Synthesis of New Iridium N-Heterocyclic Carbene Complexes and Facile Intramolecular Alkyl C−H Bond Activation Reactions of the Carbene Ligand

Fumihiro Hanasaka, Yusuke Tanabe, Ken-ichi Fujita, and Ryohei Yamaguchi*

Graduate School of Human Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

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The new iridium N-heterocyclic carbene complexes $Cp^NIr(I\textit{i}\text{-}PrMe)I_2$ and $CpIr(I\textit{i}\text{-}PrMe)I_2$ (Cp^N = (2-(dimethylamino)ethyl)cyclopentadienyl; I*i*-PrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) have been synthesized along with Ir(cod)(I*i*-PrMe)Cl, $Cp^NIr(I\textit{i}\text{-}PrMe)(\eta^2\text{-cod})$, and $CpIr(I\textit{i}\text{-}PrMe)(\eta^2\text{-cod})$. Facile intramolecular alkyl C−H bond activation reactions of $Cp^*Ir(I\textit{i}\text{-}PrMe)Cl_2$ (Cp^* = η^5-pentamethylcyclopentadienyl) and $Cp^NIr(I\textit{i}\text{-}PrMe)I_2$ have occurred by treatment with MeONa and AgOTf, respectively.

Introduction

There have been considerable investigations on the syntheses of transition-metal N-heterocyclic carbene (NHC) complexes and their reactivities,[1,2] and it has been disclosed that catalytic activities of NHC complexes are greater than those of phosphine complexes in Pd-catalyzed cross-coupling reactions[3] and Ru-catalyzed olefin metatheses.[4] Recently, we have reported that dicationic Cp*Ir NHC complexes (Cp^* = η^5-pentamethylcyclopentadienyl) exhibit a catalytic activity higher than those of phosphine analogues in hydrogen transfer reactions.[5] On the other hand, studies on the reactivity of $Cp^*Ir(NHC)X_2$ (X = halides) have been poorly explored,[6] although the reactivities of the phosphine analogues have been widely studied.[7]

Recently, several reports on an intramolecular alkyl C−H bond activation reaction in NHC complexes have appeared. Herrmann has reported that a cationic olefin hydrido complex was given by an intramolecular alkyl C−H bond activation reaction of the alkyl complex $[Cp^*Ir(ICy)(Me)_2]$ (ICy = 1,3-dicyclohexylimidazol-2-ylidene) with trifluoromethanesulfonic acid,[6a] and Whittlesey has also reported an intramolecular alkyl C−H activation of $Ru(IEtMe)(PPh_3)_2(CO)H_2$ (IEtMe = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene) by treatment with $CH_2{=}CHSiMe_3$.[8] Nolan and Caddick have shown that an intramolecular alkyl C−H activation of 1,3-di-*tert*-butylimidazol-2-ylidene (I*t*-Bu) ligand led to the formation of cyclometalated iridium and rhodium complexes[9] and nickel complexes,[10] respectively. Very recently, an intramolecular alkyl C−H activation of a triruthenium cluster containing an NHC ligand (IMe = 1,3-dimethylimidazol-2-ylidene) has been disclosed by Cabeza.[11]

In this paper, we report the synthesis of new iridium NHC complexes and facile intramolecular alkyl C−H bond activation reactions which may provide valuable information on the reactivity of iridium NHC dihalide complexes. In addition, we have found that the basic alkoxo and amino ligands could play a critical role in the C−H bond cleavage process.

Results and Discussion

Reaction of $Cp^*Ir(I\textit{i}\text{-}PrMe)Cl_2$ (1) with MeONa. Reaction of $Cp^*Ir(I\textit{i}\text{-}PrMe)Cl_2$ (**1**; I*i*-PrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) with MeONa (1 equiv) gave the cyclometalated carbene complex $Cp^*Ir(I\textit{i}\text{-}PrMe')Cl$ (**2**) in 99% yield by an intramolecular C−H bond activation reaction (Scheme 1). Reaction of **1** with *t*-BuONa in *t*-BuOH gave the cyclometalated complex **2** in 62% yield along with the unchanged **1**. However, no cyclometalation was observed by treatment with 2,2,6,6-tetramethylpiperidine or NaOTf (OTf = triflate) instead of MeONa. The ^1H NMR spectrum of **2** in C_6D_6

* To whom correspondence should be addressed. E-mail: yama@kagaku.mbox.media.kyoto-u.ac.jp.

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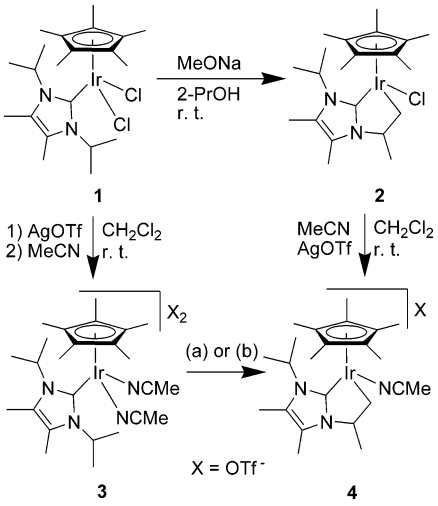
Scheme 1. Intramolecular Alkyl C−H Bond Activation Reactions of Cp*Ir NHC Complexes[a]



[a] Legend: (a) MeONa, MeOH, room temperature; (b) NEt_3, CH_2Cl_2, room temperature.

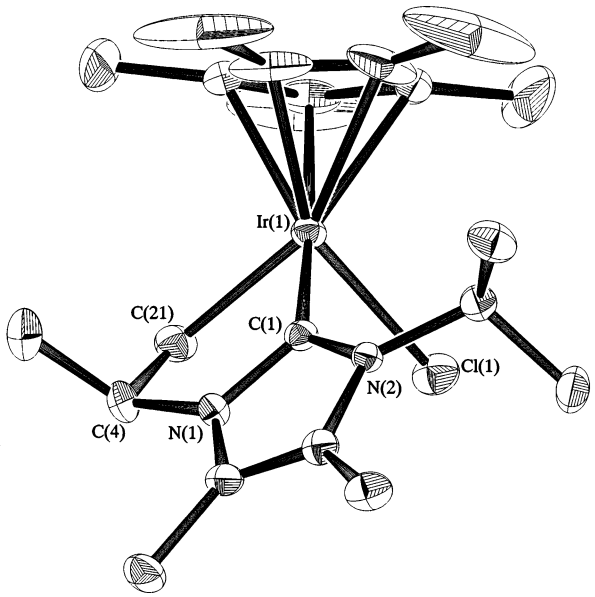
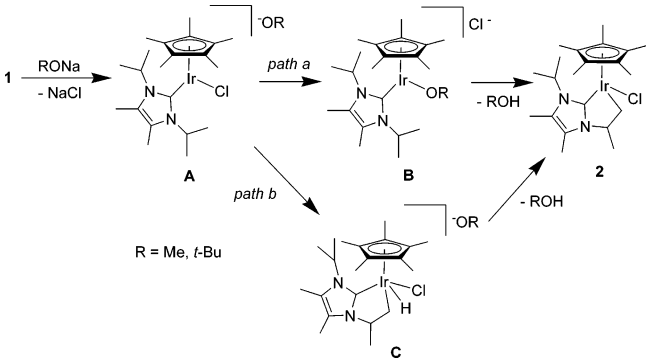


Figure 1. ORTEP drawing (ellipsoids at 50% probability) of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(1), 2.010(6); Ir(1)−C(21), 2.108(6); Ir(1)−Cl(1), 2.424(2); C(1)−Ir(1)−C(21), 77.7(2); C(1)−Ir(1)−Cl(1), 86.0(2); C(21)−Ir(1)−Cl(1), 87.3(2).

showed signals due to nonequivalent geminal protons on the carbon cyclometalated to the iridium center at δ 3.95 and 2.26 ppm with the coupling constant $^2J_{HH} = 10$ Hz. No signal was observed in the hydride region. The resonance assigned as a cyclometalated methylene carbon was observed at δ 18.5 ppm in the $^{13}C\{^1H\}$ NMR and DEPT spectra. The structure of **2** was confirmed by an X-ray diffraction study. The ORTEP drawing of **2** is illustrated in Figure 1. The structure of **2** was revealed as a five-membered iridacycle bearing one chlorine ligand. The geometry around the iridium center can be described as a distorted three-legged piano stool, showing that the iridium center is coordinated with chlorine, C(21), and the carbene C(1) as well as Cp* ring carbons. The newly formed Ir−C(21) bond length is 2.108(6) Å, which is compatible with bond lengths (2.081−2.210 Å) between iridium and cyclometalated carbons reported by Nolan.[9] Furthermore, the carbene carbon (C(1)) is

Scheme 2. Possible Mechanism for the Intramolecular Alkyl C−H Bond Activation Reaction of 1

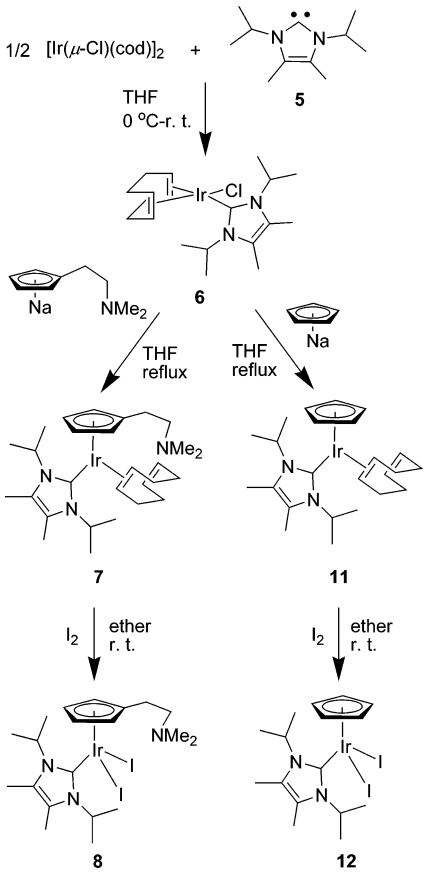


located at a single-bond length, 2.010(6) Å, from the iridium center (Ir(1)).

A possible mechanism for the intramolecular C−H bond activation reactions of **1** promoted by RONa (R = Me, *t*-Bu) is shown in Scheme 2. The initial step would be a dechlorination reaction of **1** with basic RONa to generate the intermediate **A**. At this point, two reaction pathways (*a* and *b*) should be possible. The pathway *a* is as follows: the ligand exchange on **A** from Cl to the more strongly coordinative MeO would produce the alkoxo Ir(III) complex **B**, which would undergo intramolecular C−H bond activation induced by the basic alkoxo ligand with elimination of ROH, affording the cyclometalated product **2**. The other pathway *b* is as follows: the direct C−H bond activation could occur in the coordinatively unsaturated Ir(III) complex **A** to give an Ir(V) complex, which could afford the cyclometalated product **2**. Since we have already observed that a poorly coordinating OTf ligand produces the non-cyclometalated complex $[Cp^*Ir(Ii\text{-}PrMe)(MeCN)_2][OTf]_2$ (**3**) instead of **2** in our previous work,[5] pathway *a* would be more favored. To obtain further information on the reaction mechanism, we have conducted a low-temperature (−80 to 20 °C) ^1H NMR analysis of the cyclometalation reaction of **1** with MeONa in CD_3OD. Two distinct intermediates could be detected during the reaction (see Figure S1 in the Supporting Information). Both of the intermediates should have symmetrical axes in the bond between iridium and the carbene carbon, because an increase and a decrease of singlet absorption due to the equivalent C4 and C5 methyl protons of the NHC ring were observed. Thus, it is highly likely that the singlet signal would account for the presence of the intermediates **A** and **B**, in which the C4 and C5 methyls on the NHC ring are equivalent. The signal (δ 2.31 ppm, singlet) probably due to the intermediate **A** increased with a decrease of the signal (δ 2.34 ppm, singlet) due to **1** on warming from −80 to −30 °C. When the reaction mixture was warmed to −20 °C, the signal due to **A** disappeared and another signal (δ 2.35 ppm, singlet) probably due to **B** as well as two singlet signals (δ 2.27 and 2.15 ppm) due to the cyclometalated product **2** were observed in the NMR spectra. Finally, only two singlet signals due to **2** remained on warming to 10 °C. The above observations are consistent with pathway *a* rather than pathway *b*, which involves the unsymmetrical intermediate. Methanol generated by C−H bond activation was also observed by ^1H NMR.[12] Furthermore, it can be said that the greater steric hindrance of *t*-BuO as compared to that of the MeO ligand would account for the decreased yield of **2** in the reaction of **1** with *t*-BuONa.

(12) Intramolecular aromatic C−H activation on Cp^*Ir^{III} complexes with alkoxy and phenoxy ligands has been reported: Koike, T.; Ikariya, T. *Organometallics* **2005**, *24*, 724.

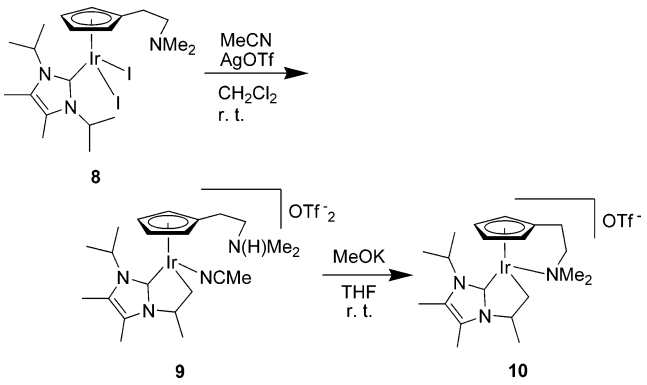
Scheme 3. Synthesis of New Ir NHC Complexes



To demonstrate the coordination of basic ligands to the cationic iridium center as a key step in the present cyclometalation, reactions of the dicationic complex **3**, which have been prepared without any cyclometalation product, with MeONa or NEt_3 were carried out (Scheme 1). The unstable cyclometalated complex [Cp*Ir(I*i*-PrMe′)(MeCN)][OTf] (**4**) was produced. Reaction of **2** with AgOTf also gave **4** in the presence of acetonitrile. These results demonstrated that coordinations of basic ligands (MeO and NEt_3) to the dicationic iridium center would proceed prior to the cyclometalation, suggesting pathway *a* in Scheme 2.

Synthesis of New Ir NHC Complexes Bearing a Cp^N Ligand. To examine the intramolecular coordination of a basic ligand causing a prompt C−H bond activation, we set out to synthesize new iridium(III) NHC complexes bearing a Cp^N (Cp^N = (2-(dimethylamino)ethyl)cyclopentadienyl) ligand.[13] The synthesis of new iridium complexes is summarized in Scheme 3. Reaction of $[Ir(\mu\text{-Cl})(cod)]_2$ (cod = 1,5-cyclooctadiene) with free I*i*-PrMe (**5**) gave the η^4-cod complex Ir(cod)(I*i*-PrMe)Cl (**6**) in 96% yield.[14] Reaction of **6** with Cp^NNa afforded the Ir(I) complex $Cp^NIr(Ii\text{-PrMe})(\eta^2\text{-cod})$ (**7**) in 84% yield. The introduction of a Cp^N ligand to the Ir(I) center induced a transformation of the coordination mode of COD from η^4 to η^2. The complex **7** was characterized by IR and NMR spectroscopy. In the IR spectrum of **7**, the uncoordinated olefinic moiety of an η^2-cod ligand showed a characteristic absorption band at 1616 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) of **7**, signals due to uncoordinated and coordinated olefinic carbons were observed at δ 131.6 and 32.1 ppm, respectively. Additionally, signals due to cyclopentadienyl carbons in the Cp^N ligand were observed at δ 101.2, 78.6, and 74.7 ppm and those due to the methylene carbons of the (dimethylamino)ethyl group in the Cp^N ligand appeared at δ 62.8 and 27.8 ppm. Finally, a diiodo iridium complex analogous to **1**, $Cp^NIr(Ii\text{-PrMe})I_2$ (**8**), was prepared in 78% yield by reaction of **7** with iodine. The structure of **8** was elucidated by the NMR spectral data and the elemental analysis. The $^{13}C\{^1H\}$ NMR spectrum of **8** in C_6D_6 showed signals due to the carbene carbon (δ 146.0 ppm), cyclopentadienyl carbons (δ 103.8, 80.3, and 73.6 ppm) in the Cp^N ligand, and the methyl carbon (δ 45.2 ppm) of the dimethylamino group.

Scheme 4. Intramolecular Alkyl C−H Bond Activation Reactions of Iridium NHC Complexes Bearing the Cp^N Ligand



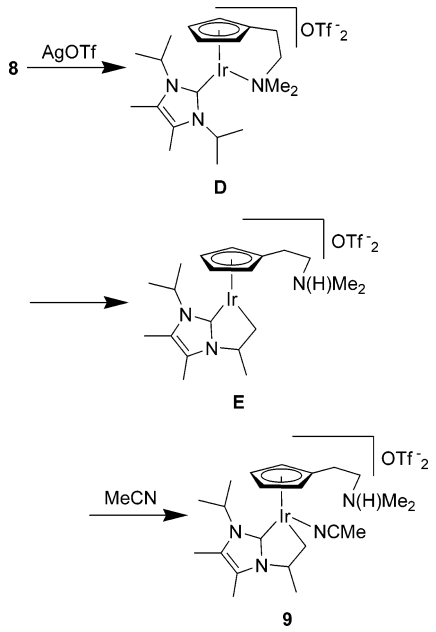
Reaction of $Cp^NIr(Ii\text{-PrMe})I_2$ with AgOTf. Because the cationic iridium(III) complex would be a possible intermediate for the C−H bond activation reaction as shown in Scheme 2, treatment of the diiodo complex **8** with 2 equiv of AgOTf was examined in the presence of acetonitrile (Scheme 4). The cyclometalated carbene complex $[Cp^{N(H)}Ir(Ii\text{-PrMe}')(MeCN)][OTf]_2$ (**9**), containing a dimethylammonium moiety, was directly obtained in 85% yield. The complex **9** was characterized by NMR and IR spectroscopy. The ^1H NMR spectrum of **9** in $CDCl_3$ showed signals due to nonequivalent geminal protons on the carbon cyclometalated to the iridium center at δ 3.08 and 2.63 ppm with the coupling constant $^2J_{HH}$ = 11 Hz. Signals due to the ammonium proton and the methyl protons of acetonitrile were also observed at δ 8.91 (this signal disappeared by addition of D_2O) and 2.55 ppm, respectively, while no signal due to a hydrido ligand was observed. The resonance due to the cyclometalated methylene carbon was observed at δ 6.9 ppm in the $^{13}C\{^1H\}$ NMR and DEPT spectra. In addition, signals due to the carbene carbon, the nitrile carbon, and the methyl carbon of acetonitrile were also observed at δ 146.9, 117.3, and 4.0 ppm, respectively. In the IR spectrum of **9**, the ammonium proton ($-N^+H$) of $Cp^{N(H)}$ showed a characteristic absorption band at 2754 cm^{-1}. These results demonstrated that the amino group can play an important role as the acceptor of a proton generated by C−H bond activation.

A possible mechanism for the intramolecular C−H bond activation reaction is shown in Scheme 5. The intermediate **D** would be formed by reaction of **8** with 2 equiv of AgOTf followed by intramolecular coordination of the dimethylamino group to the iridium center. Although C−H bond activation via the Ir(V) complex was not ruled out, the basic dimethylamino ligand would break the C−H bond of the isopropyl group to generate the Ir(III) complex **E** with the formation of a di-

(13) To the best of our knowledge, there have been only two reports on the synthesis of cobalt NHC complexes bearing functionalized Cp ligands: (a) Foerstner, J.; Kakoschke, A.; Goddard, R.; Rust, J.; Wartchow, R.; Butenschön, H. *J. Organomet. Chem.* **2001**, *617*−*618*, 412. (b) Delgado, S.; Moreno, C.; Macazaga, M. J. *Polyhedron* **1991**, *10*, 725.

(14) (a) Herrmann, W. A.; Köcher, C. *J. Organomet. Chem.* **1997**, *532*, 261. (b) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461.

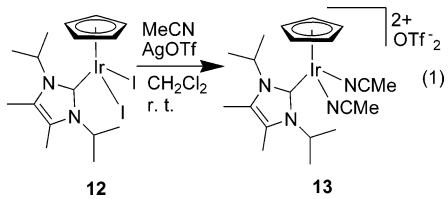
Scheme 5. Possible Mechanism for the Intramolecular Alkyl C−H Bond Activation Reaction of 8



methylammonium moiety. The subsequent coordination of acetonitrile would give the dicationic complex **9**.

Reaction of [Cp$^{N(H)}$Ir(I*i*-PrMe′)(MeCN)][OTf]$_2$ with MeOK. To remove a proton from the ammonium moiety of the Cp$^{N(H)}$ ligand in **9**, reaction of **9** with MeOK was carried out. A cationic tethered complex (**10**) was obtained in almost quantitative yield (Scheme 4). In the ^{1}H NMR spectrum ($CDCl_3$) of **10**, signals due to nonequivalent methyl protons of the dimethylamino group were observed at δ 2.64 and 2.34 ppm, indicating the intramolecular coordination of the dimethylamino group to the iridium center. As a result of the intramolecular coordination, four signals (δ 4.16, 3.89, 2.60, and 2.6−2.5 ppm) due to the methylene protons of the (dimethylamino)ethyl group were observed, and the η^5-C_5H_4 ligand also independently showed four signals at δ 5.82, 5.18, 5.09, and 4.98 ppm. In the ^{13}C-{^{1}H} NMR spectrum ($CDCl_3$) of **10**, signals due to the dimethylamino group were observed at δ 55.6 and 54.2 ppm. Signals due to the methylene chain of the (dimethylamino)-ethyl group were observed at δ 88.2 and 25.2 ppm, and signals due to cyclopentadienyl carbons in the η^5-C_5H_4 ligand were also observed at δ 118.7, 76.6, 74.0, 73.1, and 72.6 ppm. Furthermore, the structure of **10** was confirmed by an X-ray diffraction study. The ORTEP drawing of **10** is illustrated in Figure S6 (see the Supporting Information).

Reaction of CpIr(I*i*-PrMe)I$_2$ (12) with AgOTf. CpIr-(I*i*-PrMe)(η^2-cod) (**11**) and CpIr(I*i*-PrMe)I$_2$ (**12**) were prepared in 79% and 87% yields, respectively, in a manner similar to the preparation of **7** and **8** (Scheme 3). To clarify the necessity of a basic ligand for the C−H bond activation in iridium(III) NHC complexes, we examined the reaction of complex **12** with 2 equiv of AgOTf. The reaction gave dicationic [CpIr(I*i*-PrMe)-(MeCN)$_2$][OTf]$_2^{2+}$ (**13**) analogous to the preceding dicationic complexes,[5] and no formation of an intramolecular C−H activated product was observed (eq 1).[2a] This result indicated that the basic dimethylamino group coordinated to the iridium center is essential to the C−H bond cleavage.



(1)

Conclusion

We have accomplished the synthesis of new iridium NHC complexes. Facile intramolecular alkyl C−H bond activation reactions have been found, showing a fundamental reactivity of an iridium dihalide complex bearing an NHC ligand. These reactions have demonstrated that alkoxo and amino groups coordinated to the iridium center served as acceptors of the proton generated by the C−H bond cleavage. In addition, the captured proton could be removed from the side chain of the Cp$^{N(H)}$ ligand by treatment with conventional base.

Experimental Section

General Procedures. All the reactions and manipulations were carried out under an atmosphere of argon by means of Schlenk techniques. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on JEOL A-500 and EX-270 spectrometers. IR spectra were recorded on a HORIBA FT-300 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University.

Materials. Solvents were dried by using standard procedures and distilled prior to use. THF was distilled from sodium benzophenone ketyl and stored in the presence of metallic potassium. [Ir(μ-Cl)(cod)]$_2$,[15] complex **1**,[5] dicationic complex (**3**),[5] N-heterocyclic carbene **5**,[16] and Cp^{N}Na[17] were prepared by the literature methods. Other reagents were used as obtained from commercial sources.

Cp*Ir(I*i*-PrMe′)Cl (2). A 50 mL flask was charged with **1** (0.201 g, 0.347 mmol) and 2-propanol (15 mL). To the suspension was added MeONa (18.7 mg, 0.346 mmol), and the mixture was stirred for 2 h to give an orange solution. After evaporation of the solvent, the residue was extracted with benzene (5.0 mL × 3). The solvent was removed in vacuo to give a yellow solid of **2** (0.347 mmol, 99%). Crystals suitable for an X-ray diffraction study were grown from the slow diffusion of pentane into the ether solution of **2**. Mp: 218.6−220.0 °C. ^{1}H NMR (C_6D_6): δ 5.25 (sept, J = 7 Hz, 1H, NC*H*Me$_2$), 4.14 (quintet, J = 7 Hz, 1H, NC*H*MeCH$_2$), 3.95 (dd, J = 10, 7 Hz, 1H, Ir−CH$_2$), 2.26 (d, J = 10 Hz, 1H, Ir−CH$_2$), 1.80 (s, 3H, MeC═C), 1.72 (s, 15H, Cp*), 1.59 (d, J = 7 Hz, 3H, NCH*Me*Me), 1.55 (s, 3H, C═CMe), 1.31 (d, J = 7 Hz, 3H, NCHMe*Me*), 0.98 (d, J = 6 Hz, 3H, NCH*Me*CH$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 161.8 (s, Ir−C), 122.9 (s, *C*═C), 122.3 (s, C═*C*), 88.1 (s, *C*$_5$Me$_5$), 57.5 (s, N*C*HMeCH$_2$), 53.4 (s, N*C*HMe$_2$), 24.7 (s, NCH*Me*CH$_2$), 23.5 (s, NCH*Me*Me), 23.0 (s, NCHMe*Me*), 18.5 (s, Ir−CH$_2$), 10.2 (s, *Me*C═C), 9.8 (s, C$_5$*Me*$_5$), 9.1 (s, C═C*Me*). Anal. Calcd for $C_{21}H_{34}N_2ClIr$: C, 46.51; H, 6.33; N, 5.17; Cl, 6.54. Found: C, 46.25; H, 6.31; N, 5.05; Cl, 6.26.

Reaction of 1 with *t*-BuONa. A 30 mL flask was charged with **1** (31.7 mg, 54.8 μmol) and *tert*-butyl alcohol (2.0 mL). To the suspension was added *t*-BuONa (5.2 mg, 54.1 μmol), and the mixture was stirred for 2 h to give a deep red solution. After evaporation of the solvent, the residual complex was extracted with benzene (3.0 mL × 3). The solvent was removed in vacuo to give a red-brown solid (32.6 mg). The residual mixture was analyzed by means of ^{1}H NMR. The ^{1}H NMR spectrum showed the existence of complexes **2** (62%) and **1** (38%).

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Monitoring of the Intramolecular C−H Bond Activation Reaction of 1 at a Low Temperature. An NMR tube was charged with the complex **1** (29.3 mg, 50.6 μmol) and CD_3OD (0.4 mL), and the resulting suspension was precooled to a temperature below −80 °C. A solution of MeONa (3.0 mg, 55.5 μmol) in CD_3OD (0.1 mL) was added into the resulting suspension by a syringe. The resulting suspension was monitored from −80 to 20 °C by an NMR spectrometer.

Monitoring of the Intramolecular C−H Bond Activation Reaction of 1 at Room Temperature. An NMR tube was charged with the complex **1** (31.4 mg, 54.3 μmol) and CD_3OD (0.5 mL). MeONa (3.0 mg, 55.5 μmol) was added into the resulting suspension. The resulting solution was monitored at room temperature by an NMR spectrometer. The ^{1}H NMR spectrum showed the existence of complex **2** (81%), **1** (19%), and CH_3OH after 5 min.

[Cp*Ir(I*i*-PrMe′)(MeCN)][OTf] (4). A 30 mL flask was charged with complex **2** (52.5 mg, 96.8 μmol), CH_2Cl_2 (2.0 mL), and acetonitrile (19.8 mg, 0.482 mmol). To the solution was added AgOTf (25.8 mg, 0.100 mmol), and the reaction mixture was stirred for 2 h. After the solvent was removed in vacuo, the residue was extracted with CH_2Cl_2 (2.0 mL × 3), and the solution was filtered by a pad of Celite. The solvent was removed to give the pale yellow-green solid **4** in almost quantitative yield. ^{1}H NMR ($CDCl_3$): δ 4.93 (sept, J = 7 Hz, 1H, NC*H*Me$_2$), 4.31 (m, 1H, NC*H*MeCH$_2$), 2.64 (m, 1H, Ir−CH$_2$), 2.55 (s, 3H, NCMe), 2.27 (s, 3H, MeC═C), 2.18 (s, 3H, C═CMe), 1.98 (d, J = 10 Hz, 1H, Ir−CH$_2$), 1.81 (s, 15H, Cp*), 1.66 (d, J = 7 Hz, 3H, NCH*Me*Me), 1.38 (d, J = 6 Hz, 3H, NCHMe*Me*), 1.09 (d, J = 6 Hz, 3H, NCH*Me*CH$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.7 (s, Ir−C), 124.6 (s, *C*═C), 124.3 (s, C═*C*), 120.7 (q, J = 320 Hz, CF_3), 116.1 (s, N*C*Me), 90.8 (s, *C*$_5$Me$_5$), 57.1 (s, N*C*HMeCH$_2$), 53.5 (s, N*C*HMe$_2$), 23.9 (s, NCH*Me*CH$_2$), 22.5 (s, NCH*Me*Me), 22.4 (s, NCHMe*Me*), 14.5 (s, Ir−CH$_2$), 10.4 (s, *Me*C═C), 9.3 (s, C$_5$*Me*$_5$ and C═C*Me*), 3.6 (s, NC*Me*). Further purification by means of recrystallization or chromatography was unsuccessful. Instead, ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** are cited in the Supporting Information.

A 30 mL flask was charged with the complex **3**·0.5CH_3COCH_3 (40.0 mg, 43.6 μmol) and methanol (1.0 mL). To the solution was added MeONa (2.4 mg, 44.4 μmol), and the reaction mixture was stirred for 2 h to give a pale yellow solution. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 (2.0 mL × 3) and the solution was filtered through a pad of Celite. The solvent was removed in vacuo to give a yellow solid of **4** in almost quantitative yield.

A 30 mL flask was charged with the complex **3**·0.5CH_3COCH_3 (37.0 mg, 40.3 μmol) and CH_2Cl_2 (1.0 mL). To the solution was added NEt_3 (4.2 mg, 41.5 μmol), and the reaction mixture was stirred for 2 h to give a pale yellow solution. The solvent was removed in vacuo to give a yellow solid of **4** and NEt_3·HOTf.

Ir(I*i*-PrMe)(cod)Cl (6). 1,3-Diisopropyl-4,5-dimethylimidazole-2(3*H*)-thione (0.441 g, 2.08 mmol) was stirred in THF (16 mL) at 0 °C, and metallic potassium (0.874 g, 22.4 mmol) was added. After 15 min, the resulting mixture was heated at reflux for 4 h. The reaction mixture was cooled to room temperature and filtered through a glass filter. The filtrate was dropped through a cannula into an orange suspension of [Ir(μ-Cl)(cod)]$_2$ (0.697 g, 1.04 mmol) in THF (8.0 mL) at 0 °C with stirring. After 15 min, the reaction mixture was warmed to room temperature and stirred for an additional 30 min. The solvent was removed in vacuo to give a yellow solid of **6** (2.00 mmol, 96%). Mp: 231.0−232.2 °C. ^{1}H NMR ($CDCl_3$): δ 5.92 (sept, J = 7 Hz, 2H, NC*H*Me$_2$), 4.49 (m, 2H, COD CH), 3.00 (m, 2H, COD CH), 2.2−2.1 (m, 4H, COD CH$_2$), 2.17 (s, 6H, C═CMe), 1.7−1.5 (m, 4H, COD CH$_2$), 1.57 (d, J = 7 Hz, 6H, NCH*Me*Me), 1.48 (d, J = 7 Hz, 6H, NCHMe*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 177.3 (s, Ir−C), 124.6 (s, C═C), 82.2 (s, COD CH), 53.3 (s, N*C*HMe$_2$), 50.9 (s, COD CH), 33.6 (s, COD CH$_2$), 29.5 (s, COD CH$_2$), 22.3 (s, NCH*Me*Me), 21.7 (s, NCHMe*Me*), 10.3 (s, C═C*Me*). Anal. Calcd for $C_{19}H_{32}N_2ClIr$: C, 44.21; H, 6.26; N, 5.43; Cl, 6.87. Found: C, 44.42; H, 6.17; N, 5.29; Cl, 6.42.

Cp^{N}Ir(I*i*-PrMe)(η^2-cod) (7). A 50 mL flask was charged with Cp^{N}Na (0.246 g, 1.54 mmol) and **6** (0.798 g, 1.54 mmol). After the flask was cooled to 0 °C, THF (30 mL) cooled to 0 °C was added in a stream. The mixture was heated at reflux for 3 h. After removal of THF, the residue was extracted with hexane (8 mL × 5) to give a red-brown solution. The solvent was removed to give a brown solid of **7** (1.30 mmol, 84%). Mp: 124.4−127.3 °C dec. IR (cm^{-1}, Nujol): ν_{COD} 1616 br s. ^{1}H NMR (C_6D_6): δ 6.76 (sept, J = 7 Hz, 2H, NC*H*Me$_2$), 6.0−5.9 (m, 2H, uncoordinated COD CH), 5.03 (t, J = 2 Hz, 2H, C$_5$*H*$_4$CH$_2$), 4.77 (t, J = 2 Hz, 2H, C$_5$*H*$_4$CH$_2$), 2.7−2.6 (m, 4H, C$_5$H$_4$C*H*$_2$ and COD CH$_2$), 2.6−2.5 (m, 4H, C*H*$_2$NMe$_2$ and COD CH$_2$), 2.4 (m, 2H, COD CH$_2$), 2.19 (s, 6H, NMe$_2$), 2.0−1.9 (m, 2H, COD CH$_2$), 1.8 (m, 2H, coordinated COD CH), 1.76 (s, 6H, C═CMe), 1.30 (d, J = 7 Hz, 6H, NCH*Me*Me), 1.12 (d, J = 7 Hz, 6H, CHMe*Me*). ^{13}C{^{1}H} NMR (C_6D_6): δ 162.9 (s, Ir−C), 131.6 (s, uncoordinated COD CH), 122.7 (s, C═C), 101.2 (s, *C*$_5$H$_4$CH$_2$), 78.6 (s, *C*$_5$H$_4$CH$_2$), 74.7 (s, *C*$_5$H$_4$CH$_2$), 62.8 (s, *C*H$_2$NMe$_2$), 55.2 (s, N*C*HMe$_2$), 45.8 (s, NMe$_2$), 37.4 (s, COD CH$_2$), 33.5 (s, COD CH$_2$), 32.1 (s, coordinated COD CH), 27.8 (s, C$_5$H$_4$*C*H$_2$), 22.2 (s, NCH*Me*Me), 22.1 (s, NCHMe*Me*), 10.0 (s, C═C*Me*). Anal. Calcd for $C_{28}H_{46}N_3Ir$: C, 54.50; H, 7.53; N, 6.81. Found: C, 53.07; H, 7.35; N, 6.52. Because **5** is less stable, the elemental analysis was unsatisfactory.

Cp^{N}Ir(I*i*-PrMe)I$_2$ (8). A 50 mL flask was charged with **7** (0.805 g, 1.30 mmol) and ether (15 mL). Into the resulting solution was dropped a solution of iodine (0.315 g, 1.24 mmol) in ether (9.0 mL) through a cannula to give the brown precipitate of **8**. After 1 h, the resulting precipitate was filtered by a glass filter and washed with ether (5.0 mL × 4). The precipitate was dried to give a brown solid of **8** (1.02 mmol, 78%). Mp: 114.9−116.1 °C. ^{1}H NMR (C_6D_6): δ 6.19 (sept, J = 7 Hz, 2H, NC*H*Me$_2$), 5.27 (t, J = 2 Hz, 2H, C$_5$*H*$_4$CH$_2$), 4.68 (t, J = 2 Hz, 2H, C$_5$*H*$_4$CH$_2$), 2.96 (t, J = 7 Hz, 2H, C$_5$H$_4$C*H*$_2$), 2.52 (t, J = 7 Hz, 2H, C*H*$_2$NMe$_2$), 2.10 (s, 6H, NMe$_2$), 1.69 (s, 6H, C═CMe), 1.3−1.1 (br s, 12H, NCH*Me*$_2$). ^{13}C-{^{1}H} NMR (C_6D_6): δ 146.0 (s, Ir−C), 126.7 (s, C═C), 103.8 (s, *C*$_5$H$_4$CH$_2$), 80.3 (*C*$_5$H$_4$CH$_2$), 73.6 (*C*$_5$H$_4$CH$_2$), 59.2 (s, *C*H$_2$NMe$_2$), 57.0 (s, N*C*HMe$_2$), 45.2 (s, NMe$_2$), 26.7 (s, C$_5$H$_4$*C*H$_2$), 22.8 (s, NCH*Me*$_2$), 10.3 (s, C═C*Me*). Anal. Calcd for $C_{20}H_{34}N_3I_2Ir$: C, 31.50; H, 4.50; N, 5.51; I, 33.28. Found: C, 31.80; H, 4.39; N, 5.42; I, 33.16.

[Cp$^{N(H)}$Ir(I*i*-PrMe′)(MeCN)][OTf]$_2$ (9). A 50 mL flask was charged with **8** (0.299 g, 0.392 mmol), CH_2Cl_2 (30 mL), and acetonitrile (86.4 mg, 2.10 mmol). To the solution was added AgOTf (0.203 g, 0.790 mmol), and the reaction mixture was stirred for 30 min. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 (3.0 mL × 3) and the solution was filtered through a pad of Celite. After removal of the solvent, the residue was washed with benzene. The oily product was dried in vacuo to give the hygroscopic complex **9** (0.333 mmol, 85%). IR (cm^{-1}, CH_2Cl_2): ν_{N^+H} 2754 m, ν_{CN} 2339 w, 2254 w. ^{1}H NMR ($CDCl_3$): δ 8.91 (br s, 1H, N(*H*)Me$_2$), 5.78 (s, 1H, C$_5$*H*$_4$CH$_2$), 5.46 (s, 1H, C$_5$*H*$_4$CH$_2$), 5.10 (sept, J = 7 Hz, 1H, NC*H*Me$_2$), 5.07 (s, 1H, C$_5$*H*$_4$CH$_2$), 4.96 (s, 1H, C$_5$*H*$_4$CH$_2$), 4.29 (quintet, 1H, NC*H*MeCH$_2$), 3.49 (m, 2H, C*H*$_2$N(H)Me$_2$), 3.08 (d, J = 11 Hz, 1H, Ir−CH$_2$), 3.01 (t, J = 5 Hz, 6H, N(H)*Me*$_2$), 3.0−2.9 (m, 2H, C$_5$H$_4$C*H*$_2$), 2.63 (dd, J = 11, 7 Hz, 1H, Ir−CH$_2$), 2.55 (s, 3H, NCMe), 2.29 (s, 3H, C═CMe), 2.20 (s, 3H, MeC═C), 1.57 (d, J = 7 Hz, 3H, NCH*Me*Me), 1.47 (d, J = 7 Hz, 3H, NCHMe*Me*), 1.04 (d, J = 7 Hz, 3H, NCH*Me*CH$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.9 (s, Ir−C), 124.3 (2 × s, *C*═*C*), 120.5 (q, J = 320 Hz, CF_3), 117.3 (s, Me*C*N), 102.5 (s, *C*$_5$H$_4$CH$_2$), 84.5 (s, *C*$_5$H$_4$CH$_2$), 78.5 (s, *C*$_5$H$_4$CH$_2$), 77.0 (s, *C*$_5$H$_4$CH$_2$), 72.9 (s, *C*$_5$H$_4$CH$_2$), 58.1 (s, *C*H$_2$N(H)Me$_2$), 57.8 (s, N*C*HMeCH$_2$), 55.2 (s, N*C*HMe$_2$), 43.5 (s, N(H)*Me*Me), 43.4 (s, N(H)Me*Me*), 23.1 (NCH*Me*CH$_2$), 22.5 (s, C$_5$H$_4$*C*H$_2$), 22.3 (s,

NCH*Me*Me), 21.7 (s, NCHMe*Me*), 10.7 (s, C═C*Me*), 9.5 (s, *Me*C═C), 6.9 (s, Ir−CH_2), 4.0 (s, *Me*CN). Further purification by means of recrystallization or chromatography was unsuccessful. Instead, ^{1}H and ^{13}C{^{1}H} NMR spectra of **9** are cited in the Supporting Information.

[η^5:η^1-Cp^{N}Ir(I*i*-PrMe′)][OTf] (10). A 50 mL flask was charged with **9** (37.1 mg, 43.7 μmol) and THF (2.0 mL). To the solution was added MeOK (6.4 mg, 91 μmol), and the reaction mixture was stirred for 6 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 (2.0 mL × 4). After removal of the solvent, the residue was extracted with benzene (2.0 mL × 3) to give a yellow-orange solution. After removal of benzene, the residual complex was washed with hexane (2.0 mL × 3) to give a yellow-brown solid of **10** in almost quantitative yield. Crystals suitable for an X-ray diffraction study were grown from the slow diffusion of ether into the $CDCl_3$ solution of **10**. Mp: 133.4−134.6 °C. ^{1}H NMR ($CDCl_3$): δ 5.82 (m, 1H, $C_5H_4CH_2$), 5.45 (sept, J = 7 Hz, 1H, NC*H*Me_2), 5.18 (m, 1H, $C_5H_4CH_2$), 5.09 (m, 1H, C_5H_4-CH_2), 4.98 (m, 1H, $C_5H_4CH_2$), 4.35 (quintet, J = 6 Hz, 1H, NC*H*MeCH$_2$), 4.16 (dt, J = 12, 6 Hz, 1H, C*H*$_2$NMe_2), 3.89 (ddd, J = 12, 5, 2 Hz, 1H, C*H*$_2$NMe_2), 3.45 (d, J = 11 Hz, 1H, Ir−CH_2), 2.64 (s, 3H, N*Me*Me), 2.60 (dd, J = 6, 2 Hz, 1H, $C_5H_4CH_2$), 2.6−2.5 (m, 1H, $C_5H_4CH_2$), 2.43 (dd, J = 11, 7 Hz, Ir−CH_2), 2.34 (s, 3H, NMe*Me*), 2.30 (s, 3H, C═C*Me*), 2.19 (s, 3H, *Me*C═C), 1.69 (d, J = 7 Hz, 3H, NCH*Me*Me), 1.52 (d, J = 6 Hz, 3H, NCHMe*Me*), 0.90 (d, J = 6 Hz, 3H, NCH*Me*CH$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.5 (s, Ir−C), 124.4 (s, *C*═C), 124.1 (s, C═*C*), 121.2 (q, J = 321 Hz, CF_3), 118.7 (s, $C_5H_4CH_2$), 88.2 (s, *C*H$_2$NMe_2), 76.6 (s, $C_5H_4CH_2$), 74.0 (s, $C_5H_4CH_2$), 73.1 (s, $C_5H_4CH_2$), 72.6 (s, $C_5H_4CH_2$), 58.0 (s, N*C*HMeCH$_2$), 55.6 (s, Ir−N*Me*Me), 54.9 (s, N*C*HMe_2), 54.2 (s, Ir−NMe*Me*), 25.2 (s, $C_5H_4CH_2$), 23.8 (s, NCH*Me*CH$_2$), 23.1 (s, NCH*Me*Me), 21.8 (s, NCHMe*Me*), 11.6 (s, Ir−CH_2), 11.2 (s, C═C*Me*), 9.8 (s, *Me*C═C). Anal. Calcd for $C_{21}H_{33}N_3F_3O_3SIr$: C, 38.40; H, 5.07; N, 6.40. Found: C, 38.17; H, 4.98; N, 6.68.

CpIr(I*i*-PrMe)(η^2-cod) (11). A 50 mL flask was charged with **6** (0.305 g, 0.591 mmol) and THF (9.0 mL). To the solution was added a THF solution of CpNa (1.95 M, 0.30 mL), and the reaction mixture was heated at reflux for 5 h. The resulting mixture was cooled, and the solvent was removed in vacuo. The residue was extracted with hexane (8.0 mL × 3 and 5.0 mL × 2) to give a yellow-orange solution, and the solution was filtered through a pad of Celite. The solvent was removed to give a creamy solid as a mixture of **11** (0.468 mmol, 79%) and an unidentified isomer. Mp: 129.6−132.1 °C dec. IR (cm^{-1}, Nujol): ν_{COD} 1622 br s. ^{1}H NMR (C_6D_6): δ 6.78 (sept, J = 7 Hz, 2H, NC*H*Me_2), 6.0−5.9 (m, 2H, uncoordinated COD CH), 5.05 (s, 5H, Cp), 2.8−2.7 (m, 2H, COD CH_2), 2.6 (m, 2H, COD CH_2), 2.4−2.3 (m, 2H, COD CH_2), 2.0−1.9 (m, 2H, COD CH_2), 1.9−1.8 (m, 2H, coordinated COD CH), 1.74 (s, 6H, C═CMe), 1.28 (d, J = 7 Hz, 6H, NCH*Me*Me), 1.03 (d, J = 7 Hz, 6H, CHMe*Me*). ^{13}C{^{1}H} NMR (C_6D_6): δ 162.0 (s, Ir−C), 131.5 (s, uncoordinated COD CH), 122.6 (s, C═C), 77.8 (s, Cp), 55.4 (s, N*C*HMe_2), 38.3 (s, COD CH_2), 33.7 (s, COD CH_2), 33.3 (s, coordinated COD CH), 22.0 (s, NCH*Me*Me), 21.9 (s, NCHMe*Me*), 10.1 (s, C═C*Me*). Anal. Calcd for $C_{24}H_{37}N_2Ir$: C, 52.81; H, 6.85; N, 5.13. Found: C, 51.49; H, 6.78; N, 4.91.

CpIr(I*i*-PrMe)I_2 (12). A 50 mL flask was charged with isomers **11** (0.273 g, 0.500 mmol) and ether (10 mL). Into the resulting solution was dropped a solution of iodine (0.121 g, 0.477 mmol) in ether (5.0 mL) through a cannula to give the red-brown precipitate of **12**. After 1 h, the resulting precipitate was filtered by a glass filter and washed with ether (5.0 mL × 2 and 3.0 mL × 1). The precipitate was dried to give a red-brown solid of **12** (0.432 mmol, 87%). Mp: 182.1−184.1 °C. ^{1}H NMR ($CDCl_3$): δ 6.05 (sept, J = 7 Hz, 2H, NC*H*Me_2), 5.53 (s, 5H, Cp), 2.32 (s, 6H, C═CMe), 1.47 (d, J = 7 Hz, 12H, NCH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.3 (s, Ir−C), 127.2 (s, C═C), 79.4 (s, Cp), 57.1 (s, N*C*HMe_2), 22.7 (s, NCH*Me*$_2$), 10.7 (s, C═C*Me*). Anal. Calcd for $C_{16}H_{25}N_2I_2Ir$: C, 27.79; H, 3.65; N, 4.05. Found: C, 27.86; H, 3.50; N, 4.30.

[CpIr(I*i*-PrMe)(MeCN)$_2$][OTf]$_2$ (13). A 50 mL flask was charged with **12** (0.231 g, 0.334 mmol), CH_2Cl_2 (9.0 mL), and acetonitrile (72.9 mg, 1.78 mmol). To the solution was added AgOTf (0.171 g, 0.666 mmol), and the reaction mixture was stirred at room temperature for 2.5 h to give a pale yellow-green suspension. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 (8.0 mL × 3 and 5.0 mL × 2), and the solution was filtered by a pad of Celite. The solvent was removed to give the pale yellow-brown solid **13** (0.288 mmol, 86%). Compound **13** was recrystallized from the slow diffusion of ether into an acetone solution of the crude product. Mp: 107.2−110.02 °C. IR (cm^{-1}, Nujol): ν_{CN} 2332 w, 2303 w. ^{1}H NMR (acetone-d_6): δ 6.42 (s, 5H, Cp), 5.11 (sept, J = 7 Hz, 2H, NC*H*Me_2), 2.88 (s, 6H, MeCN), 2.47 (s, 6H, C═CMe), 1.8−1.4 (2 × br s, 12H, NCH*Me*$_2$). ^{13}C{^{1}H} NMR (acetone-d_6; the CF_3 group was not detected within a suitable number of scans): δ 138.8 (s, Ir−C), 129.7 (s, C═C), 126.0 (s, Me*C*N), 83.2 (s, Cp), 55.9 (s, N*C*HMe_2), 22.0 (s, NCH*Me*$_2$), 10.7 (s, C═C*Me*), 4.4 (s, *Me*CN). Anal. Calcd for $C_{22}H_{31}N_4F_6O_6S_2Ir\cdot 0.5CH_3COCH_3$: C, 33.32; H, 4.05; N, 6.62. Found: C, 34.00; H, 4.10; N, 6.34.

X-ray Structure Analysis of 2 and 10. The crystal data and experimental details for **2** and **10** are summarized in Tables S1 and S6, respectively (see the Supporting Information). Diffraction data for **2** were obtained with a Rigaku AFC-5S instrument. The reflection intensities were monitored by 3 standard reflections every 150 measurements. Diffraction data for **10** were obtained with a Rigaku RAXIS RAPID instrument. Reflection data for **2** and **10** were corrected for Lorentz and polarization effects. Absorption corrections were empirically applied. The structure of **2** was solved by heavy-atom Patterson methods[18,19] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. The structure of **10** was solved by direct methods[20,21] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[22] The hydrogen atoms were located on the idealized positions. The calculations were performed using the program systems teXsan[23] and CrystalStructure.[24]

Supporting Information Available: An ORTEP drawing of **10**, CIF files and tables giving crystallographic data for **2** and **10**, and figures giving ^{1}H and ^{13}C{^{1}H} NMR spectra for compounds **4** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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