Ir(III)-Induced C-Bound to N-Bound Tautomerization of a N-Heterocyclic Carbene

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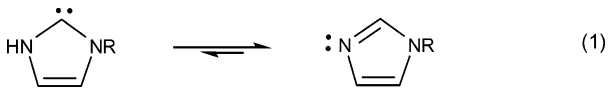
Summary: An iridium N-heterocyclic carbene (NHC) complex with a rare hydrogen wing tip was obtained via C−N bond cleavage. The C-bound to N-bound tautomerization of this carbene cannot be achieved in this neutral 18-electron Ir(III) complex. Chloride abstraction in MeCN afforded an NHC−acetimidamide complex, where the N-bound to C-bound tautomerization of this carbene was observed in $CDCl_3$ at 110 °C. Crystal structures of iridium complexes with these rare ligands were reported.

Introduction

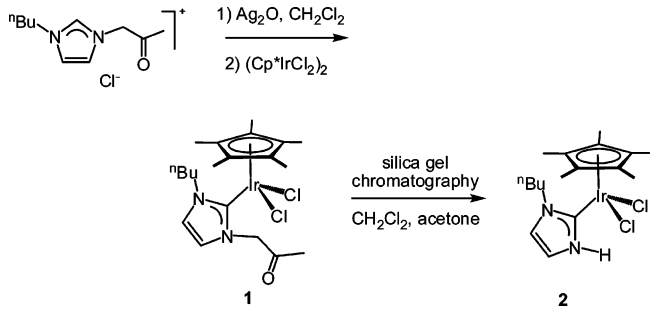
N-heterocyclic carbenes (NHCs) are widely used in organometallic chemistry and in homogeneous catalysis. They are rapidly challenging the ubiquitous phosphine ligands.[1] This is probably due to their strong σ-donating ability with a high trans effect and tunable steric and electronic properties in addition to strong NHC−M bonds. In spite of the unusual strength of the NHC−M bonds, there is an increasing number of reports on the nonspectator behavior of NHCs, such as in C−H activation at the N-substituent (the wing tip),[2] reductive elimination,[3] and migratory insertion.[4] Imidazole-based NHCs, derived from imidazoliums, are the most common ones. Almost all the imidazole-based NHC ligands have alkyl or aryl wing tips, and it is very rare to have a hydrogen atom as a wing tip although it can greatly tune the properties of an NHC. Such an NHC is intrinsically different in that tautomerization of this NHC to a N-bound imidazole can happen (eq 1), as was reported only in



(1)

several experimental studies.[5] This tautomerization was also proposed as a key step in several catalytic processes.[6] The imidazole tautomer is thermodynamically more stable than the carbene tautomer for free ligands (eq 1), with $\Delta E = -28.9$ and -28.5 kcal/mol for R = H and Me, respectively.[7] Crabtree and Eisenstein recently reported on the basis of theoretical studies that once coordinated to a metal either the N-bound imidazole or the corresponding C-bound carbene can be thermodynamically favored, depending on the environment of the metal.[7] Very recently, tautomerizations between other C-bound and N-bound heterocycles have also been reported; they are induced by Os, Ru, Ir, and Rh, and either the N-bound or the C-bound form can be thermodynamically stable.[6d,8] We now report the synthesis of Ir(III)−NHC complexes with a rare hydrogen wing tip and the subsequent observation of the C-bound to the N-bound tautomerization in the coordination sphere of Ir(III).

Scheme 1



Results and Discussion

We used the silver tansmetalation method for the synthesis of the desired Ir(III)−NHC complexes.[9] Stirring of a mixture of 1-(*n*-butyl)-3-(2-oxopropyl)imidazolium chloride and 0.5 equiv of Ag_2O in CH_2Cl_2 quickly gave a clear solution of the corresponding silver carbene (Scheme 1), to which was added $(Cp^*IrCl_2)_2$. A rapid filtration afforded complex **1** (89%), where the NHC processes a $-CH_2C(O)Me$ wing tip. This wing tip is interesting in that the presence of the carbonyl group can make this NHC a hemilabile bidentate ligand, and this feature may

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(1) For reviews, see: (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815. (c) Mata, J. A.; Poyatos, M.; Peris, E. *Coord. Chem. Rev.* **2007**, *251*, 841. (d) Glorius, F. *Top. Organomet. Chem.* **2007**, *21*, 1. (e) Lappert, M. F. *J. Organomet. Chem.* **2005**, *690*, 5467.

(2) (a) Corberan, R.; Sanau, M. Peris, E. *J. Am. Chem. Soc.* **2006**, (b) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944. (c) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516.

(3) (a) McGuinness, D. A.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029. (b) McGuinness, D. A.; Cavell, K. J. *Organometallics* **2000**, *19*, 4918.

(4) (a) Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756. (b) Becker, E.; Stingl, V.; Dazinger, G.; Puchberger, M.; Mereiter, K.; Kirchner, K. *J. Am. Chem. Soc.* **2006**, *128*, 6572.

(5) (a) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F., Jr.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381. (b) Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702.

(6) (a) Muller, J.; Stock, R. *Angew. Chem., Int. Ed.* **1983**, *22*, 993. (b) Tan, K. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2003**, *124*, 3203. (c) Caballero, A.; Jalon, F. A.; Manzano, B. R.; Espino, G.; Perez-Manrique, M.; Mucientes, A.; Poblete, F. J.; Maestro, M. *Organometallics* **2004**, *23*, 5694. (d) Wiedemann, S. H.; Lewis, J. C.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2006**, *128*, 2452.

(7) Sini, G.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **2002**, *41*, 602.

(8) (a) Esteruelas, M.; Fernandez-Alvarez, F. J.; Onate, E. *J. Am. Chem. Soc.* **2006**, *128*, 13044. (b) Alvarez, E.; Conejero, S.; Paneque, M.; Petronilho, A.; Poveda, M. L.; Serrano, O.; Carmona, E. *J. Am. Chem. Soc.* **2006**, *128*, 13060. (c) Standfest-Hauser, C. M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **2002**, *21*, 4891. For a recent review, see: Kunz, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 3405.

(9) (a) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663. (b) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

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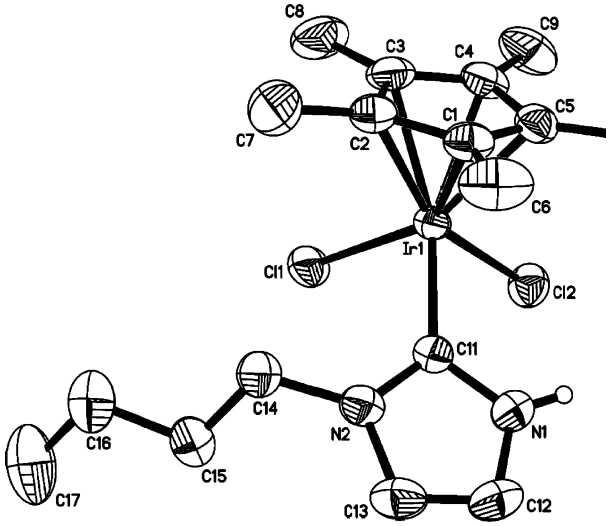


Figure 1. Molecular structure of the cation of complex **2** with the thermal ellipsoid at 50% probability. Selected lengths (Å) and angles (deg): Ir(1)−C(11), 2.034(2); Ir(1)−Cl(1), 2.4137(5); Ir(1)−Cl(2), 2.4343(5); N(1)−C(11)−N(2), 103.97(18); Cl(1)−Ir(1)−Cl(2), 88.21(2).

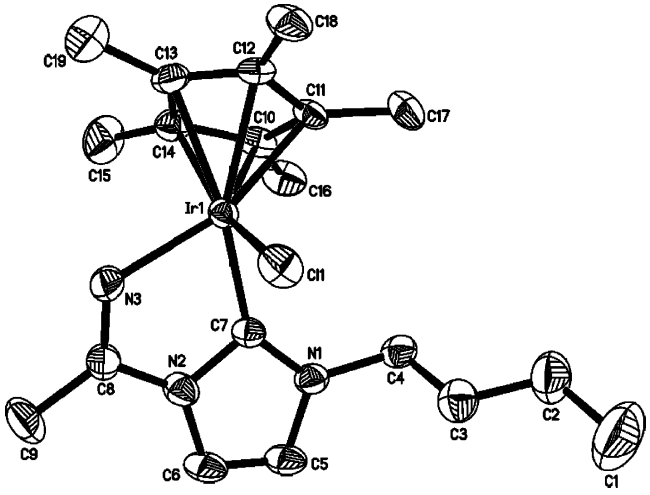
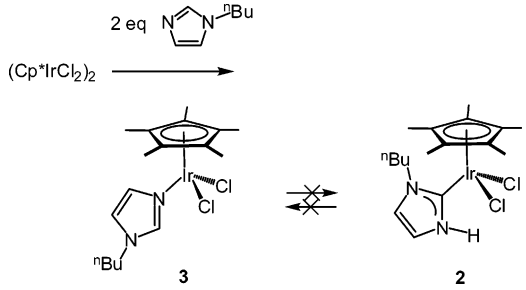


Figure 2. Molecular structure of the cation of complex **4** with the thermal ellipsoid at 50% probability. Selected lengths (Å) and angles (deg): Ir(1)−C(7), 2.001(5); Ir(1)−N(3), 2.080(4); Ir(1)−Cl(1), 2.3947(13); C(8)−N(2), 1.395(7); C(8)−N(3), 1.268(7); N(3)−Ir(1)−C(7), 75.3(2); Ir(1)−C(7)−N(2), 116.2(4); N(2)−C(8)−N(3), 113.3(5).

give rise to high catalytic activity in catalytic reactions. A prolonged silver transmetalation reaction, however, resulted in a product with impurities. Attempts to purify them by silica gel chromatography or by recrystallization failed, but decomposition of the products was observed, among which complex **2** was isolated in 30% yield as the major component as a result of the removal of the $-CH_2C(O)Me$ group. Complex **2** was fully characterized by NMR spectroscopy and X-ray crystallography (see the Supporting Information). In the ^1H NMR spectrum ($CDCl_3$), the NH signal was observed at δ 10.05. The carbene resonates at δ 154.8 in the ^{13}C NMR spectra. Unlike in complex **1**, the CH_2 protons are essentially equivalent in **2**, which suggests there is a symmetry plane that interchanges the CH_2 protons. This symmetry plane is in fact the imidazole plane which is perpendicular to the plane defined by Cl−Ir−Cl, a conformation that can be easily achieved when the rate of the Ir−C(carbene) rotation is above the NMR time scale.[9a] This is clearly consistent with the small steric bulk of the NHC in **2**. X-ray crystallography unambiguously confirmed the identity of this complex (Figure 1). Metal-induced cleavage of a N−C bond of an NHC was recently reported.[5b] We feel that the high reactivity of the $-CH_2C(O)Me$ group toward nucleophiles might be responsible for the C−N cleavage. However, addition of an ethereal solution of HCl under homogeneous conditions (CH_2Cl_2 and acetone) gave no N−C bond cleavage. Furthermore, using Et_3SiOH as a mimic of silica gel also failed. Addition of $N(n\text{-}Bu)_4Cl$ to the eluent to provide an extra source of nucleophiles in chromatography also failed to give any improvement of the yield. The yield was not improved by the addition of bases such as NEt_3 and K_2CO_3. In fact, complex **2** is the impurity in complex **1** when a longer reaction time is allowed for silver transmetalation. These indicate that heterogeneous conditions might be necessary for the C−N cleavage.

The N-bound tautomer **3** of carbene complex **2** was then synthesized from the reaction of $(Cp^*IrCl_2)_2$ and 2 equiv of 1-(*n*-butyl)imidazole (Scheme 2). Complexes **2** and **3** were separately heated in $CDCl_3$ at 130 °C (bath temperature) for 3 days in a J. Young type NMR tube sealed with a PTFE valve. ^1H NMR analysis revealed no interconversion for either complex, nor was there much decomposition. This indicates that the barrier of the tautomerization must be too high. It is possible that this

Scheme 2

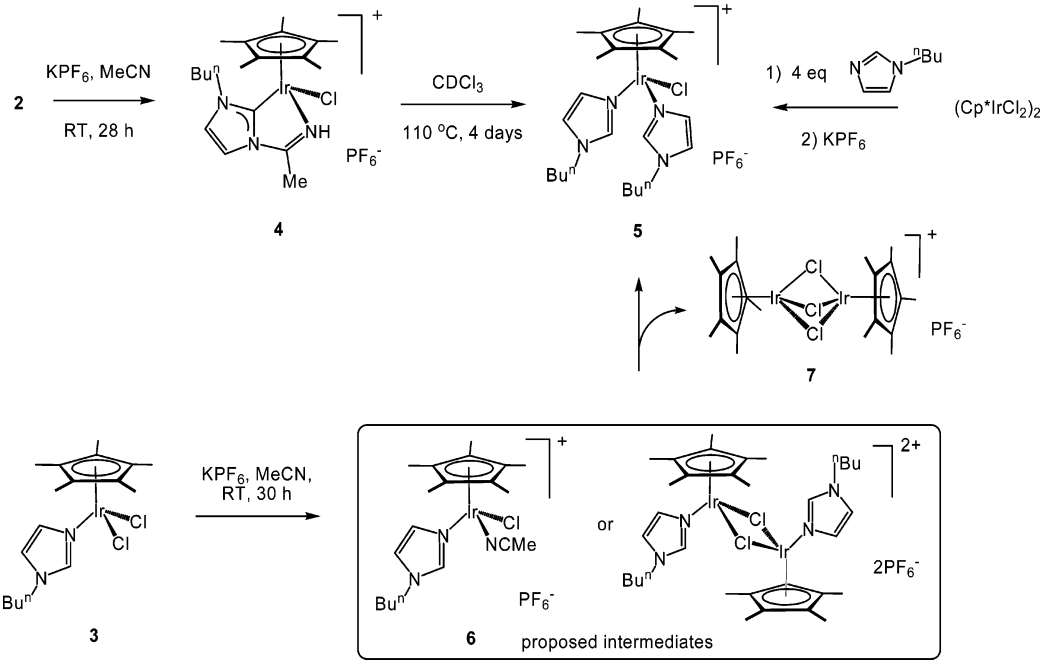


tautomerization might involve the dissociation of a chloride, and therefore, having a coordinatively unsaturated Ir(III) complex might lower this barrier. Chloride abstraction was then attempted using AgOTf or $AgPF_6$ in CH_2Cl_2, MeCN, or acetone, but all resulted in unidentifiable mixtures. Fortunately, milder chloride abstraction using KPF_6 (10 equiv) in MeCN slowly but cleanly led to a cationic complex, **4**. Both ^1H NMR spectroscopy and elemental analysis suggest the incorporation of one MeCN unit. In the ^1H NMR spectra, the N*H* resonates at δ 9.63 and diasterotopicity of CH_2 was noted. The identity of **4** was confirmed by X-ray crystallography (Figure 2), and there is no N-bound MeCN, but a chelating NHC−acetimidamide ligand, as a result of a formal *anti* addition of the N−H bond to the C≡N bond (see Figure 1 and the Supporting Information). The Ir−carbene distance is 2.001(5) Å and is slightly shorter than that in **2** [2.034(2) Å]. The bite angle of the chelating ligand is 75.3(2)°. The NHC ring and the iridacycle are nearly coplanar. We propose that a cationic Ir(III)−MeCN intermediate is formed after chloride abstraction, where the Lewis acidity of this Ir(III) activates MeCN toward the nucleophilic addition of the N−H bond, a process previously reported in a similar system.[10]

Although there is no vacant coordination site in **4**, the hemilability of the NHC−acetimidamide can potentially make a vacant site by losing a MeCN molecule. Heating a $CDCl_3$ solution of **4** at 110 °C in a sealed NMR tube led to a slow decay of **4** that gives NMR spectra with a clean low-field region

(10) Chin, C. S.; Chong, D.; Lee, B.; Jeong, H.; Won, G.; Do, Y.; Park, Y. J. *Organometallics* **2000**, *19*, 638.

Scheme 3



with a complete conversion achieved after 4 days. Compound **5** was identified as the major product after silica gel chromatography (Scheme 3) and was characterized by NMR spectroscopy, ESI-MS, and elemental analysis. ^{1}H NMR spectroscopy shows that the ratio of Cp* and the imidazole ligands is 1:2. More importantly, the ^{13}C NMR spectra (DEPT) show no quaternary carbon in the imidazole moiety, consistent with the N-bound mode. The identity of **5** was further confirmed by a clean independent synthesis by reacting 1-(*n*-butyl)imidazole (4 equiv) and $(Cp^*IrCl_2)_2$, followed by an anion exchange with KPF_6. Since the stoichiometry of Ir and NHC is 1:1 in the starting material **4**, while it is 1:2 in the product, a maximum yield of 50% can be expected. Indeed, the isolated yield is 31%.

To further understand this C-bound to N-bound tautomerization, we used complex **3** as a starting material, where the Ir to imidazole ratio is also 1:1. Stirring of a solution (MeCN) of **3** and KPF_6 also gave complex **5** in 40% yield (Scheme 3). In addition, ESI-MS (cation mode) gives a signal of $m/e = 761.06$ assigned to $C_{20}H_{30}Cl_3Ir_2^+$ on the basis of the isotope pattern. This signal could come from the ionization of $(Cp^*IrCl_2)_2$ with a chloride loss during mass spectrometry or directly from the stable cationic complex **7**. A closely related report showed that $(Cp^*IrCl_2)_2$ could be cleanly converted to complex 7 (with BF_4^-) using $AgBF_4$.[11] Similarly, we reacted $(Cp^*IrCl_2)_2$ and a large excess amount of KPF_6 in MeCN (room temperature, 24 h), and **7** was isolated almost quantitatively. This indicates that the presence of $(Cp^*IrCl_2)_2$ is not likely.[12] This overall transformation from **3** to **5** and **7** might proceed through a cationic intermediate, **6** (Scheme 3), or a bridging dichloride iridium dimer. Exchange between the imidazole and the chloride ligands eventually affords products **5** and **7**. This could also explain the transformation of **4** to **5**, where the intermediate **6** (or the bridging dichloride iridium dimer) can also be derived when a MeCN molecule is expelled from **4**.

In summary, we have demonstrated the synthesis of a rare Ir−NHC complex with a hydrogen wing tip via C−N bond cleavage. The C-bound to N-bound tautomerization of this carbene cannot be achieved in this neutral 18-electron Ir(III) complex, but it was observed in a cationic Ir(III) complex with a weak N-donor. Here the N-bound imidazole (a hard Lewis base) is more stable on metals of hard Lewis acids. This work supports the computational studies by Crabtree and Eisenstein.[7] The C−N bond cleavage and subsequent C-bound to N-bound tautomerization represent rare degradation pathways of NHCs and reinforce the nonspectator behavior of NHCs in some cases, which is of clear relevance to the catalysis and ionic liquid communities.

Experimental Section

General Procedures. All reactions and manipulations were carried out under a positive pressure of dry, oxygen-free nitrogen using the standard Shlenk technique, although almost all the compounds proved to be air stable. Solvents were dried and freshly distilled according to standard procedures and degassed prior to use when necessary. Analytical thin layer chromatography (TLC) was performed using a Merck 60 F254 precoated silica gel plate (0.2 mm thickness). ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance DPX 300 or a Bruker AMX 400 NMR spectrometer and were referenced to tetramethylsilane. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. High-resolution mass (HRMS) spectra were obtained on a Finnigan MAT95XP GC/HRMS system (Thermo Electron Corp.). X-ray crystallographic analysis was performed on a Bruker X8 APEX diffractometer.

Synthesis of 1-(*n*-Butyl)-3-(2-oxopropyl)imidazolium Chloride. To a solution of 1-butylimidazole (1.24 g, 10 mmol) in THF (40 mL) was slowly added chloroacetone (0.971 g, 10.5 mmol), and the resulting mixture was heated under reflux for 12 h. The reaction mixture was then cooled to room temperature and was concentrated to ca. 7 mL. The oily residue was washed with diethyl ether (4 × 20 mL) and was dried under reduced pressure to afford the desired product (2.05 g, 95%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.38 (s, 1H, imidazole C(2)*H*), 7.91 (s, 1H, imidazole CH), 7.74 (s, 1H, imidazole CH), 5.50 (s, 2H, $NCH_2C(O)$), 4.27 (t, J = 7.1 Hz, 2H, NCH_2CH_2), 2.24 (s, 3H, C(O)Me), 1.77 (quintet, J =

(11) Valderrama, M.; Scotti, M.; Campos, P.; Sariego, R.; Peters, K.; Von Schnering, H. G.; Werner, H. *New J. Chem.* **1988**, *12*, 633.

(12) We failed to isolate complex **7** by recrystallization of the reaction mixture obtained from complex **3**. However, at least a single crystal of **7** was obtainable and its use attempted for X-ray crystallographic studies. The connectivity in **7** was confirmed although no publishable data were obtained due to poor quality of the crystal.

7.2 Hz, 2H, NCH_2CH_2), 1.29−1.20 (sextet, $J = 7.1$ Hz, 2H, $NCH_2CH_2CH_2CH_2$), 0.89 (t, $J = 7.2$ Hz, 3H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 200.69 (CO), 137.54 (imidazole C), 124.20 (imidazole C), 122.37 (imidazole C), 57.99 $NCH_2C(O)$), 48.97 (NCH_2CH_2), 31.87 (NCH_2CH_2), 27.47 (C(O)Me), 19.17 ($NCH_2CH_2CH_2Me$), 13.74 (Me). This compound is highly hydroscopic, and no satisfactory elemental analysis can be obtained, so the PF_6^- salt was then synthesized for this purpose. To a MeCN solution (3 mL) of this chloride salt (20 mg, 0.092 mmol) was added KPF_6 (169.9 mg, 0.92 mmol). The mixture was stirred for 2 h, followed by removal of the solvent. CH_2Cl_2 (10 mL) was then added to the mixture followed by filtration. The solution was pumped to dryness to give analytically pure 1-(*n*-butyl)-3-(2-oxopropyl)-imidazolium hexafluorophosphate (29.4 mg, 98%). ^1H NMR (300 MHz, CD_3CN): δ 8.35 (s, 1H), 7.41 (t, $J = 1.7$ Hz, 1H), 7.26 (t, $J = 1.7$ Hz, 1H), 5.08 (s, 2H), 4.17 (t, $J = 7.2$ Hz, 2H), 2.24 (s, 3H), 1.2 (quintet, $J = 7.2$ Hz, 2H), 1.32 (sextet, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN): δ 199.01, 136.31, 123.79, 121.96, 57.52, 49.52, 31.50, 26.23, 18.92, 12.63. Anal. Calcd for $C_{10}H_{17}F_6N_2OP$: C, 36.82; H, 5.25; N, 8.59. Found: C, 36.56; H, 5.16; N, 8.52.

Synthesis of Complex 1. To a stirred solution of 1-(*n*-butyl)-3-(2-oxopropyl)imidazolium chloride (96 mg, 0.44 mmol) in dichloromethane (6 mL) was added Ag_2O (51.4 mg, 0.22 mmol). The resulting mixture was stirred for 1 h, and almost all the Ag_2O dissolved to give a light yellow solution. The mixture was then filtered, to the solution was added $[Cp^*IrCl_2]_2$ (174 mg, 0.22 mmol), and the resulting mixture was stirred at room temperature for 20 min. An orange solution was obtained after filtration through a plug of Celite. The solution was vacuumed to dryness to give a yellow solid (113 mg, 89%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.04 (s, 1H, imidazole CH), 6.83 (s, 1H, imidazole CH), 6.15 (d, $J = 19.8$ Hz, 1H, $C(O)CH_2$), 4.99 (d, $J = 19.5$ Hz, 1H, $C(O)CH_2$), 4.61−4.58 (m, 1H, NCH_2), 3.86−3.84 (m, 1H, NCH_2), 2.26 (s, 3H, C(O)Me), 1.40−1.70 (m, 19H, $Cp^* + 2CH_2$), 0.98 (t, $J = 7.35$ Hz, 3H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 203.06 (C(O), 156.76 (carbene), 123.48, 120.93, 89.03, 60.50, 50.89, 33.67, 27.37, 20.18, 13.98, 8.95. Anal. Calcd for $C_{20}H_{31}N_2OIrCl_2$: C, 41.52; H, 5.40; N, 4.84. Found: C, 41.33; H, 5.23; N, 4.79.

Synthesis of 2. Complex **1** (100 mg, 0.173 mmol) was applied to a silica gel TLC plate (25 cm × 25 cm) and was chromatographed in CH_2Cl_2 and acetone (8:1) for 1 h to give complex **2** as a light yellow solid (27 mg, 30%). Crystals suitable for X-ray analysis were obtained by layering a CH_2Cl_2 solution of **2** with hexane. ^1H NMR (400 MHz, $CDCl_3$): δ 10.05 (br s, 1H, NH), 7.02 (t, $J = 2.0$ Hz, 1H, imizadole CH), 6.95 (t, $J = 2.0$, 1H, imidazole CH), 4.12 (t, $J = 8.2$ Hz, 2H, NCH_2), 1.90−1.80 (m, 2H), 1.61 (s, 15H), 1.49−1.40 (m, 2H), 0.98 (t, $J = 7.35$ Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 154.82 (carbene), 119.87 (imidazole), 118.66 (imidazole), 88.55 (Me_5C_5), 49.66 (NCH_2), 33.28 (NCH_2CH_2), 20.25 ($NCH_2CH_2CH_2$), 13.91 ($NCH_2CH_2CH_2CH_3$), 8.90 (Me_5C_5). Anal. Calcd for $C_{17}H_{27}IrCl_2N_2$: C, 39.08; H, 5.21; N, 5.36. Found: C, 39.27; H, 5.27; N, 5.42.

Synthesis of 3. To a stirred solution of $[Cp^*IrCl_2]_2$ (65.4 mg, 0.082 mmol) in CH_2Cl_2 (5 mL) was added 1-(*n*-butyl)imidazole via syringe (20.4 mg, 0.164 mmol). The resulting mixture was stirred for 2 h at room temperature. The solvent was then removed under reduced pressure to give a light yellow powder (80 mg, 93%). ^1H NMR (400 M, $CDCl_3$): δ 7.93 (s, 1H, imidazole CH), 7.19 (s, 1H, imidazole CH), 6.86 (s, 1H, imidazole CH), 3.93 (t, $J = 7.2$ Hz, 2H, NCH_2), 1.78−1.74 (m, 2H, CH_2) 1.62 (s, 15H, Cp*), 1.35−1.30 (m, 2H, CH_2), 0.94 (t, $J = 7.20$ Hz, 3H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.19, 130.27, 119.71, 85.10, 47.99, 32.56, 19.68, 13.45, 8.75. Anal. Calcd for $C_{17}H_{27}IrCl_2N_2$: C, 39.08; H, 5.21; N, 5.36. Found: C, 39.33; H, 5.59; N, 5.40.

Synthesis of 4. To a stirred solution of **2** (40.8 mg, 0.078 mmol) in CH_3CN (4 mL) was added KPF_6 (143.5 mg, 0.78 mmol). The resulting mixture was stirred for 28 h at room temperature. The solvent was then removed under reduced pressure followed by addition of CH_2Cl_2 (15 mL). Filtration gave a light yellow solution from which **4** (45 mg, 86%) was obtained as a light yellow solid. Single crystals of **4** suitable for X-ray crystallographic studies were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of **4**. ^1H NMR (400 MHz, $CDCl_3$): δ 9.63 (br s, 1H, NH), 7.53 (s, 1H, imidazole CH), 7.22 (s, 1H, imidazole CH), 4.21 (t, $J = 7.3$ Hz, 2H, NCH_2), 2.86 (s, 3H, $CH_3C{=}NH$), 1.85 (m, 17 H, $Cp^* + CH_2$), 1.41−1.38 (m, 2H, CH_2), 0.96 (t, $J = 7.4$ Hz, 3H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 170.71, 167.71, 122.80, 118.36, 92.24, 50.71, 32.72, 19.94, 17.35, 13.77, 9.38. Anal. Calcd for $C_{19}H_{31}ClF_6IrN_3P$: C, 33.85; H, 4.64; N, 6.23. Found: C, 34.05; H, 4.55; N, 6.19.

Conversion of 4 to 5. To a J. Young NMR tube with a PTFE valve were added complex **4** (20 mg, 0.030 mol) and $CDCl_3$ (0.75 mL). The NMR tube was sealed, and the yellow solution was heated at 110 °C. The reaction was monitored by ^1H NMR spectroscopy, and complete conversion was observed after 4 days. Purification using silica gel chromatography (CH_2Cl_2 and acetone in a 4:1 ratio) afforded **5** (7.1 mg, 31%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (s, 2H), 7.36 (s, 2H), 6.94 (s, 2H), 4.04 (t, $J = 7.2$ Hz, 4H), 1.70 (quintet, $J = 7.3$ Hz, 4H), 1.52 (s, 15H), 1.31−1.23 (m, 4H), 0.90-(t, $J = 7.2$ Hz, 6H). $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$): δ 138.39, 129.54, 120.33, 87.04, 48.11, 32.75, 19.47, 13.45, 8.54. Anal. Calcd for $C_{24}H_{39}ClF_6IrN_4P$: C, 38.12; H, 5.20; N, 7.41. Found: C, 38.19; H 5.07; N, 7.27. ESI-MS (cation mode, MeOH): $m/z = 611.14$ [$C_{24}H_{39}IrClN_4$, $Cp^*Ir(butylimidazole)_2Cl^+$ (the cation part of complex **5**)], 487.13 [$C_{17}H_{27}IrClN_2$, $Cp^*Ir(butylimidazole)_2Cl^+$ (**5** cation − butylimidazole)], 288.21 [$Cp^*Ir(butylimidazole)_2^{2+}$, **5** cation − Cl^-], 577.22 [$C_{24}H_{40}IrN_4$, $Cp^*Ir(butylimidazole)_2H$ (the chloride is changed to a hydride)], 453.25 [$C_{17}H_{28}IrN_2$, $Cp^*Ir(butylimidazole)H$].

An Independent Synthesis of 5. To a stirred solution of $[Cp^*IrCl_2]_2$ (58.5 mg, 0.073 mmol) in CH_2Cl_2 (5 mL) was added via syringe 1-(*n*-butyl)imidazole (36.5 mg, 0.294 mmol). The resulting mixture was stirred for 2 h at room temperature. Removal of CH_2Cl_2 gave a light-yellow powder (90 mg, 96%) which is the chloride analogue of complex **5**. ^1H NMR (300 MHz, $CDCl_3$): δ 9.42 (s, 2H), 7.50 (s, 2H), 6.85 (s, 2H), 4.10−4.28 (m, 4H), 1.76 (quintet, $J = 7.2$ Hz, 4H), 1.55 (s, 15H), 1.21−1.29 (m, 4H), 0.89 (t, $J = 7.4$ Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 140.74, 129.16, 119.14, 86.94, 47.96, 32.82, 19.52, 13.57, 8.81. To this chloride salt (40.6 mg, 0.063 mmol) were then added CH_3CN (3 mL) and KPF_6 (46.2 mg, 0.251mmol, 4 equiv). The resulting mixture was stirred for 24 h at room temperature, followed by removal of CH_3CN. CH_2Cl_2 (15 mL) was then added, and the mixture was filtered to give **5** (44.8 mg, 94%). Both ^1H and ^{13}C NMR spectra are identical to those of **5** obtained from the conversion of **4**.

Observation of the Conversion of 3 to 5 and 7. To a solution of **3** (50 mg, 0.096 mmol) in MeCN (3 mL) was added KPF_6 (176 mg, 0.96 mmol). The mixture was stirred for 30 h. ESI-MS (acetone, cation mode) gave $m/z = 611.13$ [$C_{24}H_{39}IrClN_4$, $Cp^*Ir(butylimidazole)_2Cl^+$ (the cation part of complex **5**)], 487.12 [$C_{17}H_{27}IrClN_2$, $Cp^*Ir(butylimidazole)_2Cl^+$ (**5** cation − butylimidazole)], 288.18 [$Cp^*Ir(butylimidazole)_2^{2+}$, **5** cation − Cl^-], 761.06 ($C_{20}H_{30}Cl_3Ir_2$, cation of **7**), and 818.95 ($C_{23}H_{46}Cl_3Ir_2O$, **7** cation + acetone). ^1H NMR spectroscopy also showed the presence of complex **5** in this mixture.

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Supporting Information Available: NMR spectra of complexes **1**−**5** and X-ray crystal data for **2** and **4** (PDF and CIF). This material is available free of charge via the Internet at http://www.pubs.acs.org.

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