Scope and Mechanistic Studies of Intramolecular Aliphatic C−H Bond Activation of N-Heterocyclic Carbene Iridium Complexes§

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The series Cp*Ir(NHC) (Cp* = η^5-pentamethylcyclopentadienyl; NHC = N-heterocyclic carbene) complexes, Cp*Ir(IEt)Cl_2 (**1a**), Cp*Ir(IPr)Cl_2 (**1b**), and Cp*Ir(IBu)Cl_2 (**1c**) (IEt = 1,3-diethylimidazol-2-ylidene; IPr = 1,3-di-*n*-propylimidazol-2-ylidene; IBu = 1,3-di-*n*-butylimidazol-2-ylidene) have been prepared by the carbene-transfer method using silver salts. The reactions of **1a**−**c** with 1 equiv of *i*-PrONa in isopropyl alcohol give chloro hydrido complexes Cp*Ir(NHC)(H)(Cl) (**2a**−**c**). The reaction of **1a** with 2 equiv of *i*-PrONa in isopropyl alcohol results in the intramolecular C−H activation of the ethyl group in the NHC ligand to give Cp*Ir(IEt′)(H) (**3**), while the similar reactions of **1b** and **1c** give dihydrido complexes Cp*Ir(IPr)$(H)_2$ (**4b**) and Cp*Ir(IBu)$(H)_2$ (**4c**) as main products, respectively. These reactions proceed via alkoxo species, [Cp*Ir(NHC)(O*i*-Pr)]Cl and Cp*Ir(NHC)(O*i*-Pr)(H), as the key intermediates. Derivation of **3** into the chloro complex Cp*Ir(IEt′)(Cl) (**5**) and cationic complexes [Cp*Ir(IEt′)(L)]OTf [L = acetonitrile (**6**); pyridine (**7**)] is also described.

Introduction

Over the past decade, N-heterocyclic carbene (NHC) ligands have been extensively studied in the field of organometallic chemistry.[1] A number of transition metal complexes bearing NHC ligands have been synthesized, and their unique reactivities have been revealed.[2] Not only the fundamental properties involving electronic and structural characters of such ligands[3] but also catalytic performance of their transition metal complexes for the synthetic organic reactions have been disclosed.[4] The high electron-donating property of NHC ligands and their inertness toward decomplexation were beneficial for their use in a variety of coupling reactions and metathesis reactions, etc. However, recent reports have demonstrated that the NHC ligands are not always inert, and several interesting reactions involving the activation of the C−H bond in NHC ligands have appeared.[5] For example, Nolan has reported the intramolecular C−H activation of the tertiary butyl group of 1,3-di(*tert*-butyl)-imidazol-2-ylidene (I*t*-Bu) ligand in Rh^I and Ir^I complexes to afford coordinatively unsaturated cyclometalated Rh^{III} and Ir^{III} complexes.[5a] Whittlesey has reported the C−H activation of the ethyl group of 1,3-diethyl-4,5-dimethylimidazol-2-ylidene (IEt-Me) in a dihydrido Ru complex induced by the treatment with olefin.[5b] These findings obviously suggest that the NHC complexes are promising for the activation of unreactive C−H bonds, which have been one of the most challenging subjects in recent organometallic chemistry.

Among organometallic systems, Cp*Ir(phosphine) (Cp* = η^5-pentamethylcyclopentadienyl) complexes are known to be the most capable of achieving C−H activation reactions, and their performances have been extensively studied by Bergman[6] and other researchers.[7] Considering the similarity of the tertiary phosphines and NHCs, it can be anticipated that Cp*Ir(NHC)[8] would also exhibit a high capability for C−H activation reactions. Actually, Herrmann has reported the first intramolecular C−H activation of the cyclohexyl group in Cp*Ir(ICy)-$(Me)_2$ (ICy = 1,3-dicyclohexylimidazol-2-ylidene) induced by

§ Dedicated to the memory of Professor Yoshihiko Ito for his great contribution to organometallic chemistry.

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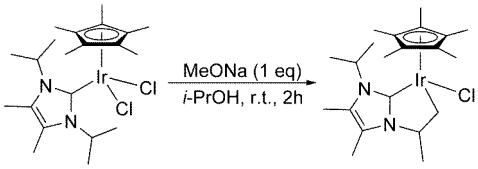
addition of acid (H^+).[9] We have also recently disclosed the facile aliphatic C−H activation of the isopropyl group in Cp*Ir(I*i*-PrMe)Cl_2 (I*i*-PrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) induced by treatment with base (MeONa) (eq 1).[10] Quite recently, Peris reported the activation of a tertiary butyl group and phenyl ring in Cp*Ir(1-*tert*-butyl-3-methylimidazol-2-ylidene)I_2 and Cp*Ir(1-benzyl-3-methylimidazol-2-ylidene)-Cl_2.[11] However, the scope of such C−H activation reactions should be brought out by systematic studies with different alkyl groups on the nitrogen, and the detailed mechanisms for the activations should be clarified.

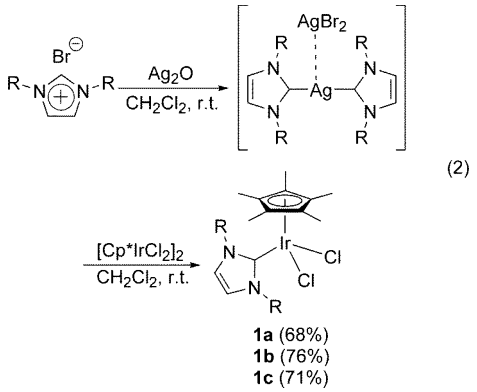
Herein, we report the synthesis of a series of Cp*Ir(NHC)-Cl_2 complexes and the important insights toward the C−H activations obtained by their reactions with base.



(1)

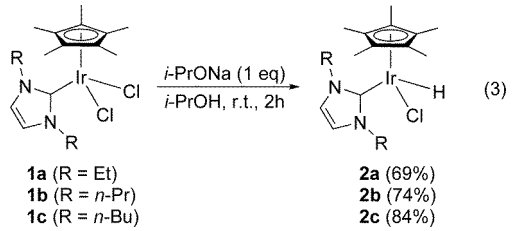
Results and Discussion

Synthesis of Cp*Ir(NHC)Cl_2 (1a−c). The Cp*Ir(NHC) complexes having ethyl, *n*-propyl, and *n*-butyl groups on the nitrogen atom in NHC ligands were synthesized by the reactions illustrated in eq 2. Complexes **1a**−**c** could be obtained by the carbene-transfer method[12] using Ag^I(NHC) complexes generated by treatment of imidazolium salts with Ag_2O. The reactions of $[Cp^*IrCl_2]_2$ with Ag^I(NHC) in CH_2Cl_2 gave **1a**−**c** in reasonable yields after recrystallization. The complexes **1a**−**c** were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectra and elemental analyses. These complexes were thermally stable in both solution and the solid state, which is in contrast to the fact that some Cp*Ir(NHC)X_2 (X = Cl or I) complexes having a *t*-Bu or benzyl group on nitrogen undergo spontaneous cyclometalation (C−H activation) under ambient conditions, reported by Peris.[11]



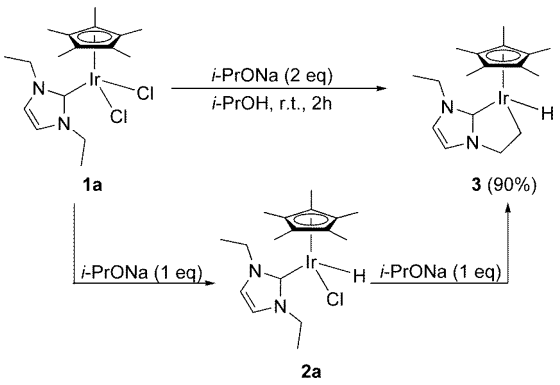
(2)

Reactions of Cp*Ir(NHC)Cl_2 (1a−c) with 1 equiv of Base: Conversion into Hydrido Complexes. We previously reported that the reaction of Cp*Ir(NHC)Cl_2 (NHC = I*i*-PrMe), having isopropyl group on the nitrogen, with 1 equiv of base in isopropyl alcohol resulted in the C−H activation of the isopropyl group (eq 1).[10] To explore the scope of this reaction, the reactions of **1a**−**c** with base (*i*-PrONa) in isopropyl alcohol were carried out. However, these reactions did not result in C−H activation; instead, they gave hydrido complexes **2a**−**c** in 69, 74, and 84% NMR yields, respectively (eq 3).[13] The structures of **2a**−**c** were elucidated by ^1H and $^{13}C\{^1H\}$ NMR and IR spectra as well as elemental analyses.[14] In the ^1H NMR spectra of **2a**−**c** in CD_2Cl_2, characteristic signals due to iridium hydrides were observed at δ −13.2, −13.3, and −13.3, respectively, which were reasonable chemical shifts for a terminal hydride in $Cp^*Ir^{III}(L)(H)(Cl)$.[15] The signals for two alkyl groups on the nitrogen were observed nonequivalently in the ^1H and $^{13}C\{^1H\}$ NMR, reflecting the unsymmetrical configuration around the iridium center. Similar conversions of Cp*Ir(L)Cl_2 into Cp*Ir-(L)(H)(Cl) by the reaction with base in alcoholic solvents are well-known with phosphine complexes.[15a]



(3)

Scheme 1



Reaction of Cp*Ir(IEt)Cl_2 (1a) with 2 equiv of Base: C−H Activation of the Ethyl Group. We next examined the reaction of **1a** with 2 equiv of *i*-PrONa in isopropyl alcohol. As illustrated in Scheme 1, the cyclometalated hydrido complex Cp*Ir(IEt′)-(H) (**3**) was obtained in high yield via intramolecular C−H activation of the ethyl group. The structure of **3** was determined by ^1H and $^{13}C\{^1H\}$ NMR spectra. In the ^1H NMR spectrum of

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(13) A similar result was obtained when MeONa was employed as a base instead of *i*-PrONa.

(14) The yields of the reactions in eq 3 were determined by ^1H NMR analysis using an internal standard method. The complexes **2a** and **2b** could also be prepared by another route: reactions of **1a** and **1b** with a small excess amount of $NaBH_4$ in THF resulted in the selective formation of **2a** and **2b**. A detailed procedure is shown in the Experimental Section.

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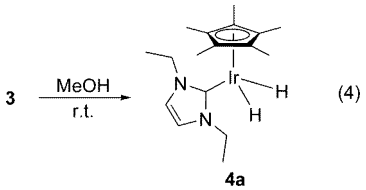
Table 1. Crystal Data and Structure Refinement Parameters for 3′ and 5

	3′	5
Description of Crystal		
color, habit	pale yellow, block	orange, block
max. cryst dimens (mm)	0.15 × 0.15 × 0.25	0.70 × 0.20 × 0.20
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a (Å)	9.140(3)	28.220(6)
b (Å)	11.718(5)	8.722(2)
c (Å)	17.275(6)	14.760(3)
α (deg)	90	90
β (deg)	99.56(1)	105.81(2)
γ (deg)	90	90
V (Å^3)	1824(1)	3495(1)
Z	4	8
formula	$C_{19}H_{31}N_2Ir$	$C_{17}H_{26}N_2ClIr$
fw	479.69	486.08
D_{calc} (g cm^{-3})	1.746	1.847
Data Collection		
radiation (λ, Å)	Mo Kα (0.71075)	Mo Kα (0.71075)
temp (K)	133	173
no. of data images	55 exposures	44 exposures
ω oscillation range ($\chi = 45.0$, $\phi = 0.0$) (deg)	130.0−190.0	130.0−190.0
exposure rate (s/deg)	180.0	200.0
ω oscillation range ($\chi = 45.0$, $\phi = 180.0$) (deg)	0.0−160.0	0.0−160.0
exposure rate (s/deg)	180.0	200.0
detector position (mm)	127.40	127.40
pixel size (mm)	0.100	0.100
$2\theta_{max}$ (deg)	50.7	55.0
no. of reflns measd	total: 13 017	total: 17 118
	unique: 3150 ($R_{int} = 0.045$)	unique: 3984 ($R_{int} = 0.033$)
Structure Determination		
no. of observations ($I > 3.00\sigma(I)$)	2735	3099
no. of variables	229	216
refln/param ratio	11.94	14.35
transmn factor	0.4990−1.2213	0.2753−1.0000
residuals: R ($I > 3.00\sigma(I)$)	0.059	0.035
residuals: R_w ($I > 3.00\sigma(I)$)	0.065	0.043
goodness of fit indicator	1.816	0.998

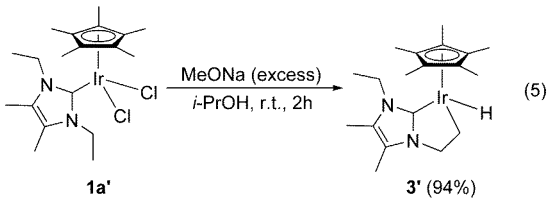
[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$.

3 in benzene-d_6, signals due to nonequivalent geminal protons on the carbon cyclometalated to the iridium center were observed at δ 2.31 and 2.87. The signal due to iridium hydride was observed at δ −16.3. In the $^{13}C\{^1H\}$ NMR spectrum in benzene-d_6, a characteristic signal for the cyclometalated carbon was observed at δ −5.4.[16] The complex **3** was stable in isopropyl alcohol; however, it slowly converted into dihydrido complex **4a** in methanol without treatment with any other reagents (eq 4). Related ring-opening reactions of a cyclometalated NHC complex by treatment with ethanol has been reported by Whittlesey.[5b]



(4)

The reaction of Cp*Ir(IEtMe)Cl$_2$ (**1a′**)[8a,b] with an excess amount of base (MeONa) also gave the similar cyclometalated complex **3′** in high yield (94%) (eq 5). The NMR signal patterns of **3′** were closely similar to those of **3**. The results of an X-ray diffraction study on **3′** are shown in Table 1 and Figure 1. It is apparent that **3′** includes a five-membered iridacycle structure, although the position of the hydride could not be determined by the difference Fourier map. The Ir−C(2) distance is 2.09(1) Å, which is similar to those in related cyclometalated Cp*Ir-(NHC) complexes[10,11] and other Cp*Ir^{III} metallacyclic complexes.[17]



(5)

To obtain information concerning the role of base, we reacted chloro hydrido complex **2a** with 1 equiv of *i*-PrONa in isopropyl alcohol. This reaction resulted in the selective formation of **3** (Scheme 1), indicating that 2 equiv of base was certainly required for the C−H activation and that conversion of **1a** to **3** would proceed via the chloro hydrido species **2a** as an intermediate.

Reactions of Cp*Ir(IPr)Cl$_2$ (1b) and Cp*Ir(IBu)Cl$_2$ (1c) with 2 equiv of Base: Conversion into Dihydrido Complexes. Then we set out to react **1b** with 2 equiv of *i*-PrONa as depicted in eq 6. This reaction was relatively complicated, but gave the dihydrido complex **4b** as the main product (40%) in addition

(16) The resonances of the iridium-bound alkyl carbon in Cp*Ir(NHC) complexes are known to be found in the range from δ 27.5 to −20.9 in the ^{13}C NMR. See refs 9, 10, and 11a.

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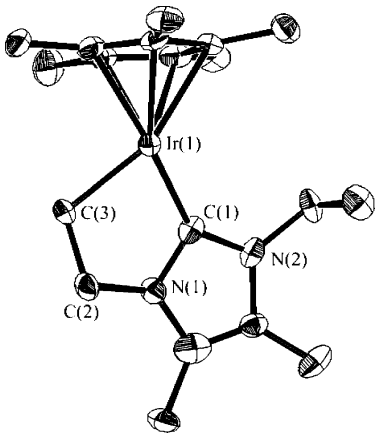
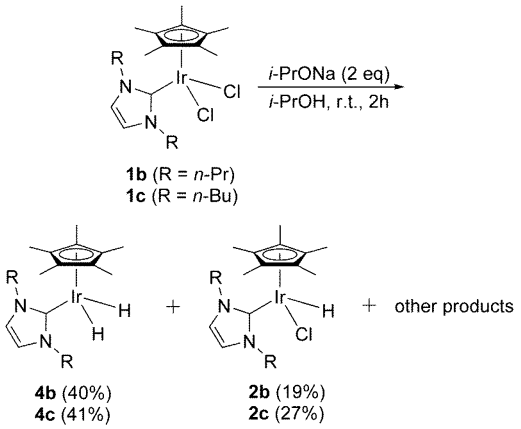


Figure 1. ORTEP drawing of Cp*Ir(IEt′Me)H (**3′**) (50% probability). The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir−C(1) 1.97(1), Ir−C(3) 2.09(1), C(2)−C(3) 1.51(2), C(1)−Ir−C(3) 77.8(5), Ir−C(3)−C(2) 112.0(8).

to a small amount of chloro hydrido complex **2b** (19%). In this reaction, cyclometalated species could not be detected.[18] The structure of **4b** was determined by ^{1}H and ^{13}C{^{1}H} NMR and IR spectra. In the ^{1}H NMR spectrum of **4b** in benzene-d_6, signals for two hydrides were equivalently observed at δ −16.9.[8a,19] Signals for the two *n*-propyl groups were observed equivalently in the ^{1}H and ^{13}C{^{1}H} NMR, reflecting the symmetric configuration around the iridium center. The reaction of **1c** with 2 equiv of *i*-PrONa also resulted in the formation of dihydrido complex **4c** as the main product (eq 6). These results are obviously different from that by the reaction of **1a** with 2 equiv of *i*-PrONa to give the cyclometalated complex via the C−H activation.



Mechanistic Consideration. A possible mechanism for the reactions of Cp*Ir(NHC)Cl$_2$ with base is summarized in Scheme 2. The first step of the reaction would be a nucleophilic attack of the isopropoxide to the iridium center followed by dechlorination, affording the cationic isopropoxide intermediate **A**. The spectroscopic evidence for the formation of this intermediate has been already mentioned in our earlier publication.[10] When the NHC ligand is I*i*-PrMe, rapid C−H activation induced by a Brønsted basic isopropoxide ligand occurs to give the cyclometalated product.[10] On the other hand, when the NHC is IEt, IPr, or IBu, β-hydrogen elimination preferentially occurs from iridium isopropoxide in **A** to afford **2**. The different reactivity of **A** can be attributed to the steric effect of substituents on the nitrogen in the NHC ligand; when the NHC is IEt, IPr, or IBu, the β'-C−H bond in the alkyl group on the nitrogen might be oriented far from the iridium center. Therefore, it would be very hard to undergo C−H activation affording the five-membered iridacycle.[20] Then, nucleophilic attack of the isopropoxide to the iridium center in **2** and dechlorination occurs again to afford the hydrido isopropoxide intermediate **B**. A phosphine complex Cp*Ir(PPh$_3$)(OEt)(H) closely related to **B**, which can be prepared by the reaction of Cp*Ir(PPh$_3$)Cl$_2$ with 2 equiv of EtONa, has been reported by Bergman.[21] The reactivity of **B** again depends on the alkyl substituent in the NHC ligand. When the NHC ligand is IEt, the intramolecular C−H activation proceeds much more rapidly than the β-hydrogen elimination, and eventually, the cyclometalated product **3** is obtained.[22] When the NHC ligand is IPr or IBu, the β-hydrogen elimination from iridium isopropoxide **B** giving **4** predominates.[23] This difference could be rationalized by the following explanation: (1) C−H activation proceeds regioselectively at the β'-position with respect to the nitrogen atom in the NHC ligand, because it gives rise to five-membered iridacyles; (2) when there is no substituent at the β'-position, i.e., Et, the C−H activation would be favorable to afford **3**; (3) when there is a substituent at the β'-position, i.e., Pr and Bu, it would be sterically difficult for the β'-C−H bond to approach the iridium center and, therefore, the C−H activation hardly occurs; instead β-hydrogen elimination proceeds predominately to afford **4**.

There would be two possible reaction paths in the critical stage of the C−H activation leading to **3** (Scheme 3): (1) direct C−H activation on Ir^{III} species induced by a Brønsted basic isopropoxide ligand (*path a*); (2) stepwise reaction via Ir^{I} species **D** by reductive elimination of isopropyl alcohol followed by the oxidative addition of a C−H bond (*path b*).[24] To obtain further information concerning the C−H activation, deuterium labeling experiments were carried out. At first, **2a-*d*$_1$** (75% D) was prepared by the reaction of **1a** with NaBD$_4$. The reaction of **2a-*d*$_1$** with 1 equiv of *i*-PrONa in isopropyl alcohol gave **3-*d*$_1$** (35% D). This result indicates that the present C−H activation proceeds via *path a*; if the C−H activation proceeds via *path b*, product **3** could not contain any deuterium.[25,26]

Reactivity of Cyclometalated Cp*Ir(IEt′)(H) (3): Derivation to Chloro and Cationic Complexes. Complex **3** was readily converted into the chloro complex Cp*Ir(IEt′)Cl (**5**) upon dissolving it in chloroform with an isolated yield of 86% (eq

(18) Although formation of a very small amount of the cyclometalated compound could not be ruled out, it is apparent that the main reaction pathway is different from that of **1a**.

(19) (a) Heinekey, D. M.; Fine, D. A.; Harper, T. G. P.; Michel, S. T. *Can. J. Chem.* **1995**, *73*, 1116. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(20) When the NHC in **A** is I*i*-PrMe, at least one of the β-C−H would be oriented near the iridium center.

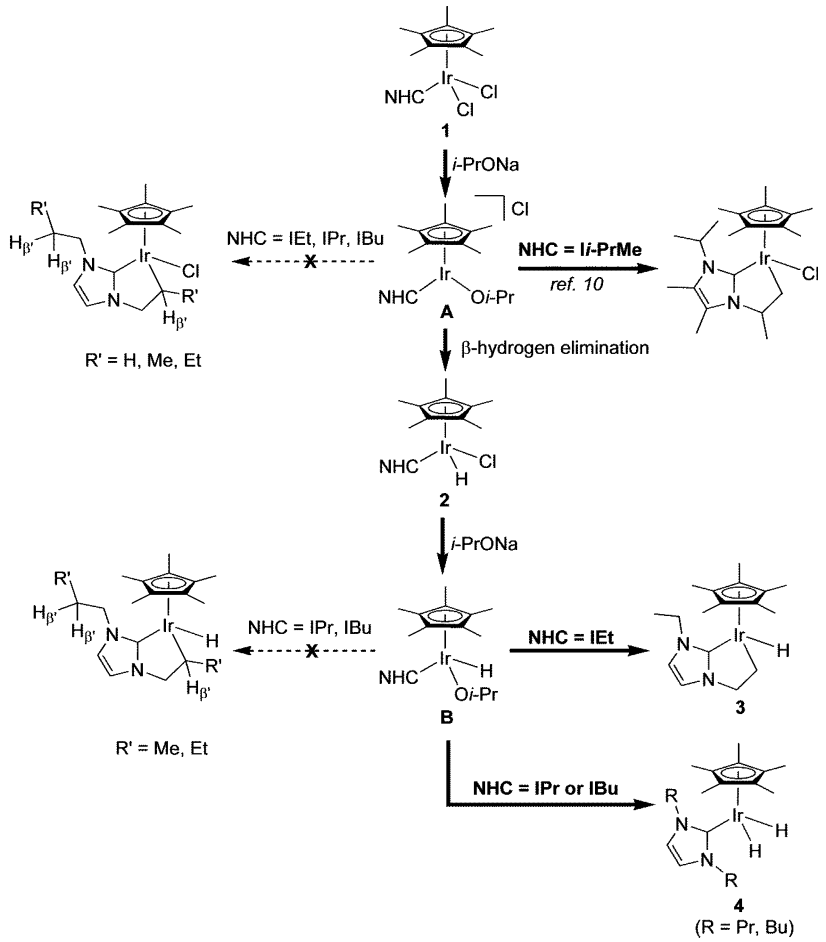
(21) Glueck, D. S.; Newman, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462.

(22) The β-hydrogen elimination in **B** would be slower than that in **A**, because **B** is a saturated 18e$^-$ species, while **A** is an unsaturated 16e$^-$ species.

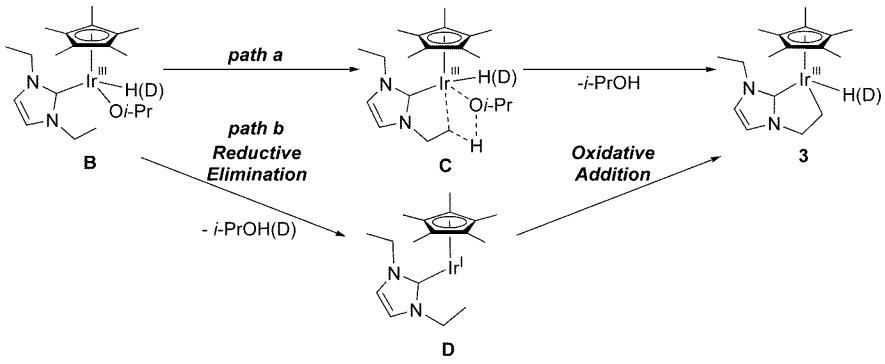
(23) The β-hydride elimination would probably proceed through the η^3-Cp* complex intermediate, which can provide a vacant coordination site.

(24) There could be two other mechanisms for the C−H activation from **2a** to afford **3**. The first one includes the reductive elimination of hydrogen chloride form **2a** to give an Ir^{I} intermediate, followed by the oxidative addition of the C−H bond. This mechanism can be ruled out by the result observed in the activation reaction using **2a-*d*$_1$**. The second one includes the oxidative addition of the C−H bond in **2a** to afford an Ir^{V} intermediate, followed by the reductive elimination of hydrogen chloride. We cannot completely rule out this possibility. However, since the Ir^{V} species are not so common, we prefer *path a*. Additionally, we have conducted a low-temperature (10 to 30 °C) ^{1}H NMR analysis of the C−H activation reaction of **2a** with *i*-PrONa in isopropyl alcohol-d_8. Only one intermediate, probably **B**, could be detected during the reaction (see Figures S1−S3 in the Supporting Information).

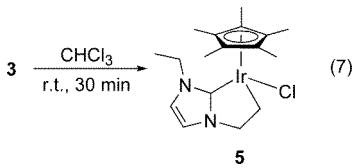
Scheme 2



Scheme 3



7).[27] The structure of **5** was determined by NMR and elemental analysis. In the $^{13}C\{^1H\}$ NMR spectrum, a signal for the cyclometalated carbon bound to iridium was observed at δ 7.8, which shifted to lower field compared to the hydrido complex **3** (δ −5.4). Other signal patterns of the NMR spectra of **5** were closely similar to those of **3** except for the hydride region. To confirm its structure, an X-ray diffraction study was performed. The results are shown in Table 1 and Figure 2.



(7)

We next tried the derivation of **5** into cationic complexes. The reactions of **5** with AgOTf in the presence of an excess amount of acetonitrile resulted in the formation of the cationic cyclometalated complex **6** in a yield of 88% (eq 8). A similar reaction in the presence of pyridine also gave the cationic

(25) Complete retention of the deuterium incorporation would be expected if the reaction proceeds via *path a*. However, about a half of a deuterium was lost (75 to 35%), probably because of H/D scrambling of **2a-*d*$_1$** with the solvent, isopropyl alcohol. Actually, when the solution of **2a-*d*$_1$** in isopropyl alcohol was stirred at room temperature for 2 h, complete conversion to **2a** with no deuterium was observed.

(26) We examined the activation reaction of **2a-*d*$_1$** in toluene and tetrahydrofuran to prevent the H/D scrambling, but the reaction did not proceed in these solvents.

(27) There are some reports on the conversion of Ir−H into Ir−Cl by treatment with chloroform. For example: (a) Sola, E.; Torres, F.; Jiménez, M. V.; López, J. A.; Ruiz, S. E.; Lahoz, F. J.; Elduque, A.; Oro, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 11925. (b) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704.

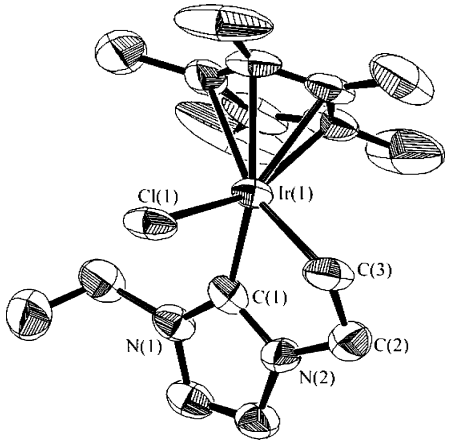
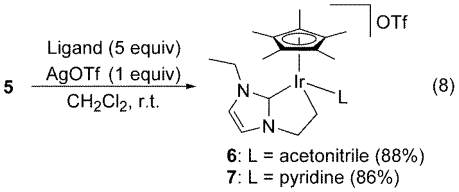


Figure 2. ORTEP drawing of Cp*Ir(IEt′)Cl (**5**) (50% probability). The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir−Cl(1) 2.429(2), Ir−C(1) 1.992(6), Ir−C(3) 2.114(7), C(2)−C(3) 1.509(8), C(1)−Ir−C(3) 77.3(2), C(1)−Ir−Cl(1) 89.2(2), Cl(1)−Ir−C(3) 88.7(2), Ir−C(3)−C(2) 110.6(5).

complex **7** in 86% yield. The structure of these cationic complexes was determined by the spectroscopic data.



Summary

We have described the reactivity of a series of Cp*Ir(NHC)-Cl_2 complexes with base changing the steric hindrance of the alkyl groups on the nitrogen atoms in the NHC ligands. The present study demonstrates that the reactivity of Cp*Ir(NHC) complexes shows great sensitivity to small steric changes in the substituent on nitrogen. The scope and detailed mechanism for the alkyl C−H activation in Cp*Ir(NHC) systems have been clarified by these systematic studies including deuterium labeling experiments. We have also represented the derivation of a cyclometalated Cp*Ir(NHC) complex into cationic complexes.

Experimental Section

General Procedures. All the reactions and manipulations were carried out under an atmosphere of argon by means of Schlenk techniques. ^{1}H, ^{2}H, and ^{13}C{^{1}H} NMR spectra were recorded on JEOL A-500 and EX-270 spectrometers. Infrared spectra were obtained on a Shimadzu IR Prestige-21 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. $[Cp^*IrCl_2]_2$,[28] Cp*Ir(IEtMe)Cl_2,[8a,b] 1-propylimidazole,[29] and imidazolium bromides[30] were prepared by the literature methods. Other reagents were used as obtained from commercial sources.

Synthesis of Cp*Ir(IEt)Cl_2 (1a). Silver oxide (0.439 g, 1.89 mmol) was added to a solution of 1,3-diethylimidazolium bromide (0.729 g, 3.55 mmol) in CH_2Cl_2 (32 mL) in the dark. The solution was stirred at room temperature for 2 h, and then $[Cp^*IrCl_2]_2$ (1.41 g, 1.77 mmol) was added. The mixture was stirred at room temperature for 1 h and filtered through Celite. The solvent was evaporated, and the crude solid was dissolved in CH_2Cl_2/acetone (9:1) and purified by SiO_2 column chromatography. After the solvent was evaporated, slow diffusion of *n*-pentane into the solution of the crude product in CH_2Cl_2 (6 mL) gave orange crystals of **1a** (1.27 g, 2.43 mmol, 69%). Mp: 263.5−265.4 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (s, 2H, C*H* imidazole), 4.68 (m, 2H, NC*H*HCH$_3$), 4.00 (m, 2H, NCH*H*CH$_3$), 1.59 (s, 15H, Cp*), 1.47 (t, J = 7 Hz, 6H, NCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 155.6 (s, Ir−C), 120.8 (s, C═C), 88.3 (s, C_5Me$_5$), 45.1 (s, NCH$_2$-CH$_3$), 16.7 (s, NCH$_2$*C*H$_3$), 8.8 (s, C$_5$*Me*$_5$). Anal. Calcd for $C_{17}H_{27}N_2Cl_2Ir$: C, 39.08; H, 5.21; N, 5.36. Found: C, 38.80; H, 5.03; N, 5.34.

Synthesis of Cp*Ir(IPr)Cl_2 (1b). Silver oxide (0.228 g, 0.98 mmol) was added to a solution of 1,3-dipropylimidazolium bromide (0.428 g, 1.84 mmol) in CH_2Cl_2 (17 mL) in the dark. The solution was stirred at room temperature for 2 h, and then $[Cp^*IrCl_2]_2$ (0.730 g, 0.917 mmol) was added. The mixture was stirred at room temperature for 1 h and filtered through Celite. The solvent was evaporated, and the crude solid was dissolved in CH_2Cl_2/acetone (9:1) and purified by SiO_2 column chromatography. After the solvent was evaporated, slow diffusion of *n*-pentane into the solution of the crude product in CH_2Cl_2 (5 mL) gave orange crystals of **1b** (0.773 mg, 1.40 mmol, 76%). Mp: 234.8−236.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (s, 2H, C*H* imidazole), 4.55 (m, 2H, NC*H*HCH$_2$CH$_3$), 3.82 (m, 2H, NCH*H*CH$_2$ CH$_3$), 2.05 (m, 2H, NCH$_2$C*H*HCH$_3$), 1.74 (m, 2H, NCH$_2$CH*H*CH$_3$), 1.60 (s, 15H, Cp*), 1.00 (t, J = 7 Hz, 6H, NCH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 155.7 (s, Ir−C), 121.0 (s, C═C), 88.4 (s, C_5Me$_5$), 52.1 (s, NCH$_2$CH$_2$CH$_3$), 24.9 (s, NCH$_2$*C*H$_2$CH$_3$), 11.1 (s, NCH$_2$-CH$_2$*C*H$_3$), 8.9 (s, C$_5$*Me*$_5$). Anal. Calcd for $C_{19}H_{31}N_2Cl_2Ir$: C, 41.45; H, 5.68; N, 5.09. Found: C, 41.18; H, 5.54; N, 5.09.

Synthesis of Cp*Ir(IBu)Cl_2 (1c). Silver oxide (0.350 g, 1.51 mmol) was added to a solution of 1,3-dibutylimidazolium bromide (0.771 g, 2.95 mmol) in CH_2Cl_2 (27 mL) in the dark. The solution was stirred at room temperature for 2 h, and then $[Cp^*IrCl_2]_2$ (1.17 g, 1.47 mmol) was added. The mixture was stirred at room temperature for 1 h and filtered through Celite. The solvent was evaporated, and the crude solid was dissolved in CH_2Cl_2/acetone (9:1) and purified by SiO_2 column chromatography. After the solvent was evaporated, slow diffusion of *n*-pentane into the solution of the crude product in CH_2Cl_2 (6 mL) gave orange crystals of **1c** (1.21 g, 2.09 mmol, 71%). Mp: 225.3−228.9 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (s, 2H, C*H* imidazole), 4.62 (m, 2H, NC*H*HCH$_2$CH$_2$CH$_3$), 3.83 (m, 2H, NCH*H*CH$_2$CH$_2$ CH$_3$), 2.01 (m, 2H, NCH$_2$C*H*HCH$_2$CH$_3$), 1.69 (m, 2H, NCH$_2$CH*H*CH$_2$CH$_3$), 1.60 (s, 15H, Cp*), 1.48 (m, 2H, NCH$_2$CH$_2$ C*H*HCH$_3$), 1.39 (m, 2H, NCH$_2$CH$_2$CH*H*CH$_3$), 0.97 (t, J = 7.5 Hz, 6H, NCH$_2$CH$_2$-CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 155.7 (s, Ir−C), 121.0 (s, C═C), 88.4 (s, C_5Me$_5$), 50.5 (s, NCH$_2$CH$_2$ CH$_2$CH$_3$), 33.7 (s, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.1 (s, NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.9 (s, NCH$_2$CH$_2$CH$_2$*C*H$_3$), 9.0 (s, C$_5$*Me*$_5$). Synthesis of the title complex has been already reported by Peris.[11b] Anal. Calcd for $C_{21}H_{35}N_2Cl_2Ir$: C, 43.59; H, 6.10; N, 4.84. Found: C, 43.44; H, 6.02; N, 4.87.

Reactions of 1a−c with 1 equiv of *i*-PrONa: Conversion into Hydrido Complexes 2a−c. *i*-PrONa (3.5 mg, 0.043 mmol) was added to the suspension of **1a** (21.0 mg, 0.040 mmol) in isopropyl alcohol (2.4 mL) at room temperature. The resulting mixture was stirred for 2 h. After evaporation of the solvent, the residue was analyzed by NMR using trimethylphenylsilane as an internal standard.

(28) Ball, R. G.; Graham, W. A. G.; Heinekey, D. M.; Hoyano, J. K.; McMaster, A. D.; Mattson, B. M.; Michel, S. T. *Inorg. Chem.* **1990**, *29*, 2023.

(29) Tosoni, M.; Laschat, S.; Baro, A. *Helv. Chim. Acta* **2004**, *87*, 2742.

(30) Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, G. R. J. *Chem.−Eur. J.* **1996**, *2*, 1627.

Similar reactions of **1b** (22.3 mg, 0.405 mmol) and **1c** (23.3 mg, 0.403 mmol) with *i*-PrONa (3.4 mg, 0.041 mmol and 3.3 mg, 0.040 mmol) in isopropyl alcohol (2.4 mL) at room temperature for 2 h were conducted, respectively. After evaporation of the solvent, the residue was analyzed by NMR using trimethylphenylsilane as an internal standard.

Synthesis of Cp*Ir(NHC)(H)Cl [NHC = IEt (2a), IPr (2b)]. $NaBH_4$ (10.3 mg, 0.272 mmol) was added to the suspension of **1a** (94.7 mg, 0.181 mmol) in THF (18 mL) at room temperature. The resulting mixture was stirred for 5.5 h. After evaporation of the solvent, the residue was dissolved in benzene (8 mL), and the solution was filtered. After the solvent was evaporated, slow addition of minimum amounts of *n*-hexane (3 mL) to the solution of the crude product in toluene (9 mL) allowed separation of byproducts, and the solution was passed through a glass filter. The filtrate was evaporated to give a yellow powder of **2a** (80.5 mg, 0.165 mmol, 91%). Mp: 103.1−104.3 °C (dec). IR (KBr): ν 2103 cm^{-1} (Ir−H). ^1H NMR (500 MHz, CD_2Cl_2): δ 6.994 (s, 1H, C═C*H* imidazole), 6.985 (s, 1H, *H*C═C imidazole), 4.58 (m, 1H, NCH*H*CH_3), 4.30 (m, 1H, CH_3CH*H*N), 4.06 (m, 1H, NC*H*HCH_3), 3.94 (m, 1H, CH_3C*H*HN), 1.78 (s, 15H, Cp*), 1.44 (t, J = 7 Hz, 3H, NCH_2CH_3), 1.33 (t, J = 7.5 Hz, 3H, C*H*$_3CH_2$N), −13.24 (s, 1H, Ir−*H*). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 159.0 (s, Ir−*C*), 119.8 (s, *C*═C), 119.3 (s, C═*C*), 89.2 (s, C_5Me_5), 46.6 (s, CH_3CH_2N), 45.4 (s, NCH_2CH_3), 17.0 (s, *C*H_3CH_2N), 15.7 (s, NCH_2CH_3), 10.1 (s, C_5Me_5). Anal. Calcd for $C_{17}H_{28}N_2ClIr$: C, 41.83; H, 5.78; N, 5.74. Found: C, 41.77; H, 5.72; N, 5.82.

A similar reaction of **1b** (99.8 mg, 0.181 mmol) with $NaBH_4$ (10.2 mg, 0.270 mmol) in THF (18 mL) at room temperature for 6 h resulted in the formation of a red-orange oil of **2b** (72.4 mg, 0.140 mmol, 77%). ^1H NMR (500 MHz, CD_2Cl_2): δ 6.98 (s, 1H, C═C*H* imidazole), 6.95 (s, 1H, *H*C═C imidazole), 4.49 (m, 1H, NCH*H*CH_2CH_3), 4.22 (m, 1H, CH_3CH_2CH*H*N), 3.86 (m, 1H, NC*H*HCH_2CH_3), 3.76 (m, 1H, CH_3CH_2C*H*HN), 1.97−1.59 (m, 4H, $NCH_2CH_2CH_3$), 1.78 (s, 15H, Cp*), 1.00−0.96 (m, 6H, $NCH_2CH_2CH_3$), −13.30 (s, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 159.3 (s, Ir−C), 119.9 (s, *C*═C), 119.8 (s, C═*C*), 89.1 (s, C_5Me_5), 52.5 (brs, $NCH_2CH_2CH_3$), 25.3 (s, $NCH_2CH_2CH_3$), 24.1 (s, $NCH_2CH_2CH_3$), 11.5 (s, $NCH_2CH_2CH_3$), 11.4 (s, $NCH_2CH_2CH_3$), 10.1 (s, C_5Me_5). Elemental analysis for **2b** was unsatisfactory because of a small amount of contaminant.

Synthesis of Cp*Ir(IBu)(H)Cl (2c). *i*-PrONa (17.0 mg, 0.207 mmol) was added to the suspension of **1c** (115.4 mg, 0.199 mmol) in isopropyl alcohol (14 mL) at room temperature. The resulting mixture was stirred for 2 h. After evaporation of the solvent, the residue was extracted with benzene (6 mL), and the solution was passed through a pad of Celite. After removal of benzene, the yellow solid was washed with *n*-hexane. After drying in vacuo, slow addition of minimum amounts of *n*-hexane to the solution of the crude product in benzene allowed separation of byproducts, and the solution was passed through a glass filter. The filtrate was evaporated to give a yellow solid of **2c** (71.0 mg, 0.130 mmol, 65%). Mp: 94.8−96.2 °C (dec). IR (KBr): ν 2137 cm^{-1} (Ir−H). ^1H NMR (500 MHz, CD_2Cl_2): δ 6.98 (s, 1H, C═C*H* imidazole), 6.95 (s, 1H, *H*C═C imidazole), 4.55 (m, 1H, NCH*H*$CH_2CH_2CH_3$), 4.30 (m, 1H, $CH_3CH_2CH_2$CH*H*N), 3.88 (m, 1H, NC*H*H$CH_2CH_2CH_3$), 3.77 (m, 1H, $CH_3CH_2CH_2$C*H*HN), 1.90−1.54 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.78 (s, 15H, Cp*), 1.46−1.36 (m, 4H, $NCH_2CH_2CH_2CH_3$), 0.98 (t, J = 7 Hz, 6H, $NCH_2CH_2CH_2CH_3$), −13.32 (s, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 159.3 (s, Ir−C), 120.0 (s, *C*═C), 119.8 (s, C═*C*), 89.1 (s, C_5Me_5), 51.6 (s, $NCH_2CH_2CH_2CH_3$), 50.8 (s, $NCH_2CH_2CH_2CH_3$), 34.0 (s, $NCH_2CH_2CH_2CH_3$), 32.8 (s, $NCH_2CH_2CH_2CH_3$), 20.7 (s, $NCH_2CH_2CH_2CH_3$), 20.5 (s, $NCH_2CH_2CH_2CH_3$), 14.1 (s, $NCH_2CH_2CH_2CH_3$), 13.9 (s, $NCH_2CH_2CH_2CH_3$), 10.1 (s, C_5Me_5). Anal. Calcd for $C_{21}H_{36}N_2ClIr$: C, 46.35; H, 6.67; N, 5.15. Found: C, 46.19; H, 6.54; N, 5.02.

Synthesis of Cp*Ir(IEt′)(H) (3). *i*-PrONa (16.2 mg, 0.197 mmol) was added to the suspension of **1a** (51.9 mg, 0.0993 mmol) in isopropyl alcohol (7 mL) at room temperature. The resulting mixture was stirred for 2 h. After evaporation of the solvent, the residue was extracted with benzene (3 mL), and the solution was passed through a pad of Celite. The filtrate was evaporated to give a pale yellow oil of **3** (40.2 mg, 0.0890 mmol, 90%). ^1H NMR (500 MHz, C_6D_6): δ 6.26 (s, 1H, C═C*H* imidazole), 6.12 (s, 1H, *H*C═C imidazole), 3.88−3.78 (m, 2H, NCH*H*CH_3, NCH*H*CH_2Ir), 3.62 (m, 1H, NC*H*HCH_3), 3.54 (m, 1H, NCH*H*CH_2Ir), 2.87 (m, 1H, NCH_2CH*H*Ir), 2.31 (m, 1H, NCH_2C*H*HIr), 2.04 (s, 15H, Cp*), 1.03 (t, 3H, J = 7.5 Hz, NCH_2CH_3), −16.33 (s, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 165.6 (s, Ir−$C_{Carbene}$), 116.3 (s, *C*═*C*), 89.0 (s, C_5Me_5), 54.2 (s, N*C*H_2CH_2Ir), 44.6 (s, N*C*H_2CH_3), 15.5 (s, NCH_2CH_3), 10.8 (s, C_5Me_5), −5.4 (s, NCH_2CH_2Ir). Anal. Calcd for $C_{17}H_{27}N_2Ir$: C, 45.21; H, 6.03; N, 6.20. Found: C, 45.55; H, 5.86; N, 5.91.

Reaction of 3 with Methanol. Complex **3** (81.2 mg, 0.180 mmol) was dissolved in methanol (5 mL). After the solution was stirred for 4 h, the solvent was removed in vacuo. The conversion into dihidrido complex **4a** was confirmed by ^1H NMR in benzene-d_6.

Synthesis of Cp*Ir(IEt)(H)$_2$ (4a). A 50 mL flask was charged with **1a** (0.105 g, 0.201 mmol), $NaBH_4$ (0.075 g, 1.99 mmol), and isopropyl alcohol (8.5 mL). After the reaction mixture was stirred for 3 h, the solvent was evaporated in vacuo. The residue was extracted with toluene (10 mL), and the solution was passed through a pad of Celite. After the solution was concentrated to the volume of 5 mL, slow addition of minimum amounts of *n*-hexane to the solution of the crude product allowed separation of byproducts, and the solution was passed through a glass filter. The filtrate was evaporated and extracted with *n*-hexane to give a white solid of **4a** (72.2 mg, 0.159 mmol, 79%). Mp: 148.5−149.0 °C (dec). IR (KBr): ν 2082 cm^{-1} (Ir−H). ^1H NMR (270 MHz, C_6D_6): δ 6.23 (s, 2H, C*H* imidazole), 4.11 (q, J = 7.3 Hz, 4H, N*C*H_2CH_3), 2.18 (s, 15H, Cp*), 1.03 (t, J = 7.3 Hz, 6H, NCH_2CH_3), −16.88 (s, 2H, Ir−H). $^{13}C\{^1H\}$ NMR (68 MHz, C_6D_6): δ 161.6 (s, Ir−C), 117.4 (s, C═C), 88.8 (s, C_5Me_5), 46.7 (s, N*C*H_2CH_3), 15.5 (s, NCH_2 *C*H_3), 12.0 (s, C_5Me_5). Anal. Calcd for $C_{17}H_{29}N_2Ir$: C, 45.01; H, 6.44; N, 6.18. Found: C, 44.87; H, 6.17; N, 5.94.

Synthesis of Cp*Ir(IEtMe′)(H) (3′). MeONa (13.7 mg, 0.254 mmol) was added to the suspension of **1a′** (31.8 mg, 0.0578 mmol) in isopropyl alcohol (3 mL) at room temperature. The resulting mixture was stirred for 2 h. After evaporation of the solvent, the residue was extracted with benzene (2 mL), and the solution was passed through a pad of Celite. After removal of benzene, the isopropyl alcohol solution (0.7 mL) of the crude product was cooled in a freezer (−30 °C) to give pale yellow crystals of **3′** (27.9 mg, 0.0543 mmol, 94%) suitable for X-ray diffraction analysis. Mp: 112.9−117.2 °C (dec). IR (KBr): ν 2047 cm^{-1} (Ir−H). ^1H NMR (500 MHz, C_6D_6): δ 4.00 (m, 1H, NCH*H*CH_3), 3.77 (m, 1H, NCH*H*CH_2Ir), 3.61 (m, 1H, NC*H*HCH_3), 3.47 (m, 1H, NC*H*HCH_2Ir), 2.90 (m, 1H, NCH_2CH*H*Ir), 2.33 (m, 1H, NCH_2C*H*HIr), 2.08 (s, 15H, Cp*), 1.62 (s, 3H, C═C*Me*), 1.55 (s, 3H, *Me*C═C), 1.10 (t, 3H, J = 7.5 Hz, NCH_2CH_3). −16.31 (s, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 162.8 (s, Ir−$C_{Carbene}$), 121.2 (s, *C*═C), 119.7 (s, C═*C*), 88.8 (s, C_5Me_5), 51.5 (s, N*C*H_2 CH_2Ir), 42.3 (s, N*C*H_2CH_3), 15.3 (s, NCH_2CH_3), 10.8 (s, C_5Me_5), 9.7 (s, C═C*Me*), 8.9 (s, *Me*C═C), −6.6 (s, *C*H_2−Ir). Anal. Calcd for $C_{19}H_{31}N_2Ir$: C, 47.57; H, 6.51; N, 5.84. Found: C, 47.28; H, 6.33; N, 5.75.

Reaction of 2a with 1 equiv of *i*-PrONa. A 30 mL flask was charged with complex **2a** (23.5 mg, 0.048 mol) and isopropyl alcohol (3.5 mL). *i*-PrONa (3.9 mg, 0.048 mmol) was added to the resulting suspension, and the reaction mixture was stirred for 2 h. After removal of the solvent in vacuo, selective conversion into **3** was confirmed by ^1H NMR in benzene-d_6.

Reaction of 1b and 1c with 2 equiv of *i*-PrONa: Conversion into Dihydrido Complexes 4b and 4c. *i*-PrONa (6.7 mg, 0.082 mmol and 6.4 mg, 0.078 mmol) was added to the suspension of **1b** (21.9 mg, 0.0398 mmol) and **1c** (23.5 mg, 0.406 mmol) in isopropyl alcohol (2.4 mL) at room temperature, respectively. The resulting mixture was stirred for 2 h. After evaporation of the solvent, the residue was analyzed by NMR using trimethylphenylsilane as an internal standard.

Synthesis of Cp*Ir(IPr)(H)$_2$ (4b) and Cp*Ir(IBu)(H)$_2$ (4c). A 50 mL flask was charged with **1b** (0.112 g, 0.203 mmol), $NaBH_4$ (0.076 g, 2.01 mmol), and isopropyl alcohol (8.5 mL). After the reaction mixture was stirred for 3 h, the solvent was evaporated in vacuo. The residue was extracted with toluene (6 mL), and the solution was passed through a pad of Celite. After the solvent was evaporated, extraction with *n*-hexane (8 mL) gave a white solid of **4b** (95.3 mg, 0.197 mmol, 97%). Mp: 66.2−67.4 °C. IR (KBr): ν 2078 cm^{-1} (Ir−H). ^{1}H NMR (270 MHz, C_6D_6): δ 6.28 (s, 2H, C*H* imidazole) 4.04 (m, 4H, NCH_2CH$_2$CH$_3$), 2.19 (s, 15H, Cp*), 1.54 (m, 4H, NCH$_2$CH_2CH$_3$) 0.80 (t, J = 7.3 Hz, 6H, NCH$_2$-CH$_2$CH_3), −16.94 (s, 2H, Ir-*H*). ^{13}C{^{1}H} NMR (68 MHz, C_6D_6): δ 162.3 (s, Ir−C), 117.8 (s, C═C), 88.8 (s, C_5Me$_5$), 53.6 (s, NCH$_2$-CH$_2$CH$_3$), 23.6 (s, NCH$_2$CH_2 CH$_3$), 12.0 (s, C$_5$*Me*$_5$), 11.6 (s, NCH$_2$-CH$_2$CH_3). Anal. Calcd for $C_{19}H_{33}N_2Ir$: C, 47.37; H, 6.91; N, 5.82. Found: C, 46.90; H, 6.87; N, 5.78.

A similar reaction of **1c** (0.116 g, 0.200 mmol) with $NaBH_4$ (0.076 g, 2.01 mmol) in isopropyl alcohol (8.5 mL) at room temperature was concucted. After the reaction mixture was stirred for 3 h, the solvent was evaporated in vacuo. The residue was extracted with *n*-hexane (8 mL), and the solution was passed through a pad of Celite. The filtrate was evaporated to give a pale yellow oil of **4c** (99.7 mg, 0.196 mmol, 98%). IR (KBr): ν 2084 cm^{-1} (Ir−H). ^{1}H NMR (270 MHz, C_6D_6): δ 6.32 (s, 2H, C*H* imidazole) 4.04 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 2.19 (s, 15H, Cp*), 1.54 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.25 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 0.85 (t, J = 7.3 Hz, 6H, NCH$_2$CH$_2$CH$_2$CH_3), −16.92 (s, 2H, Ir−H). ^{13}C{^{1}H} NMR (68 MHz, C_6D_6): δ 162.2 (s, Ir−C), 117.9 (s, C═C), 88.8 (s, C_5Me$_5$), 51.8 (s, NCH$_2$CH$_2$CH$_2$CH$_3$), 32.5 (s, NCH$_2$CH$_2$CH$_2$CH$_3$), 20.6 (s, NCH$_2$CH$_2$CH$_2$CH$_3$), 14.2 (s, NCH$_2$-CH$_2$CH$_2$CH$_3$), 12.0 (s, C$_5$*Me*$_5$). Anal. Calcd for $C_{21}H_{37}N_2Ir$: C, 49.48; H, 7.32; N, 5.50. Found: C, 49.71; H, 7.04; N, 5.38.

Synthesis of Cp*Ir(IEt)(D)Cl (2a-d_1). $NaBD_4$ (19.6 mg, 0.468 mmol) was added to the suspension of **1a** (157.6 mg, 0.302 mmol) in THF (30 mL) at room temperature. The resulting mixture was stirred for 5.5 h. After evaporation of the solvent, the residue was dissolved in benzene, and the solution was filtered. The filtrate was evaporated to give a yellow solid of **2a-d_1** (144.4 mg, 0.295 mmol, 98%). ^{1}H and ^{2}H NMR analyses in benzene-d_6 and benzene showed 75% incorporation of D atom into the iridium deuteride position.

Reaction of 2a-d_1 with 1 equiv of *i*-PrONa. *i*-PrONa (3.2 mg, 0.039 mmol) was added to the suspension of **2a-d_1** (19.5 mg, 0.040 mmol) in isopropyl alcohol (3 mL) at room temperature. The reaction mixture was stirred for 2 h. After removal of the solvent in vacuo, ^{1}H and ^{2}H NMR analyses in benzene-d_6 and benzene showed the formation of **3-d_1** and 35% incorporation of D atom into the iridium deuteride position.

Variable-Temperature Analysis of the Intramolecular C−H Bond Activation. An NMR tube was charged with the complex **2a** (7.3 mg, 0.015 mmol), and the tube was precooled to a temperature below 10 °C. A solution of *i*-PrONa (1.3 mg, 0.016 mmol) in isopropyl alcohol-d_8 (0.6 mL) was added into the NMR tube by a syringe. The resulting suspension was analyzed from 10 to 30 °C with the NMR spectrometer (see Supporting Information).

Synthesis of Cp*Ir(IEt′)Cl (5). Complex **3** (421.4 mg, 0.933 mmol) was dissolved in chroloform (9 mL). After the solution was stirred for 30 min, the solvent was removed in vacuo. The residue was washed with *n*-hexane (10 mL) and dried in vacuo to give a yellow solid of **5** (390.3 mg, 0.803 mmol, 86%). Mp: 209.9−215.8 °C (dec). ^{1}H NMR (500 MHz, C_6D_6): δ 6.28 (d, J = 2 Hz, 1H, C═C*H*), 6.22 (d, J = 2 Hz, 1H, *H*C═C), 4.23 (m, 1H, NCH*H*CH$_3$), 3.85 (m, 1H, NC*H*HCH$_2$Ir), 3.67 (m, 1H, NCH*H*CH$_3$), 3.56−3.45 (m, 2H, NC*H*HCH$_2$Ir, NCH$_2$C*H*HIr), 2.52 (m, 1H, NCH$_2$CH*H*Ir), 1.65 (s, 15H, Cp*), 1.23 (t, J = 7 Hz, 3H, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 165.6 (s, Ir−$C_{Carbene}$), 118.5 (s, C═*C*), 117.1 (s, *C*═C), 87.9 (s, C_5Me$_5$), 53.0 (s, N*C*H$_2$CH$_2$Ir), 44.7 (s, N*C*H$_2$CH$_3$), 16.7 (s, NCH$_2$*C*H$_3$), 11.1 (s, NCH$_2$*C*H$_2$Ir), 9.5 (s, C$_5$*Me*$_5$). Anal. Calcd for $C_{17}H_{26}N_2ClIr$: C, 42.01; H, 5.39; N, 5.76. Found: C, 41.55; H, 5.32; N, 5.67.

Synthesis of [Cp*Ir(IEt′)(NCMe)][OTf] (6). A 30 mL flask was charged with **5** (88.8 mg, 0.183 mmol), CH_2Cl_2 (6 mL), and CH_3CN (37.2 mg, 0.906 mmol). To the solution was added AgOTf (48.9 mg, 0.190 mmol), and the reaction mixture was stirred for 1 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 (4 mL), and the solution was filtered through a pad of Celite. After removal of the solvent, the residue was washed with diethyl ether (6 mL) to give a dark yellow solid of **6** (102.6 mg, 0.160 mmol, 88%). Mp: 127.8−129.1 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, J = 2.0 Hz, 1H, C═C*H*), 7.09 (d, J = 2.0 Hz, 1H, *H*C═C), 4.21−4.09 (m, 3H, NCH*H*CH$_2$Ir, NCH_2CH$_3$), 3.72 (m, 1H, NC*H*HCH$_2$Ir), 2.55 (s, 3H, NC*Me*), 2.44 (m, 1H, NCH$_2$CH*H*Ir), 2.31 (m, 1H, NCH$_2$C*H*HIr), 1.81 (s, 15H, Cp*), 1.46 (t, J = 7.5 Hz, 3H, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 156.6 (s, Ir−$C_{Carbene}$), 128.3 (s, N*C*Me), 120.9 (q, J = 320 Hz, CF_3), 120.5(s, C═*C*), 118.7 (s, *C*═C), 90.8 (s, C_5Me$_5$), 52.5 (s, N*C*H$_2$CH$_2$Ir), 44.9 (s, N*C*H$_2$CH$_3$), 16.3 (s, NCH$_2$*C*H$_3$), 9.2 (s, C$_5$*Me*$_5$), 7.8 (s, NCH$_2$*C*H$_2$Ir), 3.8 (s, NC*Me*). Anal. Calcd for $C_{20}H_{29}N_3F_3IrO_3S$: C, 37.49; H, 4.56; N, 6.56. Found: C, 36.72; H, 4.40; N, 6.16.

Synthesis of [Cp*Ir(IEt′)(py)][OTf] (7). A 100 mL flask was charged with **5** (0.117 g, 0.241 mmol), CH_2Cl_2 (8 mL), and pyridine (93.5 mg, 1.18 mmol). To the solution was added AgOTf (63.7 mg, 0.245 mmol), and the reaction mixture was stirred for 1 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 (3 mL × 3), and the solution was filtered through a pad of Celite. After removal of the solvent, the residue was washed with diethyl ether to give a dark yellow solid of **7** (139.7 mg, 0.206 mmol, 86%). Mp: 118.3−121.2 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (m, 2H, Py), 7.79 (m, 1H, Py), 7.35 (m, 2H, Py), 7.17 (d, J = 2.0 Hz, 1H, C═C*H*), 7.15 (d, J = 2.0 Hz, 1H, *H*C═C), 4.48−4.38 (m, 2H, NCH_2CH$_3$), 3.91 (m, 1H, NCH*H*CH$_2$Ir), 3.75 (m, 1H, NC*H*HCH$_2$Ir), 2.73 (m, 1H, NCH$_2$C*H*HIr), 1.98 (m, 1H, NCH$_2$CH*H*Ir), 1.67 (s, 15H, Cp*), 1.62 (t, J = 7.0 Hz, 3H, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.3 (s, Ir−$C_{Carbene}$), 155.3 (s, Py), 137.9 (s, *p*-Py), 127.1 (s, *m*-Py), 121.0 (q, J = 320 Hz, CF_3), 120.4 (s, C═*C*), 118.9 (s, *C*═C), 89.8 (s, C_5-Me$_5$), 52.1 (s, N*C*H$_2$CH$_2$Ir), 44.7 (s, N*C*H$_2$CH$_3$), 16.1 (s, NCH$_2$*C*H$_3$), 13.6 (s, NCH$_2$*C*H$_2$Ir), 9.0 (s, C$_5$*Me*$_5$). Anal. Calcd for $C_{23}H_{31}N_3F_3$-IrO_3S: C, 40.70; H, 4.60; N, 6.19. Found: C, 40.26; H, 4.43; N, 6.13.

X-ray Structure Analysis of 3′ and 5. The crystal data and experimental details for **3′** and **5** are summarized in Table 1 (see

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(34) *CrystalStructure*, Crystal Structure Analysis Package; Rigaku and Rigaku/Molecular Structure Corp., 2002.

the Supporting Information). Diffraction data for **3′** and **5** were obtained with a Rigaku RAXIS RAPID instrument. Reflection data for **3′** and **5** were corrected for Lorentz and polarization effects. Absorption corrections were empirically applied. The structures of **3′** and **5** were solved by direct methods[31,32] 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.[33] The hydrogen atoms were located on the idealized positions. The calculations were performed using the program system CrystalStructure.[34]

Supporting Information Available: Further details in CIF format on the crystal structures of complexes **3′** and **5**, and details for variable temperature analyses of the C−H activation reaction of **2a** with *i*-PrONa. This material is available free of charge via the Internet at http://pubs.acs.org.

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