

# Iridium Abnormal N-Heterocyclic Carbene Hydrides via Highly Selective C–H Activation

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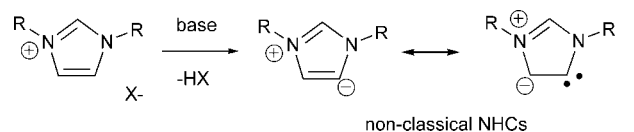
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Imidazoliums with proximal phosphines undergo C–H oxidative addition on [Ir(COD)Cl]<sub>2</sub> to give iridium(III) abnormal carbene hydrides. The effects of the length of the linker between the imidazolium and the phosphine are systematically studied. These C–H activation products can undergo base-promoted H–Cl reductive elimination to afford the corresponding Ir(I) abnormal NHC complexes.

## Introduction

N-Heterocyclic carbenes (NHCs) have become increasingly powerful ligands in organometallic chemistry and catalysis ever since the isolation of free NHCs by Arduengo and co-workers.<sup>1</sup> In many cases metal NHC complexes are highly robust and active in homogeneous catalysis.<sup>2–4</sup> Several general methods have been utilized for the preparation of transition metal NHC complexes.<sup>5</sup> These methods include metalation of free NHCs,<sup>6</sup> transmetalation from silver carbene complexes,<sup>7</sup> insertion of a metal into the C=C bond of an electron-rich olefin such as a bis(imidazolidin-2-ylidene),<sup>8</sup> metalation of carbenes generated *in situ* by the deprotonation of carbene precursors using weak bases,<sup>9</sup> and oxidative addition of C–X (X = H, halogen, and C) bonds of imidazoliums.<sup>10,11</sup> Despite the large number of NHC complexes reported, it is still necessary to prepare NHCs with tunable electronic and steric properties. In this regard, abnormal

NHCs could offer useful variants in terms of electronic and steric effects. It has been recently shown that under certain conditions metalation can take place at the C(4) or C(5) position of an imidazolium rather than at the normal C(2) position (eq 1).<sup>12–16</sup> The zwitterion in this binding mode can be treated as an “abnormal” NHC. The rarity of this binding mode of NHCs is possibly due to the low acidity of the C(4/5)–H. So far most of the abnormal NHCs are part of chelating systems if the active C(2) positions are left unblocked. Crabtree and co-workers have shown that NHCs in this mode are more donating than the most donating neutral ligands such as P<sup>t</sup>Bu<sub>3</sub> and the normal NHCs.<sup>14</sup> Nolan has reported that a palladium abnormal NHC complex is more active in catalyzing Suzuki reactions than a normal analogue.<sup>15</sup>



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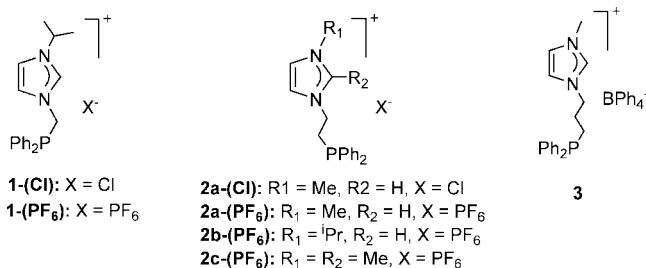
We now report the synthesis of a series of stable iridium hydrides with abnormal NHCs via highly selective cyclometalation of imidazoliums without any necessity to block the C(2) positions.

## Results and Discussion

It has been recently reported that NHC-directed C–H activation of imidazoliums can take place to afford biscarbene

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**Figure 1.** Phosphine-tethered imidazolium salts.

hydride complexes.<sup>11a,b</sup> We reason that phosphine-directed C–H activation of imidazoliums should also readily occur on low-valence metals such as an Ir(I). To the best of our knowledge, there is no report on well-characterized phosphine-directed C–H oxidative addition of imidazoliums, although many chelating phosphine–NHC complexes have been recently reported.<sup>9d,17–19</sup> Thus phosphine–imidazolium ligand precursors (Figure 1) were synthesized by following related reports with slight modifications (see the Supporting Information).<sup>9d,17,18</sup> Indeed, stirring a CD<sub>2</sub>Cl<sub>2</sub> solution of **1**-(PF<sub>6</sub>) and 0.5 equiv of [Ir(COD)Cl]<sub>2</sub> instantaneously gave Ir(I) phosphine **4** (Scheme 1), which decayed cleanly to give iridium(III) hydride **5** (99% NMR yield and 92% isolated yield). Complex **5** can also be synthesized with a similar yield by reacting ligand **1**-(Cl) with [Ir(COD)<sub>2</sub>]PF<sub>6</sub>. In the <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>) of **5**, the hydride resonates at δ –15.81 (d, <sup>2</sup>J<sub>HP</sub> = 7.5 Hz) and this small coupling constant here suggests the *cis* orientation of the hydride and the phosphine. A low-field signal at δ 8.57 was also observed in the <sup>1</sup>H NMR spectrum and was ascribed to the C(2)–H of the imidazole ring. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, the Ir–C(4/5) resonates at δ 135.4 (d, <sup>2</sup>J<sub>CP</sub> = 5.7 Hz), comparable to those reported for abnormal NHCs.<sup>12–14</sup> Diastereotopicity was noted for both the Me groups and the Ph groups. X-ray crystallography further confirmed the identity of complex **5** (Figure 2 and the Supporting Information), and the NHC has the abnormal binding mode with a Ir–C<sub>carbene</sub> distance of 2.049(4) Å.

The clean conversion of **4** to **5** allows kinetic studies of this C–H activation process. The decay of **4** in CDCl<sub>3</sub> follows first-order kinetics, consistent with the intramolecularity of this C–H activation process. The rate constants were measured by <sup>1</sup>H NMR spectroscopy at 297.1 K (*k* = 0.0179 min<sup>–1</sup>), 302.3 K (*k* = 0.0306 min<sup>–1</sup>), 307.6 K (*k* = 0.0508 min<sup>–1</sup>), and 312.9 K (*k* = 0.0847 min<sup>–1</sup>) (see Figure S1, Supporting Information). The Eyring plot from these data gave activation parameters Δ*H*<sup>‡</sup> = 17.4 kcal/mol and Δ*S*<sup>‡</sup> = –16 eu (see Figure S2, Supporting Information). The large negative Δ*S*<sup>‡</sup> value here indicates a highly ordered transition state, as would be expected in this C–H oxidative addition.

The acidity of complex **5** can be demonstrated by base-promoted reductive elimination of HCl using Cs<sub>2</sub>CO<sub>3</sub> in acetone or MeCN (Scheme 1). Thus complex **6** was isolated (92%) and was spectroscopically characterized. In the <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN), the C(2)–H resonates at δ 8.51 and the Ir–C<sub>carbene</sub> resonates at δ 130.6 (d, <sup>2</sup>J<sub>PC</sub> = 11.7 Hz) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. Base-promoted *trans* reductive elimination of HCl

from Ir(III) biscarbene complexes has been recently reported.<sup>11a,b</sup> Complex **6** can be converted back to **5** when treated with 1 equiv of ethereal HCl in acetone.

Ligands **2a–c**-(PF<sub>6</sub> or Cl) behave analogously to **1**-(PF<sub>6</sub>) in the reactions with [Ir(COD)Cl]<sub>2</sub> (Scheme 1). Complexes **7a–c** were also observed as intermediates, leading to the C–H activation products **8a–c**. Unlike the analogous complex **4**, no complete decay of **7a–c** could be observed. Instead, equilibration between complexes **7a–c** and **8a–c** was reached with oxidative addition products (**8a–c**) favored in all cases. The *K*<sub>eq</sub> is smaller in CD<sub>3</sub>CN than in CD<sub>2</sub>Cl<sub>2</sub>. Mixtures of **7a–c** and **8a–c** were spectroscopically characterized, and complex **8a**-(PF<sub>6</sub>) was further characterized by X-ray crystallography (Figure 2 and the Supporting Information). The Ir–C<sub>carbene</sub> distance [2.065(6) Å] is slightly longer than that in **5**. The most remarkable difference is the large bite angle [92.2(4)°] of the phosphine–NHC ligand, as can be accommodated by a larger metallocycle.

The effects of temperatures on this equilibrium were studied in CD<sub>3</sub>CN, and the van't Hoff plots of the equilibration systems for **7a**-(Cl), **7a**-(PF<sub>6</sub>), and **7b**-(PF<sub>6</sub>) gave thermodynamic parameters Δ*H*<sup>°</sup> –22.4, –29.1, and –29.9 kcal/mol and Δ*S*<sup>°</sup> –55.5, –73.9, and –77.5 J/(mol·K), respectively (see Table S1 and Figure S3, Supporting Information). These data indicate that the steric size of the N-alkyl group has no significant effect on the thermodynamics, while the nature of the counterion does. The large negative value of the Δ*S*<sup>°</sup> is consistent with more ordered structures of the products. Crabtree and co-workers reported that under certain conditions counterions could switch the selectivity of C(2)–H versus C(4/5)–H activation of imidazoliums.<sup>13</sup> Here C–H activation consistently occurred at the C(4/5) position regardless of the anions (Cl<sup>–</sup>, PF<sub>6</sub><sup>–</sup>, or SbF<sub>6</sub><sup>–</sup>). The <sup>19</sup>F–<sup>1</sup>H HOESY spectra of both complexes **5** and **8a**-(PF<sub>6</sub>) in CD<sub>2</sub>Cl<sub>2</sub> were obtained, and they showed the correlation between the PF<sub>6</sub><sup>–</sup> anion and the imidazole C(2)–H, suggesting an ion-pairing interaction between these two moieties in solutions (see the Supporting Information).

To make the imidazolium C(2)–H activation more favorable, ligand **10** with blocked C(4/5) positions was synthesized and was allowed to react with [Ir(COD)Cl]<sub>2</sub> (Scheme 2). Formation of Ir(I) complex **11** was clean and instantaneous, but no cyclometalation product was observed (39 °C, 5 h), nor was there any decomposition. This clearly indicates that our phosphine–imidazolium system prefers to undergo C(4/5)–H activation. While detailed reasons behind this selectivity remain unclear, the activation of the C(2)–H bond here would be more sterically unfavorable.<sup>13</sup>

Analogous to complex **5**, deprotonation of complex **8a**-(PF<sub>6</sub>) using Cs<sub>2</sub>CO<sub>3</sub> occurred in MeCN to afford **9** (91%). Field et al. recently reported the synthesis of a related Ir(I) complex with a chelating phosphine–normal NHC ligand via the deprotonation of a phosphine–imidazolium by an internal base.<sup>9d</sup> We synthesized complex **12** by directly following this method (Scheme 3), where the internal base *tert*-butoxide reacts preferably with the more acidic C(2)–H. As a comparison, an oxidative addition–base treatment sequence complementarily afforded abnormal NHC complexes **8a–c** (Scheme 1).

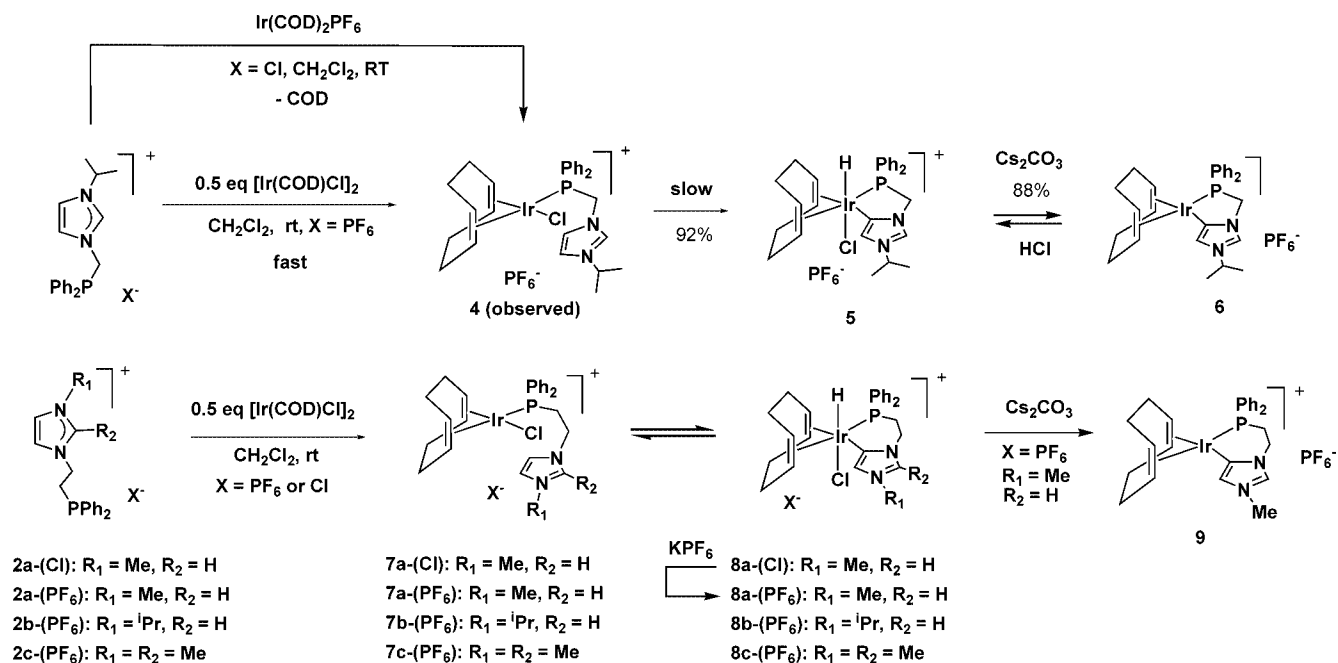
Ligand **3** (Figure 1) with a propylene linker was allowed to react with [Ir(COD)Cl]<sub>2</sub> (0.5 equiv) in CD<sub>2</sub>Cl<sub>2</sub>, but no C–H activation occurred and only phosphine coordination was observed together with partial decomposition (39 °C, 5 h). The failure of C–H activation may be due to thermodynamic and/or kinetic reasons, and the ligand is too flexible for the phosphine to exert any chelation assistance.

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## Scheme 1. Synthesis of iridium abnormal NHC complexes



## Conclusions

We have demonstrated the cyclometalation of imidazoliums with proximal phosphines on iridium(I) complexes such as  $[\text{Ir}(\text{COD})\text{Cl}]_2$  and  $\text{Ir}(\text{COD})_2\text{PF}_6$  to afford iridium(III) abnormal NHC hydrides. The linker between the imidazolium and the phosphine has a big effect. Moving from a methylene linker to an ethylene one, cyclometalation is less thermodynamically favorable. The first-order kinetics was measured for the C–H activation for a phosphine–imidazolium with a methylene linker. These cyclometalation products can be deprotonated by  $\text{Cs}_2\text{CO}_3$  to afford the corresponding Ir(I) complexes. Catalytic applications of these iridium abnormal NHC complexes in hydrogen transfer reactions will be published elsewhere.

## Experimental Section

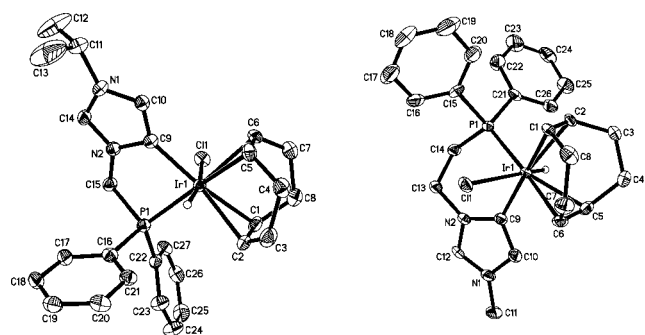
**General Considerations.** All manipulations were carried out using standard Schlenk techniques or in a nitrogen-filled glovebox. NMR spectra were recorded on Bruker DPX 300, Bruker AMX 400, or Bruker 500 spectrometers. All spectra were obtained at 298 K unless otherwise specified. Temperatures ( $\geq 290$  K) of NMR

samples in kinetic and thermodynamic studies were calibrated by using 80% ethylene glycol in  $\text{DMSO}-d_6$ . All chemical shifts are given as  $\delta$  values and are referenced relative to tetramethylsilane for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and relative to 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University, but they were not performed for imidazolium chlorides, which are highly hygroscopic. Instead, their  $\text{PF}_6^-$  salt derivatives were analyzed. HRMS spectra were obtained in ESI or EI mode on a Finnigan MAT95XP GC/HRMS spectrometer (Thermo Electron Corp.). X-ray crystallographic data were collected on a Bruker X8 APEX diffractometer.

All solvents were distilled under  $\text{N}_2$  before use and stored in a glovebox.  $\text{CDCl}_3$  was degassed and dried by 4 Å molecular sieves.  $\text{CD}_2\text{Cl}_2$ ,  $\text{CD}_3\text{CN}$ , and  $\text{DMSO}-d_6$  were obtained from the Cambridge Isotope Laboratory in sealed ampules and were used as received. Air-sensitive compounds were stored and weighed inside a glovebox. Detailed synthesis and characterization data of all the phosphine–imidazolium ligands are described in the Supporting Information.

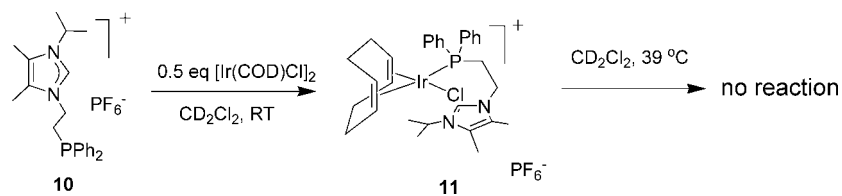
**General Procedures for the Synthesis of Ir(III) Abnormal NHC Hydride Complexes.** To a stirred solution of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (100 mg, 0.149 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added a  $\text{CH}_2\text{Cl}_2$  solution (3 mL) of a phosphine–imidazolium salt (0.297 mmol). The reaction time was 12 h for the synthesis of complex **5**, 2 h for complexes **8a**-(Cl), **8a**-(PF<sub>6</sub>), and **8c**-(PF<sub>6</sub>), and 5 h for complex **8b**-(PF<sub>6</sub>), after which time the color of the solution became pale yellow or nearly colorless. The solution was then concentrated to ca. 0.5 mL followed by addition of diethyl ether (8 mL). Off-white precipitates appeared and were filtered and dried. Analytically pure iridium hydrides were obtained by recrystallization using  $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_2\text{O}$ .

**Complex 5.** Complex **5** was synthesized by following the above general procedure using **1a**-(PF<sub>6</sub>) and  $[\text{Ir}(\text{COD})\text{Cl}]_2$  in  $\text{CH}_2\text{Cl}_2$ . Yields: 92%. Single crystals suitable for X-ray analysis were obtained by the slow diffusion of ether to a  $\text{CH}_2\text{Cl}_2$  solution of **5** after one day. Intermediate **4** was observed in both  $^{31}\text{P}$  ( $\delta$  19.1) and  $^1\text{H}$  [ $\delta$  8.70 (s, imidazole C2-H), 7.20 (d,  $J = 1.4$  Hz, imidazole C4/5-H)] NMR spectroscopy.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **5**:  $\delta$  8.57 (s, 1H, imidazole C2-H), 7.73–7.75 (m, 2H, PPh<sub>2</sub>), 7.49–7.57 (m, 8H, PPh<sub>2</sub>), 6.41 (s, 1H, imidazole H4/5), 5.51 (m, 1H, COD), 5.33–5.39 (m, 1H, COD), 5.03 (m, 1H,

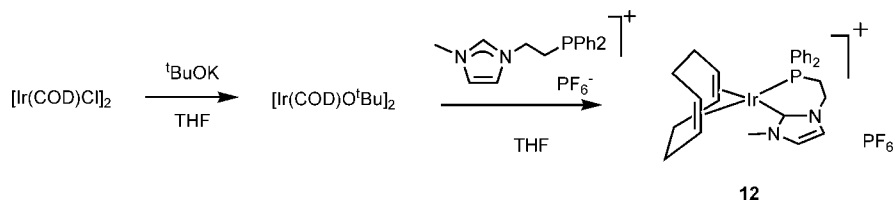


**Figure 2.** Molecular structure of complexes **5** (left) and **8a**-(PF<sub>6</sub>) (right) at the 50% thermal level. Selected lengths (Å) and angles (deg): **5** Ir(1)–C(9): 2.049(4), Ir(1)–P(1): 2.585(1), Ir(1)–Cl(1): 2.5097(9), C(9)–Ir(1)–P(1): 80.98(11), P(1)–Ir(1)–Cl(1): 85.98(3), N(2)–C(9)–Ir(1): 117.9(3). **8a**-(PF<sub>6</sub>) Ir(1)–C(9): 2.065(6), Ir(1)–P(1): 2.316(1), Ir(1)–Cl(1): 2.5076(14), C(9)–Ir(1)–P(1): 92.24(16), P(1)–Ir(1)–Cl(1): 90.83(5), N(2)–C(9)–Ir(1): 126.7(4).

## Scheme 2. Attempted Cyclometalation of a Phosphine–Imidazolium



## Scheme 3. Synthesis of a Related Ir(I) Normal NHC Complex



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COD), 4.98–5.01 (m, 2H, N-CH<sub>2</sub>-P), 4.40 (heptet, *J* = 6.7 Hz, CH of <sup>1</sup>Pr), 4.17–4.19 (m, 1H, COD), 3.03–3.05 (m, 2H, COD), 2.54–2.63 (m, 4H, COD), 2.29 (m, 1H, COD), 2.06–2.10 (m, 1H, COD), 1.50 (d, *J* = 6.6 Hz, 3H, CH<sub>3</sub>), 1.49 (d, *J* = 6.6 Hz, 3H, Me), –15.81 (d, *J*<sub>P-H</sub> = 7.5 Hz, 1H, Ir-H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 27.47 (s, PPh<sub>2</sub>), –144.4 (heptet, *J*<sub>P-F</sub> = 709 Hz, PF<sub>6</sub><sup>–</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 135.4 (d, *J*<sub>P-C</sub> = 5.7 Hz, C-Ir), 133.2 (d, *J*<sub>P-C</sub> = 11.4 Hz, *o*- or *m*-PPh<sub>2</sub>), 132.6 (d, *J*<sub>P-C</sub> = 9.0 Hz, *o*- or *m*-PPh<sub>2</sub>), 132.6 (s, imidazole C2), 132.2 (d, *J*<sub>P-C</sub> = 2.58 Hz, *p*-PPh<sub>2</sub>), 131.1 (d, *J*<sub>P-C</sub> = 11.6 Hz, *ipso*-PPh<sub>2</sub>), 129.5 (d, *J*<sub>P-C</sub> = 11.0 Hz, *o*- or *m*-PPh<sub>2</sub>), 128.9 (d, *J*<sub>P-C</sub> = 11.0 Hz, *o*- or *m*-PPh<sub>2</sub>), 125.7 (d, *J*<sub>P-C</sub> = 59.7 Hz, *ipso*-PPh<sub>2</sub>), 119.1 (s, imidazole C4/5), 95.9 (d, *J*<sub>P-C</sub> = 15.7 Hz, CH of COD), 94.3 (s, CH of COD), 91.7 (d, *J*<sub>P-C</sub> = 9.7 Hz, CH of COD), 84.7 (s, CH of COD), 52.7 (s, CH of <sup>1</sup>Pr), 49.0 (d, *J*<sub>P-C</sub> = 48.7 Hz, N-CH<sub>2</sub>-P), 35.7 (d, *J*<sub>P-C</sub> = 2.5 Hz, CH<sub>2</sub> of COD), 30.1 (s, CH<sub>2</sub> of COD), 29.9 (s, CH<sub>2</sub> of COD), 27.6 (d, *J*<sub>P-C</sub> = 2.8 Hz, CH<sub>2</sub> of COD), 22.7 (s, CH<sub>3</sub> of <sup>1</sup>Pr), 22.5 (s, CH<sub>3</sub> of <sup>1</sup>Pr). Anal. Calcd for C<sub>27</sub>H<sub>34</sub>ClF<sub>6</sub>IrN<sub>2</sub>P<sub>2</sub> (790.1): C, 41.04; H, 4.34; N, 3.55. Found: C, 41.21; H, 4.53; N, 3.48.

**Complex 6.** To a solution of **5** (50 mg, 0.063 mmol) in MeCN (3 mL) was added Cs<sub>2</sub>CO<sub>3</sub> (60 mg, 0.18 mmol), and the mixture was stirred at room temperature for 10 h, during which time the pale yellow solution turned red. A residue was obtained after the removal of MeCN under vacuum, to which was added dichloromethane (5 mL). The inorganic salt was then removed by filtration. Careful removal of all the dichloromethane gave analytically pure complex **6** as an air-sensitive solid (45.9 mg, 92%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): δ 8.51 (s, 1H, imidazole C-2), 7.51–7.60 (m, 10H, PPh<sub>2</sub>), 6.92 (s, 1H, imidazole H4/5), 4.78 (d, *J*<sub>P-C</sub> = 6.4 Hz, 2H, N-CH<sub>2</sub>-P), 4.46 (heptet, *J* = 6.7 Hz, 1H, CH of <sup>1</sup>Pr), 4.31 (br, 3H, COD), 2.09 (m, 9H, COD), 1.46 (d, *J* = 6.6 Hz, 6H, 2CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz CD<sub>3</sub>CN): δ 40.23 (s, PPh<sub>2</sub>), –143.9 (heptet, *J*<sub>P-F</sub> = 704 Hz, PF<sub>6</sub><sup>–</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>3</sub>CN): δ 133.0 (d, *J*<sub>P-C</sub> = 11.9 Hz, *o*- or *m*-PPh<sub>2</sub>), 131.3 (d, *J*<sub>P-C</sub> = 2.1 Hz, *p*-PPh<sub>2</sub>), 130.9 (d, *J*<sub>P-C</sub> = 48 Hz, *ipso*-PPh<sub>2</sub>), 130.7 (s, imidazole C2), 130.6 (d, *J*<sub>P-C</sub> = 11.7 Hz, C-Ir), 129.1 (d, *J*<sub>P-C</sub> = 10.3 Hz, *o*- or *m*-PPh<sub>2</sub>), 122.9 (s, imidazole C4/5), 76.6 (br, CH of <sup>1</sup>Pr), 52.0 (s, CH of COD), 51.4 (d, *J*<sub>P-C</sub> = 39.1 Hz, N-CH<sub>2</sub>-P), 31.3 (s, CH<sub>2</sub> of COD), 22.1 (s, CH<sub>3</sub>). Anal. Calcd for C<sub>27</sub>H<sub>33</sub>F<sub>6</sub>IrN<sub>2</sub>P<sub>2</sub> (753.7): C, 43.03; H, 4.41; N, 3.72. Found: C, 43.32; H, 4.53; N, 3.96.

**Complex 8a.** A mixture of complexes **7a**-(PF<sub>6</sub>) [Ir(I), minor] and **8a**-(PF<sub>6</sub>) [Ir(III), major] was synthesized by following the general procedure for Ir(III) abnormal NHC hydrides. Yields: 87%. Single crystals of **8a**-(PF<sub>6</sub>) suitable for X-ray crystallographic studies were obtained by the slow diffusion of ether into a CH<sub>2</sub>Cl<sub>2</sub> solution after 2 days. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for the major Ir(III) only: δ 8.17 (s, 1H, imidazole C2-H), 7.86–7.91 (m, 2H, PPh<sub>2</sub>), 7.42–7.61 (m, 8H, PPh<sub>2</sub>), 6.40 (s, 1H,

imidazole, H4/5), 5.52 (br, 1H, COD), 4.86–5.02 (m, 2H, N-CH<sub>2</sub>), 4.66 (br, 1H, COD), 3.93–3.96 (m, 1H, COD), 3.76 (s, 3H, CH<sub>3</sub>), 3.42–3.55 (m, 2H, COD), 3.00–3.04 (m, 2H, COD), 2.41–2.65 (m, 5H, 2H of P-CH<sub>2</sub> and 3H of COD), 1.96–1.99 (m, 2H, COD), –15.30 (d, *J*<sub>P-C</sub> = 8.0 Hz, Ir-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ –2.41 [s, major 98.7%, Ir(III)], 13.60 [s, minor 1.3%, Ir(I)], –143.8 (heptet, *J*<sub>P-F</sub> = 709 Hz, PF<sub>6</sub><sup>–</sup>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for Ir(III) only: δ 135.5 (s, N-CH<sub>imid-N</sub>), 134.1 (d, *J*<sub>P-C</sub> = 10.6 Hz, *o*- or *m*-PPh<sub>2</sub>), 132.7 (d, *J*<sub>P-C</sub> = 8.0 Hz, *o*- or *m*-PPh<sub>2</sub>), 132.5 (d, *J*<sub>P-C</sub> = 2.4 Hz, *p*-PPh<sub>2</sub>), 131.4 (d, *J*<sub>P-C</sub> = 2.4 Hz, *p*-PPh<sub>2</sub>), 129.5 (d, *J*<sub>P-C</sub> = 10.6 Hz, *o*- or *m*-PPh<sub>2</sub>), 128.7 (d, *J*<sub>P-C</sub> = 58.0 Hz, *ipso*-PPh<sub>2</sub>), 128.4 (d, *J*<sub>P-C</sub> = 57.2 Hz, *ipso*-PPh<sub>2</sub>), 128.1 (d, *J*<sub>P-C</sub> = 14.0 Hz, *o*- or *m*-PPh<sub>2</sub>), 124.6 (s, imidazole C4/5), 120.6 (d, *J*<sub>P-C</sub> = 9.2 Hz, C-Ir), 98.5 (d, *J*<sub>P-C</sub> = 15.3 Hz, CH of COD), 94.7 (d, *J*<sub>P-C</sub> = 9.4 Hz, CH of COD), 94.4 (s, CH of COD), 84.5 (s, CH of COD), 45.6 (s, N-CH<sub>2</sub>), 36.1 (d, *J*<sub>P-C</sub> = 3.4 Hz, CH<sub>2</sub> of COD), 35.1 (s, CH<sub>3</sub>), 30.1 (s, CH<sub>2</sub> of COD), 29.8 (d, *J*<sub>P-C</sub> = 2.2 Hz, CH<sub>2</sub> of COD), 27.6 (d, *J*<sub>P-C</sub> = 3.7 Hz, CH<sub>2</sub> of COD), 25.3 (d, *J*<sub>P-C</sub> = 39.3 Hz, P-CH<sub>2</sub>). Anal. Calcd for C<sub>26</sub>H<sub>32</sub>ClF<sub>6</sub>IrN<sub>2</sub>P<sub>2</sub>: C, 40.23; H, 4.16; N, 3.61. Found: C, 40.18; H, 4.21; N, 3.76.

**Complex 9.** Complex **9** was obtained as a red solid in 91% yield by directly following the synthesis of complex **6**. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): δ 8.22 (s, 1H, imidazole C2), 7.49–7.62 (m, 10H, PPh<sub>2</sub>), 6.88 (s, 1H, imidazole C4/5), 4.40–4.51 (m, 2H, N-CH<sub>2</sub>), 3.69 (s, 3H, CH<sub>3</sub>), 2.65–2.71 (m, 2H, P-CH<sub>2</sub>), 1.94–2.16 (m, 12H, COD). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>3</sub>CN): δ 10.28 (s, PPh<sub>2</sub>), –143.9 (heptet, *J*<sub>P-F</sub> = 703.6 Hz, PF<sub>6</sub><sup>–</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>CN): δ 149.6 (d, *J*<sub>P-C</sub> = 12.2 Hz, C-Ir), 135.3 (s, imidazole C2), 133.2 (d, *J*<sub>P-C</sub> = 10.9 Hz, *o*- or *m*-PPh<sub>2</sub>), 132.9 (d, *J*<sub>P-C</sub> = 50.4 Hz, *ipso*-PPh<sub>2</sub>), 130.9 (d, *J*<sub>P-C</sub> = 2.4 Hz, *p*-PPh<sub>2</sub>), 128.7 (d, *J*<sub>P-C</sub> = 10.1 Hz, *o*- or *m*-PPh<sub>2</sub>), 127.5 (s, imidazole C5), 48.8 (d, *J*<sub>P-C</sub> = 2.4 Hz, N-CH<sub>2</sub>), 34.5 (s, CH<sub>3</sub>), 31.0 (s, CH<sub>2</sub> of COD), 26.1 (d, *J*<sub>P-C</sub> = 34.7 Hz, CH<sub>2</sub>-P). Anal. Calcd for C<sub>26</sub>H<sub>31</sub>F<sub>6</sub>IrN<sub>2</sub>P<sub>2</sub>: C, 42.22; H, 4.22; N, 3.79. Found: C, 42.13; H, 4.38; N, 3.66.

**Complex 8a-(Cl).** A mixture of complexes **8a**-(Cl) (major) and **7a**-(Cl) (minor) was prepared by following the general synthesis of Ir(III) abnormal NHC hydrides. Yield: 81%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for the major Ir(III) only: δ 10.00 (s, 1H, N-CH<sub>imid-N</sub>), 7.89–7.94 (m, 2H, PPh<sub>2</sub>), 7.42–7.61 (m, 8H, PPh<sub>2</sub>), 6.38 (s, 1H, imidazole H4/5), 5.50 (br, 1H, COD), 5.01–5.09 (m, 2H, N-CH<sub>2</sub>), 4.67 (br, 1H, COD), 3.98–4.10 (m, 1H, COD), 3.81 (s, 3H, CH<sub>3</sub>), 3.72–3.73 (m, 1H, COD), 3.57 (br, 1H of COD), 2.98–3.08 (m, 2H, COD), 2.46–2.68 (m, 5H, 2H of P-CH<sub>2</sub> and 3H of COD), 2.01–2.19 (m, 2H, COD), –15.27 (d, *J*<sub>P-C</sub> = 7.8 Hz, Ir-H). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ –2.32 [s, major 92.4%, Ir(III), PPh<sub>2</sub>], 14.60 [s, minor, 7.6%, Ir(I), PPh<sub>2</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for the major Ir(III) only: δ 137.9 (s, N-CH<sub>imid-N</sub>), 134.2 (d, *J*<sub>P-C</sub> = 10.5 Hz,

*o*- or *m*-PPh<sub>2</sub>), 132.8 (d,  $J_{P-C}$  = 7.89 Hz, *o*-PPh<sub>2</sub>), 132.4 (d,  $J_{P-C}$  = 2.1 Hz, *p*-PPh<sub>2</sub>), 131.3 (d,  $J_{P-C}$  = 2.4 Hz, *p*-PPh<sub>2</sub>), 129.3 (d,  $J_{P-C}$  = 10.9 Hz, *o*- or *m*-PPh<sub>2</sub>), 128.9 (d,  $J_{P-C}$  = 57.9 Hz, *ipso*-PPh<sub>2</sub>), 128.6 (d,  $J_{P-C}$  = 58.5 Hz, *ipso*-PPh<sub>2</sub>), 128.0 (d,  $J_{P-C}$  = 10.4 Hz, *o*- or *m*-PPh<sub>2</sub>), 123.7 (s, imidazole C4/5), 119.8 (d,  $J_{P-C}$  = 9.2 Hz, C-Ir), 98.2 (d,  $J_{P-C}$  = 15.3 Hz, CH of COD), 94.3 (d,  $J_{P-C}$  = 9.4 Hz, CH of COD), 94.0 (s, CH of COD), 84.1 (s, CH of COD), 45.2 (s, N-CH<sub>2</sub>), 36.0 (d,  $J_{P-C}$  = 3.1 Hz, CH<sub>2</sub> of COD), 35.1 (s, CH<sub>3</sub>), 30.3 (s, CH<sub>2</sub> of COD), 29.8 (s, CH<sub>2</sub> of COD), 27.7 (d,  $J_{P-C}$  = 3.6 Hz, CH<sub>2</sub> of COD), 25.4 (d,  $J_{P-C}$  = 39.3 Hz, P-CH<sub>2</sub>). Anal. Calcd for C<sub>26</sub>H<sub>32</sub>Cl<sub>2</sub>IrN<sub>2</sub>P: C, 46.84; H, 4.84; N, 4.20. Found: C, 46.53; H, 4.87; N, 3.92.

**Complex 8b-(PF<sub>6</sub>).** A mixture of complex **8b**-(PF<sub>6</sub>) (major) and **7b**-(PF<sub>6</sub>) (minor) was prepared by following the general synthesis of Ir(III) abnormal NHC hydrides. Yield: 79%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for the major **8b**-(PF<sub>6</sub>) only: δ 8.22 (s, 1H, N-CH<sub>imid</sub>-N), 7.86–7.92 (m, 2H, PPh<sub>2</sub>), 7.39–7.60 (m, 8H, PPh<sub>2</sub>), 6.46 (s, 1H, imidazole H4), 5.51 (br, 1H, COD), 4.91–4.95 (m, 2H, N-CH<sub>2</sub>), 4.67 (br, 1H, COD), 4.37 (heptet,  $J$  = 6.7 Hz, 1H, CH of <sup>1</sup>Pr), 3.94–4.08 (m, 1H, COD), 3.40–3.47 (m, 2H, COD), 3.01–3.05 (m, 2H, COD), 2.41–2.67 (m, 5H, 2H of P-CH<sub>2</sub> and 3H of COD), 2.25 (br, 1H, COD), 1.96–1.99 (m, 1H, COD), 1.47–1.52 (m, 6H, 2CH<sub>3</sub> of <sup>1</sup>Pr), –15.29 (d,  $J_{P-C}$  = 8.1 Hz, Ir-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ –2.44 (s, major 94.7%, Ir(III), PPh<sub>2</sub>), 14.71 (s, minor, 5.3% Ir(I), PPh<sub>2</sub>), –143.8 (heptet,  $J_{P-F}$  = 707.6 Hz, PF<sub>6</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for the Ir(III) only: δ 134.1 (d,  $J_{P-C}$  = 10.6 Hz, *o*- or *m*-PPh<sub>2</sub>), 133.2 (s, N-CH<sub>imid</sub>-N), 132.6 (d,  $J_{P-C}$  = 8.0 Hz, *o*- or *m*-PPh<sub>2</sub>), 132.4 (d,  $J_{P-C}$  = 2.4 Hz, *p*-PPh<sub>2</sub>), 131.4 (d,  $J_{P-C}$  = 2.3 Hz, *p*-PPh<sub>2</sub>), 129.4 (d,  $J_{P-C}$  = 10.7 Hz, *o*- or *m*-PPh<sub>2</sub>), 128.9 (d,  $J_{P-C}$  = 58.0 Hz, *ipso*-PPh<sub>2</sub>), 128.3 (d,  $J_{P-C}$  = 57.8 Hz, *ipso*-PPh<sub>2</sub>), 128.1 (d,  $J_{P-C}$  = 10.5 Hz, *o*-PPh<sub>2</sub>), 121.1 (s, imidazole C4/5), 120.3 (d,  $J_{P-C}$  = 9.3 Hz, C-Ir), 98.2 (d,  $J_{P-C}$  = 15.4 Hz, CH of COD), 94.6 (d,  $J_{P-C}$  = 9.0 Hz, CH of COD), 94.5 (s, CH of COD), 84.6 (s, CH of COD), 52.2 (s, CH of <sup>1</sup>Pr), 45.7 (s, N-CH<sub>2</sub>), 36.1 (d,  $J_{P-C}$  = 3.4 Hz, CH<sub>2</sub> of COD), 30.0 (s, CH<sub>2</sub> of COD), 29.9 (s, CH<sub>2</sub> of COD), 27.5 (d,  $J_{P-C}$  = 3.5 Hz, CH<sub>2</sub> of COD), 25.4 (d,  $J_{P-C}$  = 39.2 Hz, P-CH<sub>2</sub>), 22.7 (s, CH<sub>3</sub>), 22.4 (s, CH<sub>3</sub>). Anal. Calcd for C<sub>28</sub>H<sub>36</sub>ClF<sub>6</sub>IrN<sub>2</sub>P<sub>2</sub>: C, 41.82; H, 4.51; N, 3.48. Found: C, 41.41; H, 4.38; N, 3.26.

**Complex 8c-(PF<sub>6</sub>).** A mixture of complexes **8c**-(PF<sub>6</sub>) (major) and **7c**-(PF<sub>6</sub>) (minor) was prepared by following the general synthesis of Ir(III) abnormal NHC hydrides. Yield: 89%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for the major Ir(III) only: 7.61–7.65 (m, 2H, PPh<sub>2</sub>), 7.45–7.65 (m, 8H, PPh<sub>2</sub>), 6.39 (s, 1H, imidazole H4/5), 5.58–5.59 (m, 1H, COD), 4.90–5.07 (m, 2H, N-CH<sub>2</sub>), 4.66 (br, 1H, COD), 3.48–3.92 (m, 3H, COD), 3.79 (s, 3H, CH<sub>3</sub>), 3.05–3.14 (m, 2H, COD), 2.46–2.68 (m, 5H, 2H of P-CH<sub>2</sub> and 3H of COD), 2.57 (s, 3H, CH<sub>3</sub>), 1.99–2.04 (m, 2H, COD), –15.34 (d,  $J_{P-C}$  = 8.4 Hz, Ir-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ –2.34 [s, major 92.2%, Ir(III), PPh<sub>2</sub>], 12.29 [s, minor, 7.8%, Ir(I), PPh<sub>2</sub>], –143.9 (heptet,  $J_{P-F}$  = 707.6 Hz, PF<sub>6</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for the major Ir(III) only: δ 142.2 (s, N-CH<sub>imid</sub>-N), 134.0 (d,  $J_{P-C}$  = 10.7 Hz, *o*- or *m*-PPh<sub>2</sub>), 132.6 (d,  $J_{P-C}$  = 8.0 Hz, *o*- or *m*-PPh<sub>2</sub>), 132.4 (d,  $J_{P-C}$  = 2.2 Hz, *p*-PPh<sub>2</sub>), 131.4 (d,  $J_{P-C}$  = 2.4 Hz, *p*-PPh<sub>2</sub>), 129.5 (d,  $J_{P-C}$  = 10.7 Hz, *o*- or *m*-PPh<sub>2</sub>), 128.7 (d,  $J_{P-C}$  = 57.8 Hz, *ipso*-PPh<sub>2</sub>), 128.3 (d,  $J_{P-C}$  = 58.0 Hz, *ipso*-PPh<sub>2</sub>), 128.1 (d,  $J_{P-C}$  = 10.4 Hz, *o*- or *m*-PPh<sub>2</sub>), 123.7 (s, imidazole C4/5), 118.2 (d,  $J_{P-C}$  = 9.6 Hz, C-Ir), 99.1 (d,  $J_{P-C}$  = 15.2 Hz, CH of COD), 95.7 (d,  $J_{P-C}$  = 9.3 Hz, CH of COD), 93.9 (s, CH of COD), 84.3 (s, CH of COD), 43.8 (s, N-CH<sub>2</sub>), 36.3 (d,  $J_{P-C}$  = 2.8 Hz, CH<sub>2</sub> of COD), 34.5 (s, CH<sub>3</sub>), 29.9 (s, CH<sub>2</sub> of COD), 29.7 (s, CH<sub>2</sub> of COD), 27.5 (d,  $J_{P-C}$  = 3.5 Hz, CH<sub>2</sub> of COD), 25.5 (d,  $J_{P-C}$  = 39.5 Hz, P-CH<sub>2</sub>), 9.8 (s, CH<sub>3</sub>). No satisfactory microanalysis of **7c**-(PF<sub>6</sub>)/**8c**-(PF<sub>6</sub>) could be obtained. However, the SbF<sub>6</sub><sup>–</sup> salt [**8c**-(SbF<sub>6</sub>)], prepared using the ligand **2c**-(SbF<sub>6</sub>) and [Ir(COD)Cl]<sub>2</sub>, gave satisfactory results.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of this **8c**-(SbF<sub>6</sub>) are almost identical to those of **8c**-(PF<sub>6</sub>). Anal. Calcd for C<sub>27</sub>H<sub>34</sub>ClF<sub>6</sub>IrN<sub>2</sub>Psb: C, 36.81; H, 3.89; N, 3.18. Found: C, 36.45; H, 3.76; N, 3.35.

**Observation of Complex 11.** Compound **10** (13.0 mg, 0.0262 mmol) and [Ir(COD)Cl]<sub>2</sub> (8.8 mg, 0.0131 mmol) were dissolved in CD<sub>2</sub>Cl<sub>2</sub> (0.6 mL), and the solution was loaded into an NMR tube for characterization. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) for complex **11**: δ 8.59 (s, 1H, N-CH<sub>imid</sub>-N), 7.57–7.63 (m, 4H, PPh<sub>2</sub>), 7.46–7.56 (m, 6H, PPh<sub>2</sub>), 5.15–5.17 (m, 2H, COD), 4.80–4.87 (m, 2H, N-CH<sub>2</sub>), 4.33–4.42 (heptet,  $J$  = 6.7 Hz, 1H, CH of <sup>1</sup>Pr), 3.03–3.13 (m, 2H, P-CH<sub>2</sub>), 2.65–2.66 (m, 2H, COD), 2.28 (s, 3H, CH<sub>3</sub>), 2.24 (s, 3H, CH<sub>3</sub>), 2.15–2.27 (m, 2H, COD), 1.90–1.95 (m, 2H, COD), 1.59–1.66 (m, 2H of COD), 1.52 (d,  $J$  = 6.7 Hz, 6H, 2CH<sub>3</sub>). No hydride was observed even after heating for 5 h at 40 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 14, 29 (s, PPh<sub>2</sub>), –143.8 (heptet,  $J_{P-F}$  = 708.0 Hz, PF<sub>6</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 133.5 (d,  $J_{P-C}$  = 10.7 Hz, *o*- or *m*-PPh<sub>2</sub>), 131.3 (s, imidazole C2), 130.9 (d,  $J_{P-C}$  = 2.2 Hz, *p*-PPh<sub>2</sub>), 130.4 (d,  $J_{P-C}$  = 49.0 Hz, *o*-PPh<sub>2</sub>), 127.4 (s, imidazole C4/5), 126.0 (s, imidazole C4/5), 94.6 (d,  $J_{P-C}$  = 14.0 Hz, CH of COD), 54.8 (s, CH of <sup>1</sup>Pr), 50.7 (s, CH of COD), 44.3 (d,  $J_{P-C}$  = 9.5 Hz, N-CH<sub>2</sub>), 33.2 (d,  $J_{P-C}$  = 3.3 Hz, CH<sub>2</sub> of COD), 29.4 (d,  $J_{P-C}$  = 28.5 Hz, P-CH<sub>2</sub>), 29.3 (s, CH<sub>2</sub> of COD), 22.1 (s, 2CH<sub>3</sub>), 8.4 (s, CH<sub>3</sub>), 8.3 (s, CH<sub>3</sub>). No C–H activation product was observed after this sample of **11** was heated at 39 °C for 5 h.

**Reaction between 3 and [Ir(COD)Cl]<sub>2</sub>.** Compound **3** (18.0 mg, 0.0286 mmol) and [Ir(COD)Cl]<sub>2</sub> (9.6 mg, 0.0143 mmol) were dissolved in CD<sub>2</sub>Cl<sub>2</sub> (0.6 mL), and the solution was loaded into an NMR tube for characterization. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.38–7.55 (m, 18H), 6.97–7.02 (m, 8H), 6.87 (s, imidazole H4/5), 6.78–6.83 (m, 4H), 6.63 (s, imidazole H4/5), 5.67 (s, 1H, N-CH<sub>imid</sub>-N), 5.03 (br, 2H, COD), 3.60–3.64 (t,  $J$  = 6.9 Hz, N-CH<sub>2</sub>), 3.24 (s, 3H, CH<sub>3</sub>), 2.62 (br, 2H, COD), 2.14–2.39 (m, 8H, 2H of P-CH<sub>2</sub> and 5H of COD), 1.84–1.87 (m, 2H, COD), 1.52–1.62 (m, 2H, CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 15.92 (s). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 164.1 (q,  $J_{B-C}$  = 48.9 Hz, *ipso*-BPh<sub>4</sub>), 135.7 (s, *o*-BPh<sub>4</sub>), 133.5 (d,  $J_{P-C}$  = 6.5 Hz, *o*- or *m*-PPh<sub>2</sub>), 131.2 (d,  $J_{P-C}$  = 48.4 Hz, *ipso*-PPh<sub>2</sub>), 130.7 (s, imidazole C2), 128.4 (d,  $J_{P-C}$  = 9.7 Hz, *o* or *m*-PPh<sub>2</sub>), 125.9 (d,  $J_{P-C}$  = 2.67 Hz, *m*-BPh<sub>4</sub>), 122.4 (s, imidazole C4/5), 122.0 (s, *p*-BPh<sub>4</sub>), 121.6 (imidazole C4/5), 94.8 (d,  $J_{P-C}$  = 14.1 Hz, CH of COD), 54.1 (s, CH of COD), 50.1 (d,  $J_{P-C}$  = 14.5 Hz, N-CH<sub>2</sub>), 36.0 (s, CH<sub>3</sub>), 33.2 (d,  $J_{P-C}$  = 3.1 Hz, CH<sub>2</sub> of COD), 29.4 (s, CH<sub>2</sub> of COD), 26.4 (s, CH<sub>2</sub>), 24.4 (d,  $J_{P-C}$  = 31.7 Hz, P-CH<sub>2</sub>). No C–H activation product was observed after this sample was heated at 39 °C for 5 h.

**Synthesis of Complex 12.** Complex **12** was synthesized on the basis of a literature report for its BPh<sub>4</sub><sup>–</sup> analogue.<sup>9d</sup> To a solution of [Ir(COD)Cl]<sub>2</sub> (180 mg, 0.268 mmol) in THF (5 mL) was slowly added <sup>t</sup>BuOK (0.54 mL, 1 M in THF, 0.54 mmol). The color of the solution turned dark red immediately. The solution was stirred for 2 h followed by addition of a suspension of **2a**-(PF<sub>6</sub>) (243 mg, 0.535 mmol) in THF. The mixture was stirred at room temperature for another 3 h followed by removal of all volatiles under reduced pressure. CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to the residue, and the inorganic salt was removed by filtration. The solution was then concentrated to ca. 0.5 mL under reduced pressure. Addition of diethyl ether (10 mL) afforded red microcrystals (313 mg, 0.423 mmol, 79%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.38–7.48 (m, 10H, PPh<sub>2</sub>), 7.02 (d,  $J$  = 1.9 Hz, 1H, H4/5), 6.82 (d,  $J$  = 1.8 Hz, 1H, H4/5), 4.89 (br, 2H, COD), 4.67 (m, 1H, NCH<sub>2</sub>), 4.59 (m, 1H, NCH<sub>2</sub>), 4.02 (br, 2H, COD), 3.84 (s, 3H, CH<sub>3</sub>), 2.69–2.70 (m, 2H, P-CH<sub>2</sub>), 2.09–2.21 (m, 8H, COD) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 17.71 (s, PPh<sub>2</sub>), 144.4 (heptet,  $J_{P-F}$  = 707 Hz). <sup>13</sup>C{<sup>1</sup>H} (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 171.8 (d,  $J_{P-C}$  = 13.9 Hz, C-Ir), 133.0 (br, *ipso* C of PPh<sub>2</sub>), 131.3 (s, *p*-C of PPh<sub>2</sub>), 129.0 (d,  $J_{P-C}$  = 10.4 Hz, *m* and *o*-C of PPh<sub>2</sub>), 123.0 (s, C4/5), 122.2 (s, C4/5), 86.2 (br, CH of

COD), 80.1 (s, CH of COD), 49.7 (d,  $J_{P-C}=2.95$  Hz, NCH<sub>2</sub>). 38.0 (s, CH<sub>3</sub>), 31.5 (br, CH<sub>2</sub> of COD), 25.4 (d,  $J_{P-C} = 38.3$  Hz, NCH<sub>2</sub>). Anal. Calcd for C<sub>26</sub>H<sub>31</sub>F<sub>6</sub>IrN<sub>2</sub>P<sub>2</sub>: C, 42.22; H, 4.22; N, 3.79. Found: C, 42.41; H, 4.41; N, 3.58.

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**Supporting Information Available:** Detailed synthesis of all phosphine–imidazoliums, NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) of all new compounds, kinetic studies and the Eyring plot for the decay of **4**, van't Hoff Plot of **7a**-(Cl), **7a**-(PF<sub>6</sub>), and **7b**-(PF<sub>6</sub>), <sup>19</sup>F–<sup>1</sup>H HOESY spectra of **5** and **8a**-(PF<sub>6</sub>), and crystal data (CIF and PDF) for complexes **5** and **8a**-(PF<sub>6</sub>). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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