)	Ir(1)–N(11)#1	2.122(5)	Ir(1)–N(211)	2.121(4)
Ir(1)–C(131)	2.166(4)	Ir(1)–C(31)	2.171(6)	Ir(1)–C(311)	2.178(5)
Ir(1)–C(132)	2.181(3)	Ir(1)–C(31)#1	2.171(6)	Ir(1)–C(312)	2.158(6)
Ir(1)–C(133)	2.155(4)	Ir(1)–C(32)	2.193(7)	Ir(1)–C(313)	2.175(5)
Ir(1)–C(134)	2.144(4)	Ir(1)–C(32)#1	2.193(7)	Ir(1)–C(314)	2.189(5)
Ir(1)–C(135)	2.155(4)	Ir(1)–C(33)	2.187(9)	Ir(1)–C(315)	2.176(6)
Ir(1)–Cl(1)	2.4025(10)	Ir(1)–Cl(1)	2.377(2)	Ir(1)–Cl(1)	2.4009(17)
Bond angle [°]					
N(111)–Ir(1)–N(121)	83.51(11)	N(11)–Ir(1)–N(11)#1	76.5(3)	N(111)–Ir(1)–N(211)	75.80(18)
N(111)–Ir(1)–Cl(1)	85.63(9)	N(11)–Ir(1)–Cl(1)	85.51(13)	N(111)–Ir(1)–Cl(1)	84.05(13)
N(121)–Ir(1)–Cl(1)	87.71(9)	N(11)#1–Ir(1)–Cl(1)	85.51(13)	–Ir(1)–Cl(1)	87.58(13)
–N(111)–Ir(1)	124.6(2)	C(11)–N(11)–Ir(1)	113.4(4)	–N(111)–Ir(1)	114.0(4)
C(112)–N(111)–Ir(1)	127.6(2)	C(21)–N(11)–Ir(1)	128.5(4)	–N(211)–Ir(1)	127.5(3)
–C(111)–C(1)	126.9(3)	N(11)–C(11)–C(11)#1	116.9(3)	N(111)–C(111)–C(1)	117.4(5)
N(112)–C(111)–C(1)	123.9(3)	C(11)–N(11)–Ir(1)	113.4(4)	N(211)–C(1)–C(111)	115.7(5)
–C(1)–C(111)	112.0(3)				

[a] Estimated standard deviation in the least significant figure are given in parentheses.

tilled from calcium hydride. CD_2Cl_2 was dried with calcium hydride and vacuum-distilled before use. 1,2,3,4,5-Pentamethylcyclopentadiene was purchased from Lancaster and used without further purification. Iridium(III) chloride hydrate and rhodium(III) chloride hydrate were obtained from Precious Metals Online (PMO) and were used without further purification. $[IrCp^*Cl_2]_2$, $[RhCp^*Cl_2]_2$,[37] bis(1-pyrazolyl)methane,[38] bis(1-methylimidazol-2-yl)methane,[39] bis(1-methylimidazol-2-yl) ketone,[40] bis(2,4,6-trimethylphenylimino)acenapthene[41,42] and 2-formyl-1-methylimidazole[43] were prepared following literature methods.

^1H, ^{13}C and ^{19}F NMR spectra were recorded with Bruker DPX300 and DMX500 spectrometers. All spectra were recorded at 298 K unless otherwise specified. ^1H NMR and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. ^{19}F NMR was referenced externally using α,α,α-trifluorotoluene in $CDCl_3$. Melting points were recorded using a Mel-Temp apparatus and are uncorrected. IR spectra were recorded using an ATI Mattson Genesis Series FT-IR spectrometer. Electrospray mass spectra were performed by the Biomedical Mass Spectrometry Facility (BMSF) at the University of New South Wales, Sydney, Australia. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago, New Zealand. Single-crystal X-ray structure analyses were obtained at the Research School of Chemistry at the Australian National University, Canberra, Australia.

Synthesis of [Cp*IrCl(bpm)][Cp*IrCl$_3$] (1c): A toluene suspension (25 mL) of $[IrCp^*Cl_2]_2$ (90 mg, 0.11 mmol) was stirred for 30 min and a toluene solution (10 mL) of bis(pyrazolyl)methane, bpm (38 mg, 0.25 mmol) was added dropwise. On addition of the ligand, the suspension immediately changed colour from orange–red to yellow. The mixture was stirred for a further 45 min. The yellow solid was collected by filtration, washed with toluene (2 × 5 mL) and dried in vacuo to give the compound as a yellow air stable solid. The solid was recrystallised by slow diffusion of pentane into a CH_2Cl_2 solution of the complex to give **1c** as small orange crystals which were suitable for X-ray analysis. Yield: 31% (32 mg). M.p. > 230 °C. $C_{27}H_{38}Cl_4Ir_2N_4$ (944.9): calcd. C 34.32, H 4.05, N 5.93; found C 34.23, H 4.14 N 5.30. IR (KBr): ṽ = 3475 (br), 3111 (m), 2962 (w), 2915 (m), 2341 (w), 1635 (w), 1558 (w), 1421 (vs), 1273 (vs), 1096 (m), 1067 (m), 1031 (m), 772 (m), 754 (m) cm^{-1}. MS (ES$^+$, CH_2Cl_2): *m*/*z* (%) = 511 (10) [Cp*IrCl(bpm)]$^+$, 363 (100) [Cp*IrCl]$^+$. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 8.79 (d, $^3J_{H5\text{-}H4}$ = 2.3 Hz, 2 H, H5), 8.35 (d, $^2J_{Ha\text{-}Hb}$ = 15.1 Hz, 1 H, Ha), 7.60 (d, $^3J_{H3\text{-}H4}$ = 2.3 Hz, 2 H, H3), 6.44 (m, 2 H, H4), 5.67 (d, $^2J_{Ha\text{-}Hb}$ = 15.1 Hz, 1 H, Hb), 1.66 [s, 15 H, $CH_3(Cp^*)_{cation}$], 1.58 [s, 15 H, $CH_3(Cp^*)_{anion}$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 143 (C5), 136 (C3), 107 (C4), 88 (Cp*), 84 (CH_2), 8.8 [CH_3(Cp*)], 8.6 [CH_3(Cp*)] ppm.

Synthesis of [Cp*IrCl(bim)][Cp*IrCl$_3$] (2c) and [Cp*IrCl(bim)]Cl (2a): A toluene suspension (25 mL) of $[IrCp^*Cl_2]_2$ (99 mg, 0.11 mmol) was stirred for 30 min. A toluene solution (10 mL) of bis(1-methylimidazol-2-yl)methane, bim, (43 mg, 0.24 mmol) was then added dropwise and the mixture was stirred for 45 min. The yellow solid was collected by filtration, washed with toluene (2 × 5 mL) and recrystallised from dichloromethane and pentane. A yellow powder was isolated by filtration and dried in vacuo. This crude compound was a mixture of [Cp*IrCl(bim)]Cl and [Cp*IrCl(bim)][Cp*IrCl$_3$] and was recrystallised by slow diffusion of petroleum into a CH_2Cl_2 solution of the complex. Two sets of analytically pure crystals were obtained; microcrystalline yellow [Cp*IrCl(bim)]Cl Yield: 28% (40 mg) and large red cubic crystals of [Cp*IrCl(bim)][Cp*IrCl$_3$]$_3$. Yield: 17% (16 mg). The crystals of **2a** and **2c** were separated physically. The red cubic crystals of **2c** were suitable for X-ray crystal structure analysis.

[Cp*IrCl(bim)]Cl (2a): M.p. 225–228 °C. IR (KBr disc): ṽ 3427 (br), 3118 (m), 2918 (m), 1637 (w), 1508 (m), 1450 (m), 1412 (m), 1381 (w), 1279 (w), 1261 (w), 1150 (m), 1096 (m), 1032 (vs), 796 (m) 7,61 (m) cm^{-1}. MS (ES$^+$, CH_2Cl_2): *m*/*z* (%)= 539 (100) [M$^+$], 540 (90), 537 (80), 541 (70), 503 (50). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.00 (s, 4 H, H4 and H5), 5.36 (d, $^2J_{Hb\text{-}Ha}$ = 18.8 Hz, 1 H, Ha), 4.52 (d, $^2J_{Ha\text{-}Hb}$ = 19.2 Hz, 1 H, Hb), 4.10 (s, 6 H, N–CH_3), 1.62 [s, 15 H, CH_3(Cp*)] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 141.3 (C2), 128.7 (C4), 122.7 (C5), 86.9 (Cp*), 35.4 (N–CH_3), 26.1 (CH_2), 8.7 [CH_3(Cp*)] ppm.

[Cp*IrCl(bim)][Cp*IrCl$_3$] (2c): M.p. 270–275 °C. $C_{29}H_{42}Cl_4Ir_2N_4 \cdot CH_2Cl_2$ (1057.9): calcd. C 34.06, H 4.19, N 5.30; found C 33.76, H 4.17, N 5.03. IR (KBr disc): ṽ = 3466 (br), 3143 (m), 3117 (m), 2977 (w), 2910 (m), 1635 (m), 1551 (w), 1514 (vs), 1452 (s), 1377 (m), 1292 (w), 1178 (w), 1144 (w), 1081 (w), 1035 (s), 758 (s) cm^{-1}. MS (ES$^+$, CH_2Cl_2): *m*/*z* (%) = 539 (10) [Cp*IrCl(bim)]$^+$), 503 (100). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 6.95 (s, 4 H, H4 and H5), 5.01

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(d, $^2J_{Hb-Ha}$ = 19.2 Hz, 1 H, Ha), 4.73 (d, $^2J_{Ha-Hb}$ = 19.2 Hz, 1 H, Hb), 4.04 (s, 6 H, N–CH_3), 1.61 [s, 15 H, $CH_3(Cp^*)_{cation}$], 1.54 [s, 15 H, $CH_3(Cp^*)_{anion}$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 141.8 (C2), 128.1 (C4), 122.5 (C5), 86.9 (Cp), 35.9 (N–CH_3), 25.2 (CH_2), 8.8 [$CH_3(Cp^*)$] ppm.

Synthesis of [Cp*RhCl(bpm)][Cp*RhCl$_3$] (3c): $[RhCp^*Cl_2]_2$ (215 mg, 0.35 mmol) and bpm (383 mg, 2.5 mmol) were suspended in toluene and stirred for 3 h. The orange-brown solid which formed was collected by filtration and was recrystallised by layering a CH_2Cl_2 solution of the compound with pentane. The product crystallised both as large red plates and small orange crystals. Both crystal forms were found to be analytically pure [Cp*RhCl(bpm)][Cp*RhCl$_3$]. The red plates of [Cp*RhCl(bpm)][Cp*RhCl$_3$] were suitable for X-ray crystal structure analysis. Yield: 32% (105 mg). M.p. > 310 °C. IR (KBr disc): $\tilde{\nu}$ = 3409 (br), 3120 (w), 2965 (w), 1635 (m), 1522 (m), 1489 (m), 1458 (m), 1403 (s), 1375 (m), 1288 (s), 1264 (m), 1096 (s), 1058 (s), 1017 (s), 799 (s), 168 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 8.76 (d, $^3J_{H5-H4}$ = 2.5 Hz, 2 H, H5), 8.07 (d, $^2J_{Hb-Ha}$ = 15.1 Hz, 1 H, Ha), 7.60 (d, $^3J_{H3-H4}$ = 2.3 Hz, 2 H, H3), 6.39 (m, 2 H, H4), 5.84 (d, $^2J_{Ha-Hb}$ = 15.1 Hz, 1 H, Hb), 1.69 [s, 15 H, $CH_3(Cp^*)_{cation}$], 1.61 [br. s, 15 H, $CH_3(Cp^*)_{anion}$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 145.0 (C5), 137.5 (C3), 108.3 (C4), 97.3 (d, $^1J_{Rh-Cp^*}$ = 8.7 Hz, Cp), 64.3 (CH_2), 9.8 (Cp–CH_3), 9.6 [$CH_3(Cp^*)$] ppm.

Synthesis of [Cp*IrCl(bpm)]BF$_4$ (1b): $[IrCp^*Cl_2]_2$ (53 mg, 0.067 mmol) was suspended in toluene (10 mL) and stirred for 10 min. A toluene (5 mL) solution of bpm (23 mg, 0.16 mmol) was added and the mixture was stirred for 30 min before a methanol solution (5 mL) of $NaBF_4$ (14 mg, 0.127 mmol) was added. The solid dissolved to generate a yellow solution which was allowed to stir overnight. The solvent volume was reduced to ca. 5 mL, filtered and layered with pentane (10 mL). The resulting precipitate was collected by filtration, washed with pentane (5 mL) and dried in vacuo to give [Cp*IrCl(bpm)]BF$_4$ as a yellow solid. Yield: 53% (42 mg). M.p. 275–285 °C. $C_{17}H_{23}Cl_1BF_4Ir_1N_1$ (597.2): calcd. C 34.15, H 3.88, N 9.37; found C 34.18, H 3.91, N 9.14. IR (KBr disc): $\tilde{\nu}$ = 3649 (w), 3427 (br), 3119 (m), 3081 (m), 2984 (w), 2913 (w), 1636 (m), 1489 (w), 1456 (m), 1418 (s), 1288 (s), 1277 (m), 1084 (vs), 989 (vs), 764 (m) cm^{-1}. MS (ES$^+$, CH_2Cl_2): *m/z* (%) = 511 (100) [Cp*IrCl(bpm)]$^+$), 509 (80), 513 (80). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 8.07 (d, $^3J_{H5-H4}$ = 2.7 Hz, 2 H, H5), 7.58 (d, $^3J_{H3-H4}$ = 2.5 Hz, 2 H, H3), 7.03 (d, $^2J_{Hb-Ha}$ = 14.5 Hz, 1 H, Ha), 6.43 (dd, $^3J_{H5-H4}$ = 2.7 Hz, $^3J_{H5-H4}$ = 2.5 Hz, 2 H, H4), 5.68 (d, $^2J_{Ha-Hb}$ = 14.5 Hz, 1 H, Hb), 1.56 [br. s, 15 H, $CH_3(Cp^*)$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 144.8 (C3), 135.0 (C5), 108.7 (C4), 88.8 (Cp*), 62.7 (CH_2), 8.7 [$CH_3(Cp^*)$] ppm. ^{19}F NMR (CD_2Cl_2, 282.41 MHz): δ = –151.4 ppm.

Synthesis of [Cp*IrCl(bim)]BF$_4$ (2b): $[IrCp^*Cl_2]_2$ (58.8 mg, 0.073 mmol), bim (27.2 mg, 0.154 mmol) and $NaBF_4$ (19.2 mg, 0.175 mmol) were dissolved in toluene (10 mL) and MeOH (5 mL) and stirred for 2 h. The solution was reduced in volume, filtered and layered with pentane. The product was allowed to precipitate overnight, collected by filtration, washed with pentane and dried in vacuo to isolate [Cp*IrCl(bim)]BF$_4$ as a yellow powder. Yield: 73% (67.3 mg). Yellow crystals of [Cp*IrCl(bim)]BF$_4$ obtained by layering a CH_2Cl_2 solution of **2b** with petroleum in air were suitable for X-ray crystal structure analysis. M.p. 273–278 °C. $C_{19}H_{27}ClBF_4IrN_4{\cdot}H_2O$ (625.9): calcd. C 35.44, H 4.54, N 8.70; found C 35.81, H 4.37, N 8.73%. IR (KBr disc): $\tilde{\nu}$ = 3432 (br), 3108 (m), 1716 (w), 1699 (w), 1652 (m), 1655 (m), 1557 (w), 1514 (m), 1456 (w), 1413 (w), 1290 (w), 1084 (br. s), 1032 (vs), 820 (w), 758 (m) cm^{-1}. MS (ES$^+$, CH_2Cl_2): *m/z* (%) = 539 (100) [Cp*IrCl(bim)]$^+$, 537 (30). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.02 (d, $^3J_{H4-H5}$ = 1.8 Hz, 2 H, H4 or H5), 6.99 (d, $^3J_{H4-H5}$ = 1.8 Hz, 2 H, H4 or H5), 4.52 (d, $^2J_{Hb-Ha}$ = 19.0 Hz, 1 H, Ha), 4.14 (d, $^2J_{Ha-Hb}$ = 19.0 Hz, 1 H, Hb), 3.86 (s, 6 H, N-CH_3), 1.59 [s, 15 H, $CH_3(Cp^*)$] ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 141.1 (C2), 129.3 (C4), 123.7 (C5), 86.9 (Cp*), 35.9 (N–CH_3), 25.2 (CH_2), 8.8 [$CH_3(Cp^*)$] ppm. ^{19}F NMR (CD_2Cl_2, 282.41 MHz): δ = –154.1 ppm.

Synthesis of [Cp*IrCl(dmbpm)]BF$_4$ (5b): A toluene (10 mL) suspension of $[IrCp^*Cl_2]_2$ (52.4 mg, 0.066 mmol) was stirred for 10 min prior to the addition of a toluene solution (5 mL) of bis(3,5-dimethylpyrazolyl)methane, dmbpm (24.1 mg, 0.139 mmol). The suspension was stirred for 45 min before addition of a methanol solution of $NaBF_4$ (24.2 mg, 0.221 mmol). The orange solid dissolved producing a yellow solution which was stirred overnight. The volume of the solution was reduced in vacuo, filtered and was layered with pentane. The precipitate was collected, washed with pentane and dried to give [Cp*IrCl(dmbpm)]BF$_4$ as a yellow solid. Yield: 50% (42.5 mg). $C_{21}H_{31}BClF_4IrN_4$ (654.0): calcd. C 38.57, H 4.78, N 8.57; found C 38.30, H 4.78., N 8.40%. IR (KBr disc): $\tilde{\nu}$ = 3448 (br), 3136 (w), 2986 (w), 1699 (w), 1652 (w), 1561 (s), 1490 (m), 1472 (s), 1426 (s), 1396 (s), 1288 (vs), 1156 (vs), 843 (m), 806 (m), 705 (w), 686 (m), 658 (w), 624 (w), 520 (m), 456 (m) cm^{-1}. MS (ES$^+$, CH_2Cl_2): *m/z* (%) = 568 (100) [Cp*IrCl(dmbpm)]$^+$), 567 (90), 569 (80), 565 (60). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 6.48 (d, $^2J_{Hb-Ha}$ = 15.9 Hz, 1 H, Ha), 6.14 (s, 2 H, H4), 5.67 (d, $^2J_{Hb-Ha}$ = 15.9 Hz, 1 H, Hb), 2.54 (s, 6 H, CH_3), 2.42 (s, 6 H, CH_3), 1.56 [s, 15 H, $CH_3(Cp^*)$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 155.1 (C3 or 5), 144.04 (C3 or 5), 109.51 (C4), 89.35 (Cp*), 58.4 (CH_2), 15.2 (Me), 11.6 (Me), 9.7 [$CH_3(Cp^*)$] ppm. ^{19}F NMR (CD_2Cl_2, 282.41 MHz): δ = –152.5 ppm.

Synthesis of [Cp*IrCl(bik)]BF$_4$ (6b): A toluene (10 mL) suspension of $[IrCp^*Cl_2]_2$ (46.3 mg, 0.058 mmol) was stirred for 30 min prior to the addition of a MeOH solution (5 mL) of bis(1-methylimidazol-2-yl) ketone, bik, (44.1 mg, 0.231 mmol). The suspension was stirred for 30 min before addition of a MeOH solution (5 mL) of $NaBF_4$ (24.2 mg, 0.221 mmol). The yellow solution was stirred for 2 h before the volume of the solution was reduced, filtered and was layered with pentane. The yellow solid obtained was collected, washed with pentane and dried in vacuo to give [Cp*IrCl(bik)]BF$_4$. Yield: 31% (23 mg). M.p. 301–305 °C. $C_{19}H_{25}BClF_4IrN_4O$ (639.9): calcd. C 35.66, H 3.94, N 8.76; found C 35.44, H 4.13, N 8.47. IR (KBr disc): $\tilde{\nu}$ = 3522 (br), 3442 (br), 3374 (br), 3153 (w), 3128 (w), 1634 (vs), 1558 (w), 1481 (w), 1421 (vs), 1386 (m), 1293 (m), 1189 (m), 1083 (m), 1032 (m), 904 (vs) cm^{-1}. MS (ES$^+$, CH_2Cl_2): *m/z* (%) = 554 (100), 552 (95), 555 (92), 553 (90) [Cp*IrCl(bik)]$^+$), 551 (50). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.52 (d, $^3J_{H5-H4}$ = 1.10 Hz, 2 H, H4 or H5), 7.36 (d, $^3J_{H5-H4}$ = 1.10 Hz, 2 H, H4 or H5), 4.23 (s, 6 H, N–Me) 1.53 [s, 15 H, $CH_3(Cp^*)$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 172.7 (C=O), 132.7 (C2), 129.9 (C4), 128.0 (C5), 88.5 (Cp*), 38.2 (N–Me), 8.3 [$CH_3(Cp^*)$] ppm. ^{19}F NMR (CD_2Cl_2, 282.41 MHz): δ = –153.9 ppm

Synthesis of [Cp*IrCl(mesBIAN)]BF$_4$ (7b): A toluene (20 mL) suspension of $[IrCp^*Cl_2]_2$ (110.5 mg, 0.139 mmol) was stirred for 30 min prior to the addition of a toluene solution (5 mL) of 1,2-bis(2,4,6-trimethylphenylimino)acenapthene, mesBIAN, (129.2 mg, 0.310 mmol). The suspension was stirred for 30 min before drop wise addition of a MeOH/toluene solution (5 mL, 1: 4) of $NaBF_4$ (34.1 mg, 0.310 mmol). The dark brown solution was stirred overnight; the solvent was removed in vacuo to give a brown solid. The solid was recrystallised from CH_2Cl_2, by slow diffusion of pentane. Dark brown crystals of [Cp*IrCl(mesBIAN)]BF$_4$ were collected,

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washed with pentane (2 5 mL) and dried. Yield: 54% (129 mg). The dark brown crystals of **6b** obtained were suitable for X-ray crystal structure analysis. M.p. > 230 °C. $C_{40}H_{43}BClF_4IrN_2{\cdot}H_2O{\cdot}CH_2Cl_2{\cdot}CH_3OH$[44] (1001.3): calcd. C 50.38, H 5.13, N 2.80; found C 50.07, H 4.75, N 2.80%. IR (KBr disc): $\tilde{\nu}$ = 3629 (w), 3588 (w), 3433 (br), 2917 (w), 2361 (w), 1624 (w), 1064 (m),1473 (m) 1436 (m), 1417 (m), 1382 (m), 1302 (m), 1058 (vs), 1031 (vs), 778 (m) cm^{-1}. MS (ES^+, CH_2Cl_2): *m*/*z* (%) = 782 (100) [Cp*IrCl(mesBIAN)]$^+$), 783 (60), 784 (10), 743 (10). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 8.19 (d, $^3J_{H5\text{-}H4}$ = 8.4 Hz, 2 H, H5), 7.55 (m, 2 H, H4), 7.23 (s, 2 H, H10), 7.10 (s, 2 H, H12), 6.89 (d, $^3J_{H3\text{-}H4}$ = 7.3 Hz, 2 H, H3), 2.48 (s, 6 H, *o*-Me), 2.46 (p, 6 H, *p*-Me), 1.92 (s, 6 H, *o*′-Me), 1.27 [s, 15 H, CH_3(Cp*)] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 178.7 (C1), 145.0 (C7), 142.1 (C8), 139.9 (C11), 133.2 (C5), 132.0 (C6), 131.7 (C9), 131.5 (C10), 130.6 (C12), 130.0 (C4), 129.2 (C13), 126.8 (C2), 125.5 (C3), 93.5 (Cp*), 21.3 (*p*-Me), 20.5 (*o*-Me), 18.6 (*o*′-Me), 8.6 [CH_3(Cp*)] ppm. ^{19}F NMR (CD_2Cl_2, 282.41 MHz): δ = –154.0 (br. s, BF_4) ppm.

Synthesis of [(2,4,6-Trimethylphenyl)imino](1-methyl-2-imidazolyl)-methane: 2-Formyl-1-methylimidazole (1.38 g, 12.5 mmol) and 2,4,6-trimethylaniline (4 mL, 26.5 mmol) were dissolved in ethanol (12 mL) and heated to reflux for 3 h. The solvent was removed in vacuo to give a brown oil which was purified by kugelrohr distillation. The product [(2,4,6-trimethylphenyl)imino](1-methyl-2-imidazolyl)methane was obtained as a viscous yellow oil. Yield: 25% (878 mg). $C_{14}H_{17}N_3$ (227.3): calcd. C 73.98, H 7.54, N 18.49; found C 73.49, H 7.88, N 17.73. MS (GC-EI, CH_2Cl_2): *m*/*z* (%) = 120 (100), 135 (90) [M^+]. ^1H NMR ([D_6]acetone, 300 MHz): δ = 8.18 (s, 1 H, N=CH), 7.27 (s, 1 H, H5), 7.12 (s, 1 H, H4), 6.87 (s, 2 H, *m*-H), 4.14 (s, 3 H, N–Me), 2.23 (s, 3 H, *p*-Me), 2.11 (s, 6 H, *o*-Me) ppm. $^{13}C\{^1H\}$ NMR ([D_6]acetone, 75 MHz): δ = 154.8 (N=CH), 148.4 (C7), 142.9 (C1), 129.4 (C4), 128.6 (*p*), 128.5 (*o*), 126.5 (*o*), 126.0 (C5), 35.0 (N–Me), 19.9 (*p*-Me), 17.6 (*o*-Me) ppm.

Synthesis of [Cp*IrCl(mesim-mim)]BF_4 (8b): $[IrCp^*Cl_2]_2$ (75.6 mg, 0.095 mmol) and 2,4,6-trimethylphenylimino-(1-methyl-2-imidazolyl)methane (**7**) (86.3 mg, 0.400 mmol) were dissolved in toluene (10 mL) and stirred for 30 min prior to the addition of a methanol solution (5 mL) of $NaBF_4$ (24.2 mg, 0.221 mmol). The dark orange solution was stirred for 2 h before the volume was reduced, filtered and the solution was layered with pentane (10 mL). Orange crystals of [Cp*IrCl(mesim-mim)]BF_4 were collected in air and dried. Yield: 38% (49.1 mg) M.p. 283–288 °C. $C_{24}H_{32}BClF_4IrN_3$ (677.0): calcd. C 42.58, H 4.76, N 6.21; found C 42.44, H 4.74, N 6.09. IR (KBr disc): $\tilde{\nu}$ = 3853 (w), 3736 (w), 3394 (br), 3153 (w), 2190 (m), 1584 (m), 1488 (m), 1424 (s), 1386 (m), 1309 (m), 1298 (m), 1142 (m), 1061 (vs), 989 (m), 853 (m), 782 (m) cm^{-1}.

MS (ES^+, CH_2Cl_2): *m*/*z* (%) = 590 (100) [Cp*IrCl(mesim-mim)]$^+$) 588 (80), 592 (50). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 8.57 (s, 1 H, H6), 7.42 (d, $^3J_{H5\text{-}H4}$ = 1.51 Hz, 1 H, H5) 7.32 (d, $^3J_{H4\text{-}H5}$ = 1.51 Hz, 1 H, H4), 6.96 (s, 1 H, H10), 6.93 (s, 1 H, H12), 3.99 (s, 3 H, N–Me), 2.26 (s, 3 H, *p*-Me), 2.20 (s, 3 H, *o*′-Me), 2.00 (s, 3 H, *o*-Me), 1.49 [s, 15 H, CH_3(Cp*)] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 156.6 (C6), 149.8 (C2), 144.7 (C8), 138.5 (C11), 131.9 (C13), 130.0 (C12), 129.9 (C9), 128.6 (C4), 128.3 (C5), 89.7

Table 5. Crystal structure and refinement data for **1c**, **2c** and **3c**.

Compound	**1c**	**2c**	**3c**
Empirical formula	$C_{27}H_{38}Cl_4Ir_2N_4$	$C_{31}H_{46}C_{18}Ir_2N_4$	$C_{27}H_{38}Cl_4N_4Rh_2$
Formula weight	944.81	1142.72	766.23
Temperature [K]	200(2)	200(2)	200(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	*P*21/*a*	*P*212121	*P*21/*a*
Crystal size [mm]	0.19 × 0.12 × 0.11	0.34 × 0.31 × 0.28	0.51 × 0.43 × 0.12
a [Å]	14.626(3)	12.001(2)	14.596(2)
b [Å]	14.413(3)	15.082(3)	14.436(2)
c [Å]	14.918(3)	21.807(4)	14.876(2)
α [°]	90	90	90
β [°]	103.20(3)	90	103.1620(10)
γ [°]	90	90	90
V [Å^3]	3061.7(11)	3947.0(14)	3052.0(7)
Z	4	4	4
$D_{calcd.}$ [Mg/m^3]	2.05	1.923	1.668
μ [mm^{-1}]	9.057	7.305	1.455
F(000)	1800	2200	1544
θ Range for data collection [°]	3.14–27.50	3.11–27.49	3.15–27.49
Limiting indices	$-18 \le h \le 18$, $-17 \le k \le 18$, $-19 \le l \le 19$	$-15 \le h \le 12$, $-19 \le k \le 19$, $-28 \le l \le 28$	$-18 \le h \le 18$, $-18 \le k \le 17$, $-19 \le l \le 18$
Reflections collected	63766	55293	63992
Independent reflections	7009 [R_{int} = 0.0820]	9054 [R_{int} = 0.1317]	6976 [R_{int} = 0.0685]
Completeness to theta	27.50°, 99.8%	27.49°, 99.8%	27.49°, 99.6%
Max. and min. transmission	0.451 and 0.285	0.356 and 0.161	0.921 and 0.719
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	7009/0/345	9054/0/418	6976/0/344
Goodness-of-fit on F^2	1.022	1.01	1.009
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0334, wR_2 = 0.0757	R_1 = 0.0346, wR_2 = 0.0752	R_1 = 0.0324, wR_2 = 0.0855
R indices (all data)	R_1 = 0.0530, wR_2 = 0.0846	R_1 = 0.0464, wR_2 = 0.0796	R_1 = 0.0401, wR_2 = 0.0914
Extinction coefficient	0.00088(6)	–0.014(7)	
Largest diff. peak and hole [e·Å^{-3}]	1.385 and –2.072	0.936 and –1.096	1.521 and –0.932

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Table 6. Crystal structure and refinement data for **2b**, **7b** and **8b**.

Compound	**2b**	**7b**	**8b**
Empirical formula	$C_{19}H_{27}BClF_4IrN_4$	$C_{42}H_{51}BCl_5F_4IrN_2O_2$	$C_{25}H_{34}BCl_3F_4IrN_3$
Formula weight	625.91	1072.11	761.91
Temperature [K]	200(2)	200(2)	200(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	*Pcab*	*Pbnm*	$P\bar{1}$
Crystal size [mm]	$0.19 \times 0.17 \times 0.12$	$0.20 \times 0.18 \times 0.18$	$0.25 \times 0.10 \times 0.05$
a [Å]	15.2650(10)	15.265(3)	9.5200(19)
b [Å]	16.6330(10)	16.509(4)	12.287(3)
c [Å]	17.4210(10)	17.182(3)	13.418(3)
α [°]	90	90	68.51(3)
β [°]	90	90	85.49(3)
γ [°]	90	90	77.04(3)
V [Å^3]	4423.2(5)	4330.0(15)	1423.2(5)
Z	8	4	2
$D_{calcd.}$ [Mg/m^3]	1.88	1.645	1.778
μ [mm^{-1}]	6.204	3.448	5.019
$F(000)$	2432	2144	748
θ Range for data collection [°]	2.91–27.49	2.94–27.47	3.11–25.04
Limiting indices	$-19 \le h \le 19$, $-21 \le k \le 21$, $-22 \le l \le 22$	$-19 \le h \le 19$, $-21 \le k \le 21$, $-22 \le l \le 22$	$-11 \le h \le 10$, $-14 \le k \le 14$, $-15 \le l \le 15$
Reflections collected	65229	81934	16560
Independent reflections	5070 [R_{int} = 0.0948]	5091 [R_{int} = 0.1034]	5027 [R_{int} = 0.0709]
Completeness to theta	27.49°, 99.9%	27.50°, 99.3%	25.04°, 99.7%
Max. and min. transmission	0.512 and 0.336	0.712 and 0.557	0.805 and 0.478
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	5070/0/278	5091/47/308	5027/0/343
Goodness-of-fit on F^2	1.006	1.007	1.019
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0306, wR_2 = 0.0716	R_1 = 0.0514, wR_2 = 0.1398	R_1 = 0.0343, wR_2 = 0.0783
R indices (all data)	R_1 = 0.0456, wR_2 = 0.0797	R_1 = 0.0680, wR_2 = 0.1520	R_1 = 0.0439, wR_2 = 0.0827
Largest diff. peak and hole [e·Å^{-3}]	0.898 and –1.747	0.765 and –0.640	1.193 and –1.008

($^1J_{Rh\text{-}Cp}$ = 8.7 Hz, Cp*), 35.5 (N–Me), 20.4 (*p*-Me), 19.6 (*o*′-Me), 18.6 (*o*-Me), 8.3 [CH_3(Cp*)] ppm. ^{19}F NMR (CD_2Cl_2, 282.41 MHz): δ = 153.7 ppm.

Synthesis of [Cp*RhCl(bpm)]BF$_4$ (3b): [RhCp*Cl$_2$]$_2$ (99 mg, 0.16 mmol), bpm (86 mg, 0.58 mmol) and $NaBF_4$ (67 mg, 0.61 mmol) were suspended in toluene and stirred for 12 h at room temp. The yellow-orange solid was collected in air by filtration and was recrystallised from a CH_2Cl_2/hexane (1:1) mix. [Cp*RhCl(bpm)]BF_4 was obtained as an orange powder. Yield: 47% (77 mg). MP > 230 °C dec. $C_{17}H_{23}BClF_4N_4Rh$ (508.55): calcd. C 40.15, H 4.56, N 11.02; found C 39.97, H 4.77, N 10.94. IR (KBr disc): $\tilde{\nu}$ = 3144 (m), 3117 (w), 3081 (w), 2959 (w), 2922 (w), 1493 (m), 1457 (m), 1430 (m), 1403 (s), 1288 (vs), 1278 (s), 1098 (vs), 1038 (vs), 986 (m), 767 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 8.27 (d, $^3J_{H5\text{-}H4}$ = 2.64 Hz, 2 H, H5), 7.73 (d, $^3J_{H3\text{-}H4}$ = 2.26 Hz, 2 H, H3), 7.28 (d, $^2J_{Hb\text{-}Ha}$ = 14.7 Hz, 1 H, Ha), 6.50 (dd, $^3J_{H5\text{-}H4}$ = 2.64 Hz, $^3J_{H3\text{-}H4}$ = 2.26 Hz, 2 H, H4), 6.00 (d, $^2J_{Ha\text{-}Hb}$ = 14.7 Hz, 1 H, Hb), 1.71 [br. s, 15 H, CH_3(Cp*)] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ = 144.8 (C3), 135.0 (C5), 108.7 (C4), 88.8 (Cp*), 62.7 (CH_2), 8.7 [CH_3(Cp*)] ppm. ^{19}F NMR (CD_2Cl_2, 282.41 MHz): δ = –151.6 ppm.

Synthesis of [Cp*RhCl(bim)]BF$_4$ (4b): [RhCp*Cl$_2$]$_2$ (104 mg, 0.17 mmol), bim (115 mg, 0.65 mmol) and $NaBF_4$ were suspended in toluene and stirred for 12 h at room temp. The orange solid was collected via filtration and recrystallised from CH_2Cl_2: pentane. Red cubic crystals of [Cp*RhCl(bim)]BF_4 were obtained. Yield: 63% (115 mg). M.p. 290 °C (dec.). $C_{19}H_{27}BClF_4N_4Rh$ (536.6): calcd. C 42.53, H 5.07, N 10.44; found C 42.56, H 5.20, N 10.50. IR (KBr disc): $\tilde{\nu}$ = 3129 (m), 2961 (w), 1621 (w), 1547 (m), 1515 (s), 1456 (m), 1417 (s), 1378 (m), 1288 (m), 1171 (w), 1143 (m), 1057 (br. s), 819 (w), 762 (s), 618 (m), 521 (m), 436 (m), 409 (m) cm^{-1}. MS (ES$^+$, CH_2Cl_2) *m*/*z*: 449 (M$^+$, 100%), 451 (80%), 413 (70%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.03 (d, 4 H, H4 and H5), 4.47 (d, $^2J_{Hb\text{-}Ha}$ = 19.0 Hz, 1 H, Ha), 4.16 (d, $^2J_{Ha\text{-}Hb}$ = 19.0 Hz, 1 H, Hb), 3.83 (s, 6 H, N–CH_3), 1.60 [s, 15 H, CH_3(Cp*)] ppm. ^{13}C NMR [CD_2Cl_2, 75 MHz]: δ = 142.0 (C2), 129.1 (C4 or 5), 123.8 (C5 or 4), 96.0 ($^1J_{Rh\text{-}Cp}$ = 8.0 Hz, Cp*), 34.9 (N–CH_3), 22.8 (CH_2), 9.4 [CH_3(Cp*)] ppm. ^{19}F NMR (CD_2Cl_2, 282.41 MHz): δ = –152.2 ppm.

X-ray Crystallography

Details of the crystals and their refinements are given in Table 5 and Table 6. CCDC- 291178, -291179, -291180, -291478, -609638 and -609639 contain the supplementary crystallographic information for **1c**, **7b**, **2c**, **3c**, **8b** and **2b**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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