



# Synthesis of monodentate bis(N-heterocyclic carbene) complexes of iridium: Mixed complexes of abnormal NHCs, normal NHCs, and triazole NHCs

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## ABSTRACT

A stepwise synthesis of mixed monodentate bis-NHC complexes of Ir(I), employing Ag(I)NHC complexes as transfer agents, yields complexes with two monodentate NHCs having different steric and electronic characteristics. The crystal structure of the mixed complex (**5**) with both a triazole-derived NHC ligand and an imidazole-derived NHC ligand is reported and both the NHC ring geometry and the M–NHC bond lengths are similar to related complexes. The complexes maintain their integrity over time and do not disproportionate, consistent with the NHC ligands not being labile.

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## 1. Introduction

Owing to the utility of N-heterocyclic carbenes (NHCs) as spectator ligands in transition metal-mediated catalysis, the number and variety of transition metal NHC complexes reported in the literature has increased significantly in recent years [1,2]. The use of N-heterocyclic carbenes as ligands enables the variation of the steric and electronic properties of the metal center [3]. Indeed, their application as a proposed “phosphine-analog” is one of the reasons their popularity as spectator ligands in catalysis has grown so rapidly. Nonetheless, as the field has developed, significant differences have emerged in the behavior of NHCs and phosphines as spectator ligands [4].

Many different classes of NHC complexes have been described for a wide variety of metals. One exception is the limited number of Rh and Ir NHC complexes with two dissimilar NHC ligands bound to the metal, that is, complexes in which the two NHC ligands differ in their steric or electronic properties. While many examples of chelating [5] and monodentate bis(NHC) or tris(NHC) [6–18] complexes of Rh and Ir are known, to the best of our knowledge only a few have been reported in which electronically or sterically distinct types of NHC ligands are present [17,19]. Given the importance of both steric and electronic dissymmetry in many catalytic reactions [20–36], we sought a facile method to reliably

synthesize monodentate bis(NHC) complexes in which the two NHC ligands are sterically and/or electronically distinct.

Furthermore, as monodentate phosphine ligands tend to be labile, a complex with two different phosphine ligands would be likely to disproportionate to give a mixture of species [37,38]. In contrast, N-heterocyclic carbene ligands are not thought to be labile in most complexes, excluding silver carbene complexes. When NHC dissociation from the metal center occurs it is usually through irreversible cleavage of the metal–NHC bond [39,40]. Mixed NHC complexes should allow control over electronic and steric properties without the potential complications of ligand exchange inherent in a phosphine-based system. Consistent with this picture, the mixed NHC complexes described here maintain their integrity over time in solution.

This paper describes a method for the synthesis of monodentate bis(NHC) complexes of Ir(I) containing two different types of NHCs. This procedure is based on the common method of Ag–NHC transmetalation [41–44], which is widely used in the synthesis of Ir and Rh NHC complexes [45], and has been previously employed by several groups to synthesize monodentate bis(NHC) complexes with identical NHC ligands [12,14–16,46]. We demonstrate that the introduction of a second type of NHC ligand, in the form of a Ag–NHC complex, reliably yields monodentate bis(NHC) complexes with widely varying steric and electronic characteristics. This allows facile control of a dissymmetric electronic and steric environment around the metal center.

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## 2. Results and discussion

In the following sections, we will refer to imidazole-derived NHCs, bound normally via C2, as *n*NHCs, imidazole-derived NHCs bound abnormally through C4(5), as *a*NHCs, and triazole-derived NHCs bound normally through C5, as *t*NHCs (Fig. 1).

### 2.1. Synthesis of Ir bis(*n*NHC) complexes

We began by examining the synthesis of bis(*n*NHC) complexes in which the two *n*NHC ligands have different N-substituents, with the aim of generating a complex in which the two L-type ligands are electronically similar but sterically dissimilar.

The  $[\text{Ag}(\text{NHC})_n]^+$  complexes were synthesized by the method described by Youngs [47], and were used without further purification. Previous literature reports [41–44,47,48] of  $\text{Ag}(\text{NHC})$  complexes with weakly coordinating counterions, X, such as  $\text{BF}_4^-$  or  $\text{PF}_6^-$ , have the formulation  $[\text{Ag}(\text{NHC})_2]\text{X}$ , and that is the stoichiometry we assume here.

Bis(*n*NHC) complexes with two relatively large *n*NHC ligands and one large and one small *n*NHC ligand were synthesized (Scheme 1). We first examined the formation of a complex with two sterically similar, and relatively bulky, *n*NHC ligands.

Complex **1** combined with the  $[\text{Ag}(\text{NHC})_2]\text{PF}_6$  salt for 36 h in refluxing dichloromethane yielded **2** in 48% yield. The most important factors in improving the yield were long reaction times and the use of an excess of the  $\text{Ag}(\text{NHC})_2^+$  complex. We suspect the large excess is required due to decomposition of the  $\text{Ag}(\text{NHC})_2^+$  complex over the rather lengthy course of the reaction. All the reactions were carried out in degassed solvents, under an inert atmosphere, and in the dark, to minimize the degradation of the silver species. Crude **2** was contaminated with unreacted **1** and a small quantity of 1,3-di(*n*-butyl)imidazolium salt, which could arise from decomposition of the  $\text{AgNHC}$  complex, or may have been an impurity in the  $\text{AgNHC}$  starting material. Complex **2** was easily purified by column chromatography, and the unreacted **1** could be recovered in pure form and reused.

Owing to the symmetric nature of both the ligands the NMR spectra of **2** were unremarkable. Rotation about the M–carbene bonds is hindered, as evidenced by the diastereotopicity of both the *n*-butyl and *p*-tolylmethyl methylene protons in the  $^1\text{H}$  NMR spectrum. In the  $^{13}\text{C}$  NMR spectrum, the two carbene carbons res-

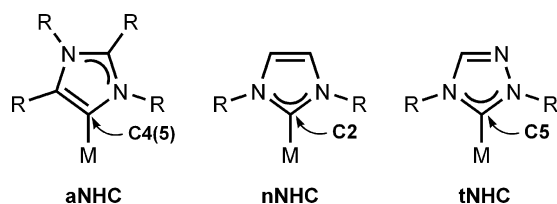


Fig. 1. Abbreviations used here for abnormal and normal imidazole-derived and normal triazole-derived NHC ligands.

onate at  $\delta$  178.97 and 175.99 ppm, both in the expected range for *n*NHC complexes of Ir(I).

We also synthesized a bis(*n*NHC) complex, **3**, with one small and one large *n*NHC ligand (Scheme 1). This reaction went at room temperature, with 2.5 eq.  $\text{Ag}(\text{NHC})_2^+$ , giving **3** in 75% yield. The improved yield under milder conditions is undoubtedly the result of reduced steric hindrance at the metal center. As with **2**, the crude product was contaminated with unreacted **1** and 1,3-dimethylimidazolium salt, but **3** was easily purified, and unreacted **1** recovered, by column chromatography. Complex **3** was recrystallized from dichloromethane/pentane as bright orange prisms.

In the  $^1\text{H}$  NMR spectrum the methylene groups of the *p*-tolylmethyl wingtips are diastereotopic, indicating that rotation around the M–carbene bond is still hindered, despite the smaller steric profile of the second NHC ligand. This is not surprising, as hindered rotation of the 1,3(di(*p*-tolylmethyl)imidazol-2-ylidene) ligand is observed even in complexes of  $\text{Ir}(\text{cod})(\text{NHC})\text{Cl}$  [45]. The two carbene carbons resonate at  $\delta$ 179.2 and 177.9 ppm in the  $^{13}\text{C}$  NMR spectrum.

### 2.2. Synthesis of Ir(*n*NHC)(*t*NHC) complexes

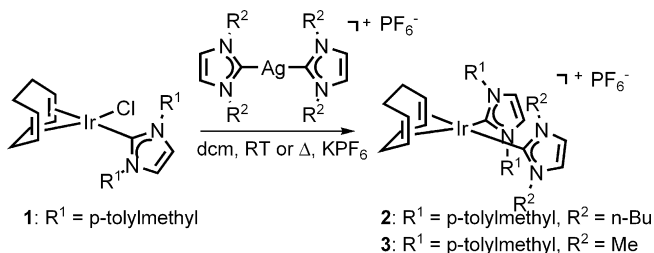
We also synthesized complexes with electronically dissimilar NHC ligands (Scheme 2). The first complex we targeted was one in which the two electronically different NHC ligands would have identical steric properties. The formation of **5** did not require an excess of the  $\text{Ag}(\text{tNHC})$  complex, and the reaction proceeded to 73% yield in just 12 h at room temperature. The crude product was purified by column chromatography and recrystallized from dichloromethane/pentane to yield bright orange crystals.

In the  $^1\text{H}$  NMR spectra the methyl groups of the *n*NHC ligand in **5** appeared as a single broad signal, indicating that there is slow rotation about the Ir–NHC bonds at room temperature. At 5 °C, the resonances resolve into two distinct singlets at  $\delta$ 3.86 and 3.85 ppm which coalesce at approximately ca. 25 °C. At 50 °C, rotation is fast on the NMR time-scale and the two methyl groups resonate as a single sharp peak at  $\delta$ 3.89 ppm.  $^1\text{H}$  NMR spectra showing the N–CH<sub>3</sub> region of **5** from 5 to 50 °C are shown in Fig. 2. The two triazole methyl groups resonate as sharp singlets at all temperatures ( $\delta$ 4.01 and 3.82 ppm at 5 °C). All four methyl groups exhibit a temperature dependent change in chemical shifts. Line-shape analysis (15 °C) gave  $\Delta G^\ddagger = 16.2$  kcal/mol for rotation about the M–C bond, corresponding to a rate of rotation of ca. 2.8 Hz at 15 °C.

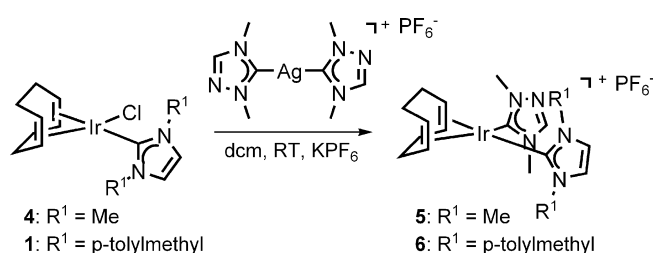
The same route (Scheme 2) is also suitable for the synthesis of an Ir(*t*NHC)(*n*NHC) complex, **6**, where the two NHC ligands are both sterically and electronically dissimilar.

The reaction proceeded at room temperature, although it required an excess of the  $\text{Ag}(\text{tNHC})$  complex (1 eq.), and a much longer reaction time (55 h) than for **5**. An 88% yield of **6** was obtained after column chromatography.

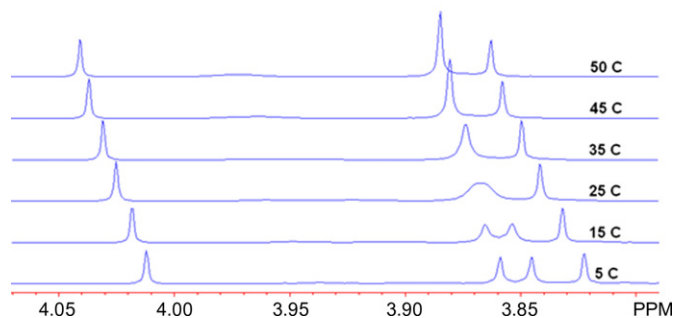
Unsurprisingly, the methylene protons are diastereotopic in the  $^1\text{H}$  NMR, indicative of hindered rotation around the M–carbene bonds. Furthermore, because rotation around the M–carbene



Scheme 1. Synthesis of  $[\text{Ir}(\text{cod})\text{bis}(\text{nNHC})]\text{PF}_6$  complexes **2** and **3**.



Scheme 2. Synthesis of the  $[\text{Ir}(\text{cod})(\text{tNHC})(\text{nNHC})]\text{PF}_6$  complexes, **5** and **6**.



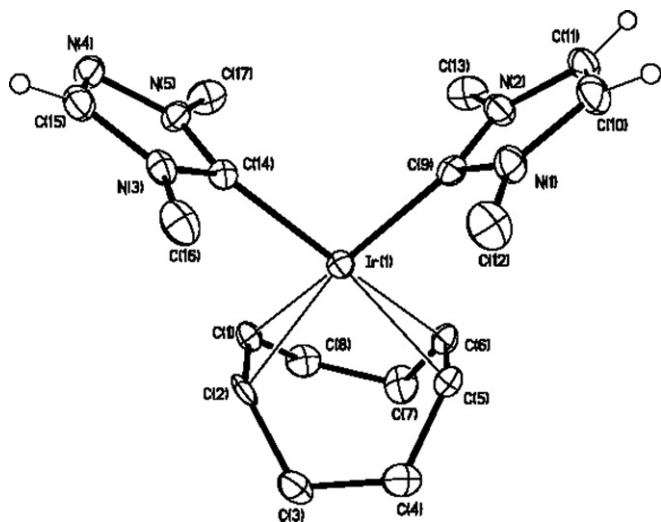
**Fig. 2.** The methyl region of the  $^1\text{H}$  NMR spectra of **5** at various temperatures showing line broadening of the imidazole methyl groups due to rotation about the M-carbene bonds.

bonds is slow on the NMR time-scale and the tNHC ligand is not symmetric, the two “halves” of the nNHC ligand are inequivalent in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The four methylene protons resonate in the  $^1\text{H}$  NMR spectrum as two overlapping AB patterns, each a pair of doublets, while the methylene carbons resonate in the  $^{13}\text{C}$  NMR spectrum as barely differentiated singlets. The aromatic carbons in the tolyl groups resonate as eight distinct peaks in the  $^{13}\text{C}$  NMR spectra and the backbone of the imidazole ring also resonates as two signals. In the  $^1\text{H}$  NMR, the two imidazole protons resonate as singlets, while the  $\text{CH}_{\text{tolyl}}$  resonances are overlapped, resonating as an apparent doublet ( $\delta 7.20$  ppm, 4H) and apparent triplet ( $\delta 6.91$  ppm, 4H) that are due to pairs of overlapped doublets.

### 2.3. Structure determination of **5**

X-ray quality crystals of **5** were grown by layering a solution of **5** in dichloromethane with hexanes, and the complex was fully characterized by single crystal X-ray diffraction (Fig. 3).

The compound crystallizes in the chiral orthorhombic space group  $P2_12_12_1$ . The iridium is square planar. Protons H(10A), H(11A), and H(15A) were located from the residual electron difference map to confirm the orientation and atom identification of the heterocycles. The Ir–C<sub>nNHC</sub> bond length Ir–C(9) is 2.033(5) Å and the Ir–C<sub>tNHC</sub> bond length Ir–C(14) is 2.045(6) Å. The Ir–C<sub>nNHC</sub> bond lengths are within the range of bond lengths reported for other cationic Ir(I)-bis(NHC) complexes [49–56] in which Ir–C<sub>nNHC</sub> bonds range from 2.02 to 2.10 Å. The Ir–C<sub>tNHC</sub> bonds (2.045 Å) are slightly



**Fig. 3.** An ORTEP diagram of **5** showing 30% probability ellipsoids.

**Table 1**  
Selected bond lengths (Å) and angles ( $^\circ$ ) for **5**

Ir(1)–C(9)	2.033(5)	C(9)–Ir(1)–C(14)	96.6(2)
Ir(1)–C(14)	2.045(6)	N(2)–C(9)–N(1)	103.3(4)
Ir(1)–C(5)	2.162(5)	N(2)–C(9)–Ir(1)	126.5(4)
Ir(1)–C(6)	2.174(5)	N(1)–C(9)–Ir(1)	129.4(4)
Ir(1)–C(1)	2.173(5)	N(5)–C(14)–N(3)	102.4(5)
Ir(1)–C(2)	2.186(5)	N(5)–C(14)–Ir(1)	128.1(4)
		N(3)–C(14)–Ir(1)	129.0(4)

longer than those (2.031–2.038 Å) in the only other reported cationic bis(tNHC) complex [15], but the difference is small and a range of bond lengths is expected. Selected bond lengths and angles are included in Table 1.

### 2.4. Synthesis of an Ir(aNHC)(tNHC) complex

Finally, we wished to target the synthesis of bis(NHC) complexes containing abnormally bound NHCs as shown in Scheme 3. Abnormal NHCs are much stronger electron donors than nNHCs and tNHCs [57–59]. In addition, because the aNHC complexes are quite sterically bulky near the metal center, this would allow us to test the synthetic method for NHCs substituted with tert-alkyl substituents at the nitrogens. Because of the increased steric bulk in the aNHC we chose a small tNHC in order to optimize the chances of forming the bis(NHC) complex (Scheme 3).

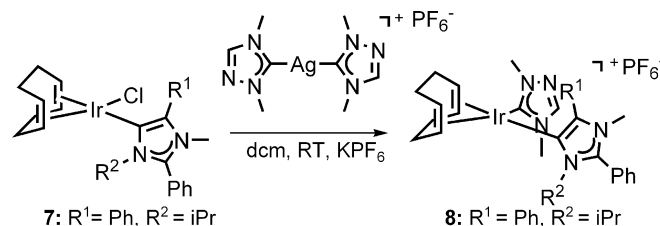
Complex **8** was synthesized in 52% yield over 24 h at room temperature, using 0.8 eq. of  $[\text{Ag}(\text{tNHC})_2]\text{PF}_6$ , and was recrystallized from dichloromethane/pentane. Complex **8** forms as a pair of diastereomers in a nearly equal ratio (53:47), which recrystallization did not significantly alter.

The  $^1\text{H}$  NMR spectra of the two diastereomers could be individually assigned, based on integration. In the  $^{13}\text{C}$  NMR spectra, there are four Ir-carbene peaks, two for each diastereomer, at  $\delta$  183.84, 183.48, 155.36, and 155.09 ppm. By comparison to literature values the downfield peaks are assigned to the tNHC carbene carbon, and the upfield peaks are assigned to the aNHC carbene carbon. Complete NMR assignments are given in Section 4.

An attempt to synthesize the Ir(nNHC)(aNHC) complex analogous to **8**, using 4 eq.  $\text{Ag}(\text{nNHC})_2\text{PF}_6$  and stirring at room temperature for 120 h (5 days), gave less than 10% conversion, insufficient for adequate characterization.

### 3. Conclusions

We describe a facile and general method for the synthesis of Ir(I) complexes with two different monodentate NHC ligands, via a stepwise approach. We demonstrated the utility of this method for complexes with combinations of nNHCs, tNHCs, and aNHCs. More hindered products, such as **2**, require more forcing conditions, but still give the desired products in satisfactory yields. The complexes do not disproportionate in solution, consistent with the non-lability of the metal–NHC bonds. This method enables control of both the steric and electronic characteristics of this non-labile bis-NHC ligand set.



**Scheme 3.** Synthesis of the  $[\text{Ir}(\text{cod})(\text{aNHC})(\text{tNHC})]\text{PF}_6$  complex, **8**.

## 4. Experimental

### 4.1. General methods

The iridium complexes **1** [45], **4** [13], and **7** [58] and the salts 1,3-di(*n*-butyl)imidazolium bromide [60], 1,4-dimethyl-1,2,4-triazolium iodide and 1,3-dimethylimidazolium iodide were synthesized as reported in the literature [61]. All other reagents were purchased commercially and used as received. Syntheses were performed in air using reagent grade solvents, unless stated otherwise. Column chromatography was performed on silica gel (Silica Gel 60, 40–63  $\mu\text{m}$ , EMD). Isolated yields are given for all products. NMR spectra were recorded on Bruker spectrometers operating at 400 or 500 MHz ( $^1\text{H}$  NMR), 100 or 125 MHz ( $^{13}\text{C}$  NMR), and 160 or 200 MHz ( $^{31}\text{P}$  NMR), and referenced to the residual solvent signal. NMR spectra were obtained at room temperature unless otherwise noted. Assignments are based on  $^1\text{H}$ ,  $^{13}\text{C}$ , HMQC, and DEPT NMR spectroscopy. Elemental analyses were performed by Atlantic Microlab Inc.

### 4.2. Synthesis of Ag NHC complexes

The Ag NHC complexes were synthesized by the method described by Youngs [47]. In the case of the dimethyl imidazolium and triazolium salts a modification was necessary because the silver NHC halide complexes are only slightly soluble in water. The desired procedure was the same except  $\text{KPF}_6$  was added prior to filtration, and the product was isolated by extraction into dichloromethane, rather than by filtration. Detailed procedures are reported in the experimental procedures for the respective metal complexes. For all products, conversion of the imidazolium salts to the silver complexes was confirmed by observing the disappearance of the C2 (imidazolium) or C5 (triazolium) protons by  $^1\text{H}$  NMR spectroscopy ( $\text{CD}_2\text{Cl}_2$ ). The silver salts begin to darken within hours if exposed to light and were used without further purification on the same day they were synthesized.

### 4.3. (1,3-Di(*n*-butyl)imidazol-2-ylidene)(1,3-di(*p*-tolylmethyl)imidazol-2-ylidene)( $\eta^4$ -1,5-cyclooctadiene)iridium (I) hexafluorophosphate (**2**)

1,3-Di(*n*-butyl)imidazolium bromide (305 mg, 1.17 mmol) was combined in water with silver (I) oxide (235 mg, 1.01 mmol) and stirred in the dark at room temperature for 30 min. The reaction mixture was filtered to remove excess silver (I) oxide. Potassium hexafluorophosphate (275 mg, 1.49 mmol) was added resulting in the immediate precipitation of the silver NHC compound as an off-white solid, which was collected by filtration (279 mg, 0.455 mmol, assuming  $\text{Ag}(\text{NHC})_2\text{PF}_6$ ). The  $\text{Ag}(\text{NHC})$  complex (209 mg, 0.341 mmol) was combined with **1** (35 mg, 0.0572 mmol) and potassium hexafluorophosphate (12 mg, 0.0652 mmol) in a small flask and placed under an inert atmosphere. Degassed dichloromethane (20 mL) was added and the reaction mixture stirred at reflux, in the dark, for 36 h. Removal of the solvent under vacuum and purification by column chromatography (50:50 ethyl acetate/hexanes followed by 100% ethyl acetate) to yield the product as a bright orange solid (25 mg, 48% yield).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500.0 MHz)  $\delta$  7.18 (4H, d,  $^3J_{\text{H-H}} = 8.0$  Hz,  $\text{CH}_{\text{tol}}$ ), 6.93 (2H, s,  $\text{CH}_{\text{imid}}$ ), 6.86 (4H, d,  $^3J_{\text{H-H}} = 8.0$  Hz,  $\text{CH}_{\text{tol}}$ ), 6.85 (2H, s,  $\text{CH}_{\text{imid}}$ ), 5.78 (2H, d,  $^1J_{\text{H-H}} = 15.2$  Hz,  $\text{NCH}_2\text{tol}$ , diastereotopic), 5.38 (2H, d,  $^1J_{\text{H-H}} = 15.2$  Hz,  $\text{NCH}_2\text{tol}$ , diastereotopic), 4.48 (2H, dq,  $^1J_{\text{H-H}} = 11.0$  Hz,  $J_{\text{H-H}} = 5.7$  Hz,  $\text{NCH}_2\text{butyl}$ , diastereotopic), 3.89 (4H, m,  $\text{CH}_{\text{cod}}$ ), 3.53 (2H, dq,  $^1J_{\text{H-H}} = 11.0$  Hz,  $J_{\text{H-H}} = 5.7$  Hz,  $\text{NCH}_2\text{butyl}$ , diastereotopic), 2.36 (6H, s,  $\text{CH}_3\text{tol}$ ), 2.19 (4H, m,  $\text{CH}_2\text{cod}$ ), 1.93 (4H, m,  $\text{CH}_2\text{cod}$ ), 1.73 (2H, m,  $\text{CH}_2\text{butyl}$ , diastereotopic), 1.64 (2H, m,

$\text{CH}_2\text{butyl}$ , diastereotopic), 1.34 (4H, m,  $\text{CH}_2\text{butyl}$ , diastereotopic), 0.94 (6H, t,  $^3J_{\text{H-H}} = 7.4$  Hz,  $\text{CH}_3\text{butyl}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125.8 MHz)  $\delta$  178.97 (s, Ir-C<sub>carbene</sub>), 175.99 (s, Clr-C<sub>carbene</sub>), 139.16 (s,  $\text{C}_{\text{tol ipso}}$ ), 132.79 (s,  $\text{C}_{\text{tol ipso}}$ ), 130.39 (s,  $\text{CH}_{\text{tol}}$ ), 127.15 (s,  $\text{CH}_{\text{tol}}$ ), 122.50 (s,  $\text{CH}_{\text{NHC}}$ ), 121.32 (s,  $\text{CH}_{\text{NHC}}$ ), 77.33 (s,  $\text{CH}_{\text{cod}}$ ), 76.76 (s,  $\text{CH}_{\text{cod}}$ ), 54.76 (s,  $\text{NCH}_2\text{tol}$ ), 50.92 (s,  $\text{CH}_2\text{butyl}$ ), 33.21 (s,  $\text{CH}_2\text{butyl}$ ), 31.94 (s,  $\text{CH}_2\text{cod}$ ), 31.86 (s,  $\text{CH}_2\text{cod}$ ), 21.40 (s,  $\text{CH}_3\text{tol}$ ), 20.70 (s,  $\text{CH}_2\text{butyl}$ ), 14.05 (s,  $\text{CH}_3\text{butyl}$ ). Anal. Calc. for  $\text{C}_{38}\text{H}_{52}\text{N}_4\text{PF}_6$ : C, 50.60; H, 5.81; N, 6.21. Found: C, 50.10; H, 5.81; N, 6.09.

### 4.4. (1,3-Dimethylimidazol-2-ylidene)(1,3-di(*p*-tolylmethyl)imidazol-2-ylidene)( $\eta^4$ -1,5-cyclooctadiene)iridium (I) hexafluorophosphate (**3**)

1,3-Dimethylimidazolium bromide (577 mg, 2.58 mmol) was combined in water with silver (I) oxide (612 mg, 2.64 mmol) and stirred in the dark at room temperature for 30 min. Potassium hexafluorophosphate (712 mg, 3.87 mmol) was added. Dichloromethane (50 mL) was added to the reaction mixture and the mixture stirred vigorously for several minutes, then filtered. The dichloromethane layer was separated and the water layer extracted two times with dichloromethane (20 mL). All organic layers were combined, dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure to yield the Ag NHC complex as a white solid (208 mg, 18% yield, assuming  $\text{Ag}(\text{NHC})_2\text{PF}_6$ ). The  $\text{Ag}(\text{NHC})$  complex (30 mg, 0.0674 mmol) was combined with **1** (16 mg, 0.0261 mmol) and potassium hexafluorophosphate (8 mg, 0.0435 mmol) in a small flask and placed under an inert atmosphere. Degassed dichloromethane (5 mL) was added and the reaction mixture stirred at room temperature, in the dark, for 72 h. Removal of the solvent under vacuum and purification by column chromatography (50:50 ethyl acetate/hexanes followed by 100% ethyl acetate) to yield the product as a bright orange solid (16 mg, 75% yield) which was recrystallized from dichloromethane/pentane.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500.0 MHz)  $\delta$  7.18 (4H, d,  $^3J_{\text{H-H}} = 7.8$  Hz,  $\text{CH}_{\text{tol}}$ ), 6.89 (4H, d,  $^3J_{\text{H-H}} = 7.8$  Hz,  $\text{CH}_{\text{tol}}$ ), 6.87 (2H, s,  $\text{CH}_{\text{NHC}}$ ), 6.84 (2H, s,  $\text{CH}_{\text{NHC}}$ ), 5.74 (2H, d,  $^1J_{\text{H-H}} = 15.5$  Hz,  $\text{CH}_{\text{tol}}$ , diastereotopic), 5.48 (2H, d,  $^1J_{\text{H-H}} = 15.5$  Hz,  $\text{CH}_{\text{tol}}$ , diastereotopic), 3.96 (2H, m,  $\text{CH}_{\text{cod}}$ ), 3.84 (2H, m,  $\text{CH}_{\text{cod}}$ ), 3.66 (6H, s,  $\text{NCH}_3$ ), 2.36 (6H, s,  $\text{CH}_3\text{tol}$ ), 2.23 (4H, m,  $\text{CH}_2\text{cod}$ ), 1.94 (4H, m,  $\text{CH}_2\text{cod}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125.8 MHz)  $\delta$  179.15 (s, Ir-C<sub>carbene</sub>), 177.90 (s, Clr-C<sub>carbene</sub>), 139.10 (s,  $\text{C}_{\text{tol ipso}}$ ), 132.94 (s,  $\text{C}_{\text{tol ipso}}$ ), 130.34 (s,  $\text{CH}_{\text{tol}}$ ), 127.20 (s,  $\text{CH}_{\text{tol}}$ ), 123.41 (s,  $\text{CH}_{\text{NHC}}$ ), 122.46 (s,  $\text{CH}_{\text{NHC}}$ ), 77.53 (s,  $\text{CH}_{\text{cod}}$ ), 77.27 (s,  $\text{CH}_{\text{cod}}$ ), 54.78 (s,  $\text{NCH}_2\text{tol}$ ), 37.90 (s,  $\text{NCH}_3\text{NHC}$ ), 31.86 (s,  $\text{CH}_2\text{cod}$ ), 21.40 (s,  $\text{CH}_3\text{tol}$ ). Anal. Calc. for  $\text{C}_{32}\text{H}_{40}\text{N}_4\text{IrPF}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$ : C, 45.37; H, 4.80; N, 6.51. Found: C, 45.55; H, 4.86; N, 6.49.

### 4.5. (1,3-Dimethylimidazol-2-ylidene)(1,4-dimethyl-1,2,4-imidazol-5-ylidene)( $\eta^4$ -1,5-cyclooctadiene)iridium (I) hexafluorophosphate (**5**)

1,4-Dimethyl-1,2,4-triazolium iodide (256 mg, 1.14 mmol) was combined in water with silver (I) oxide (146 mg, 0.630 mmol) and stirred in the dark at room temperature for 10 min after which potassium hexafluorophosphate (375 mg, 2.03 mmol) was added. Dichloromethane (30 mL) was added to the reaction mixture and the mixture stirred vigorously for several minutes, then filtered. The dichloromethane layer was separated and the water layer extracted two times with dichloromethane (10 mL). All organic layers were combined, dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure to yield the Ag NHC complex as a white solid (99 mg, 39% yield, assuming  $\text{Ag}(\text{NHC})_2\text{PF}_6$ ). The  $\text{Ag}(\text{NHC})$  complex (60 mg, 0.134 mmol) was combined with **4** (106 mg, 0.245 mmol) and potassium hexafluorophosphate (23 mg, 0.125 mmol) in a small flask and placed under an inert atmosphere. Degassed dichloromethane (5 mL) was added and the reaction mixture stirred at room temperature, in the dark, for 12 h. Removal of the solvent under vacuum and purification by column chromatography



(ethyl acetate followed by acetone/KPF<sub>6</sub>) yield the product as a bright orange solid (114 mg, 73% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500.0 MHz, 298.15 K) δ 8.06 (s, 1H, H<sub>Tz</sub>), 6.98 (s, 2H, H<sub>imid</sub>), 4.06 (s, 3H, NCH<sub>3Tz</sub>), 3.97 (br m, 1H, CH<sub>cod</sub>), 3.94 (br m, 1H, CH<sub>cod</sub>), 3.90 (s, 3H, NCH<sub>3Tz</sub>), 3.89 (br s, 6H, NCH<sub>3imid</sub>), 3.82 (br m, 2H, CH<sub>cod</sub>), 2.30 (br m, 4H, CH<sub>2cod</sub>), 2.01 (br m, 4H, CH<sub>2cod</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz, 298.15 K) δ 181.61 (s, Ir–C<sub>Tz</sub>), 176.46 (s, Ir–C<sub>imid</sub>), 144.61 (s, CH<sub>Tz</sub>), 123.49 (s, CH<sub>imid</sub>), 123.45 (s, CH<sub>imid</sub>), 79.29 (br s, CH<sub>cod</sub>), 78.72 (br s, CH<sub>cod</sub>), 77.37 (br s, CH<sub>cod</sub>), 77.17 (br s, CH<sub>cod</sub>), 40.45 (s, NCH<sub>3Tz</sub>), 38.28 (br s, NCH<sub>3imid</sub>), 35.56 (s, NCH<sub>3Tz</sub>), 31.94 (br s, CH<sub>2cod</sub>), 31.86 (br s, CH<sub>2cod</sub>), 31.52 (br s, CH<sub>2cod</sub>). Anal. Calc. for C<sub>17</sub>N<sub>5</sub>H<sub>27</sub>IrPF<sub>6</sub>: C, 31.97; H, 4.26; N, 10.97. Found: C, 31.94; H, 4.27; N, 10.80.

#### 4.6. Variable temperature NMR studies of **5**

Variable temperature NMR studies of **5** were performed using solutions of **5** in CD<sub>3</sub>CN to allow access to a wider temperature range than CD<sub>2</sub>Cl<sub>2</sub>. However, broadening of the <sup>1</sup>H and <sup>13</sup>C NMR peaks was also observed in CD<sub>2</sub>Cl<sub>2</sub> at room temperature.

#### 4.7. (1,4-Dimethyl-1,2,4-triazol-5-ylidene)(1,3-di(*p*-tolylmethyl)-imidazol-2-ylidene)(η<sup>4</sup>-1,5-cyclooctadiene)iridium (I) hexafluorophosphate (**6**)

1,4-Dimethyl-1,2,4-triazolium iodide (68 mg, 0.302 mmol) was combined in water with silver (I) oxide (70 mg, 0.302 mmol) and stirred in the dark at room temperature for 30 min after which potassium hexafluorophosphate (113 mg, 0.614 mmol) was added. Dichloromethane (30 mL) was added to the reaction mixture and the mixture stirred vigorously for several minutes. The dichloromethane layer was separated and the water layer extracted two times with dichloromethane (30 mL). All organic layers were combined, dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure to yield the Ag NHC complex as a white solid (66 mg, 98% yield, assuming Ag(NHC)<sub>2</sub>PF<sub>6</sub>). The Ag(NHC) complex (16 mg, 0.0335 mmol) was combined with **1** (22 mg, 0.0359 mmol) and potassium hexafluorophosphate (11 mg, 0.0598 mmol) in a small flask and placed under an inert atmosphere. Degassed dichloromethane (5 mL) was added and the reaction mixture stirred at room temperature, in the dark, for 54 h. Removal of the solvent under vacuum and purification by column chromatography (ethyl acetate followed by acetone/KPF<sub>6</sub>) yield the product as a bright orange solid (26 mg, 88% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500.0 MHz) δ 7.97 (s, 1H, H<sub>Tz</sub>), 7.20 (br d, 4H, <sup>3</sup>J<sub>H–H</sub> = 8.0 Hz, CH<sub>tol</sub>), 6.91 (apparent t, 4H, <sup>3</sup>J<sub>H–H</sub> = 8.0 Hz, CH<sub>tol</sub>), 6.88 (s, CH<sub>imid</sub>), 6.87 (s, CH<sub>imid</sub>), 5.75–5.49 (m, 4H, CH<sub>2</sub> methylene), 4.07 (m, 2H, CH<sub>cod</sub>), 3.82 (m, 2H, CH<sub>cod</sub>), 3.80 (s, 3H, NCH<sub>3Tz</sub>), 3.69 (s, 3H, NCH<sub>3Tz</sub>), 2.36 (s, 6H, CH<sub>3tol</sub>), 2.24 (m, 4H, CH<sub>2cod</sub>), 2.00 (m, 4H, CH<sub>2cod</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz) δ 181.08 (s, Ir–C<sub>Tz</sub>), 177.73 (s, Ir–C<sub>imid</sub>), 144.66 (s, CH<sub>Tz</sub>), 139.23 (s, C<sub>ipso tol</sub>), 132.86 (s, C<sub>ipso tol</sub>), 132.78 (s, C<sub>ipso tol</sub>), 132.72 (s, C<sub>ipso tol</sub>), 130.44 (s, CH<sub>tol</sub>), 130.43 (s, CH<sub>tol</sub>), 127.16 (s, CH<sub>tol</sub>), 127.14 (s, CH<sub>tol</sub>), 122.81 (s, CH<sub>imid</sub>), 122.66 (s, CH<sub>imid</sub>), 79.80 (s, CH<sub>cod</sub>), 79.42 (s, CH<sub>cod</sub>), 78.22 (s, CH<sub>cod</sub>), 77.95 (s, CH<sub>cod</sub>), 54.81 (s, CH<sub>2</sub> methylene), 40.06 (s, NCH<sub>3Tz</sub>), 35.28 (s, NCH<sub>3Tz</sub>), 32.17 (s, CH<sub>2cod</sub>), 32.02 (s, CH<sub>2cod</sub>), 31.90 (s, CH<sub>2cod</sub>), 31.65 (s, CH<sub>2cod</sub>), 31.64 (s, CH<sub>2cod</sub>), 21.40 (s, CH<sub>3tol</sub>). Anal. Calc. for C<sub>31</sub>H<sub>39</sub>N<sub>5</sub>IrPF<sub>6</sub>: C, 45.47; H, 4.80; N, 8.55. Found: C, 45.72; H, 4.82; N, 8.40.

#### 4.8. (1,4-Dimethyl-1,2,4-triazol-5-ylidene)(1-isopropyl-2,4-diphenyl-3-methylimidazol-5-ylidene)(η<sup>4</sup>-1,5-cyclooctadiene)iridium (I) hexafluorophosphate (**8**)

1,4-Dimethyl-1,2,4-triazolium iodide (68 mg, 0.302 mmol) was combined in water with silver (I) oxide (70 mg, 0.302 mmol) and

stirred in the dark at room temperature for 30 min after which potassium hexafluorophosphate (113 mg, 0.614 mmol) was added. Dichloromethane (30 mL) was added to the reaction mixture and the mixture stirred vigorously for several minutes. The dichloromethane layer was separated and the water layer extracted two times with dichloromethane (30 mL). All organic layers were combined, dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure to yield the Ag NHC complex as a white solid (66 mg, 98% yield, assuming Ag(NHC)<sub>2</sub>PF<sub>6</sub>). The Ag(NHC) complex (31 mg, 0.0693 mmol) was combined with **7** (50 mg, 0.0817 mmol) and potassium hexafluorophosphate (12 mg, 0.0652 mmol) in a small flask and placed under an inert atmosphere. Degassed dichloromethane (10 mL) was added and the reaction mixture stirred in the dark, at room temperature, for 24 h. Removal of the solvent under reduced pressure and purification by column chromatography (50:50 ethyl acetate/hexanes followed by 100% ethyl acetate) yields the product as a bright orange solid (35 mg, 52% yield) which was recrystallized from dcm/pentane. The compound forms as a mixture of diastereomers (53:47) and was not noticeably enriched on recrystallization. The <sup>1</sup>H NMR spectra of the diastereomers were differentiated based on integrations and <sup>1</sup>H–<sup>1</sup>H COSY NMR spectroscopy and are reported for the major and minor isomers separately. The <sup>13</sup>C NMR is reported for both diastereomers. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) (*major diastereomer*) δ 7.85 (s, 1H, CH<sub>Tz</sub>), 7.70–7.41 (m, CH<sub>Ar</sub>), 5.69 (sept, CH<sub>iPr</sub>), 4.26 (m, 2H, CH<sub>cod</sub>), 4.03 (s, 3H, NCH<sub>3Tz</sub>), 3.32 (m, 2H, CH<sub>cod</sub>), 3.10 (s, 3H, NCH<sub>3aNHC</sub>), 2.85 (s, 3H, NCH<sub>3Tz</sub>), 2.35–2.10 (m, CH<sub>2cod</sub>), 2.09–1.74 (m, CH<sub>2cod</sub>), 1.49 (apparent t, 3H, CH<sub>3iPr</sub>), 1.25 (apparent t, 3H, CH<sub>3iPr</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz), (*minor diastereomer*) δ 7.97 (s, 1H, CH<sub>Tz</sub>), 7.70–7.41 (m, CH<sub>Ar</sub>), 5.69 (sept, CH<sub>iPr</sub>), 4.35 (m, 1H, CH<sub>cod</sub>), 4.24 (m, 1H, CH<sub>cod</sub>), 3.88 (s, 3H, NCH<sub>3Tz</sub>), 3.46 (m, 2H, CH<sub>cod</sub>), 3.08 (s, 3H, NCH<sub>3aNHC</sub>), 2.95 (s, 3H, NCH<sub>3Tz</sub>), 2.35–2.10 (m, CH<sub>2cod</sub>), 2.09–1.74 (m, CH<sub>2cod</sub>), 1.49 (apparent t, 3H, CH<sub>3iPr</sub>), 1.25 (apparent t, 3H, CH<sub>3iPr</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz), (*mixture of diastereomers*) δ 183.84, 183.48 (Ir–C<sub>Tz</sub>), 155.36, 155.09 (Ir–C<sub>aNHC</sub>), 144.29, 144.21, 144.04, 134.84, 132.39, 132.37, 131.89, 131.79, 131.71, 131.67, 131.50, 131.41, 129.94, 129.68, 129.60, 129.37, 129.34, 126.37, 126.32 (C<sub>Ar</sub>), 80.34, 79.88, 77.73, 76.72, 72.19, 72.10, 72.05, 71.92 (CH<sub>cod</sub>), 58.02, 57.91 (CH<sub>iPr</sub>), 39.88, 38.33, 34.95 (NCH<sub>3Tz</sub>), 33.88, 33.77 (NCH<sub>3aNHC</sub>), 33.71 (NCH<sub>3Tz</sub>), 32.49, 32.24, 31.91, 31.78, 31.76, 31.70, 31.26, 31.13 (CH<sub>2cod</sub>), 24.84, 24.58, 23.82, 23.75 (CH<sub>3iPr</sub>). Anal. Calc. for C<sub>31</sub>N<sub>5</sub>H<sub>39</sub>IrPF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 42.53; H, 4.57; N, 7.75. Found: C, 42.66; H, 4.52; N, 7.80.

#### 4.9. Structure determination and refinement of **5**

The structure determination was performed by Dr. Chris D. Incarvito. X-ray diffraction for single crystals was measured on Nonius Kappa CCD diffractometer. Data collection were carried out at –90 °C, using graphite monochromated Mo Kα (λ = 0.71069 Å). The crystal parameters and other experimental details of the data collection are summarized in Table 2.

The compound crystallizes in the chiral orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with one molecule in the asymmetric unit and four molecules in the unit cell. The iridium is square planar (deviation = 0.032 Å) with respect to the C(1–2) and C(5–6) centroids. The heterocyclic carbene ligands are offset from the iridium coordination plane by 89.3 and 86.0 ° for N(1,2)–C(9–11) (nNHC) and N(3–4)–C(14,15) (tNHC), respectively. Protons H(10A), H(11A), and H(15A) were located from the residual electron difference map to confirm the orientation and atom identification of the heterocycles. The C–H bonds were fixed to an ideal distance for ease of refinement. The model was refined as a racemic twin [Flack parameter = 0.495(8)] with unmerged Friedel pairs. Selected bond lengths and angles are included in Table 1.

**Table 2**  
Crystallographic data for **5**

Identification code	crabtree_la04
Empirical formula	C <sub>17</sub> H <sub>27</sub> F <sub>6</sub> IrN <sub>5</sub> P
Formula weight	638.61
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	11.326(2)
<i>b</i> (Å)	13.778(3)
<i>c</i> (Å)	13.801(3)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	2153.6(8)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.970
Absorption coefficient (cm <sup>-1</sup> )	63.39
F(000)	1240
Crystal size (mm <sup>3</sup> )	0.25 × 0.10 × 0.10
Theta range for data collection (°)	2.33–27.50
Index ranges	−14 ≤ <i>h</i> ≤ 14, −17 ≤ <i>k</i> ≤ 17, −17 ≤ <i>l</i> ≤ 17
Reflections collected	4923
Independent reflections [R(int)]	4923 [0.0000]
Completeness to theta = 27.50° (%)	99.4
Absorption correction	None
Maximum and minimum transmission	0.5697 and 0.3002
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4923/0/273
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.028
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0306, <i>wR</i> <sub>2</sub> = 0.0709
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0359, <i>wR</i> <sub>2</sub> = 0.0732
Absolute structure parameter	0.495(8)
Extinction coefficient	0.0022(2)
Largest difference peak and hole (e Å <sup>-3</sup> )	0.814 and −0.847

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## Appendix A. Supplementary material

CCDC 663417 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2008.05.024](https://doi.org/10.1016/j.jorgchem.2008.05.024).

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