Aliphatic and Aromatic Intramolecular C−H Activation on Cp*Ir(NHC) Complexes

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Facile intramolecular aliphatic and aromatic C−H activations have been observed for a series of complexes based on the "Cp*Ir(NHC)" fragment (NHC = 1-diphenylmethyl-3-methylimidazol-2-ylidene, 1-*tert*-butyl-3-methylimidazol-2-ylidene, 1-benzyl-3-*tert*-butylimidazol-2-ylidene, and 1-benzyl-3-isopropylimidazol-2-ylidene). We have performed a series of experiments for elucidating the factors that determine the aromatic or aliphatic C−H activations that occur. In the cases where both aliphatic and aromatic C−H activations are possible, steric factors govern the selectivity of the reaction.

1. Introduction

During the last decade, the use of N-heterocyclic-carbene ligands (NHCs) has given a new dimension to the design of new transition metal complexes and homogeneous catalysts.[1] The unique electronic and steric properties of NHCs have given rise to a series of complexes with unprecedented chemical properties. For example, the stabilization of electron-deficient Rh and Ir species by intramolecular alkyl C−H activation of 1,3-di-*tert*-butyl-2-ylidene described by Nolan and co-workers[2,3] has never been observed for other phosphine-related complexes. The better σ-donor ability of NHCs compared to phosphines may explain this singular behavior[4] and, in fact, may facilitate intramolecular C−H activation. Some NHC-based complexes are known to undergo facile intramolecular alkyl,[2,3,5−7] vinyl,[8] and aryl[9,10] C−H activation processes, leading to stable cyclometalated species. Intermolecular C−H processes induced by NHC compounds are also known, although those used in catalytic processes are still scarce.[10,11]

In a very recent work, Yamaguchi and co-workers reported the intramolecular alkyl C−H activation of a series of isopropyl-functionalized imidazolylidenes coordinated to the Cp*Ir fragment.[7] The ability of Cp*Ir(NHC) complexes to undergo intramolecular C−H activation had been reported by Herrmann and co-workers, who described the cyclometalation of the complex Cp*Ir(ICy)(Me)$_2$ (ICy = 1,3-dicylohexylimidazol-2-ylidene).[6] For the phosphine analogue complexes with the fragment "Cp*Ir(PR$_3$)", Bergman and co-workers have extensively studied all processes regarding inter- and intramolecular C−H activations.[12]

We recently described a series of Cp*Ir(NHC) complexes that undergo facile intramolecular aromatic C−H activation (Scheme 1), which are effective catalysts in the deuteration of a wide range of organic molecules.[10] On the basis of these results, we now report the preparation and reactivity of a series of alkyl- and aryl-functionalized imidazolylidene complexes of Ir(III), leading to the corresponding cyclometalated products. In most cases, the cyclometalation occurs under very mild conditions, at room temperature and without need of addition of a base. The ability of our complexes to undergo aliphatic and/or aromatic C−H activation is also studied, and our results

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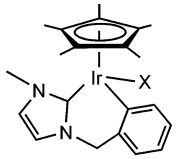
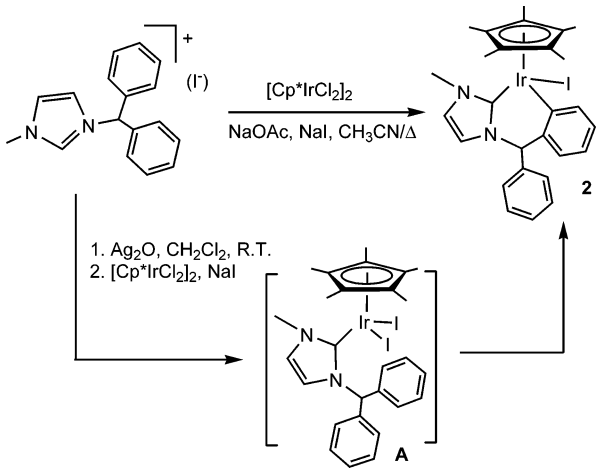
Scheme 1



1, X =Cl, I

Scheme 2



may challenge the idea that the Cp*Ir metal center shows a preference for cleavage of stronger C−H bonds.[13]

Results and Discussion

(a) Aromatic C−H Activation. We have previously reported that the orthometalation of 1-benzyl-3-methylimidazolylidene (IBzMe) in Cp^*IrCl_2(IBzMe) affords compound **1** at room temperature, with loss of HCl.[10] The facile C−H activation in this species suggested that some other similar complexes could be obtained under mild reaction conditions. In this sense, we obtained 1-diphenylmethyl-3-methylimidazolium iodide, an imidazolylidene precursor that could orthometalate, generating a chiral center in the bridging methylene carbon atom. Compound **2** can be obtained by transmetalation of 1-diphenylmethyl-3-methylimidazolium iodide from the corresponding silver carbene derivative to $[Cp^*IrCl_2]_2$ in CH_2Cl_2. Alternatively, compound **2** can be obtained by direct reaction between 1-diphenylmethyl-3-methylimidazolium iodide and $[Cp^*IrCl_2]_2$ in CH_3CN in the presence of NaOAc (Scheme 2). The addition of NaI facilitated the substitution of the Cl ligands by I in the final reaction products. Both reaction procedures led to the cyclometalated species, not allowing the detection of the monometalated species (**A**), thus suggesting that the intramolecular C−H activation is an extremely favorable process.

Compound **2** is obtained as a mixture of chiral complexes, since both the Ir atom and the carbon at the methylene bridging carbon of the cyclometalated ligand are stereogenic centers. Since none of the chiralities of the stereogenic centers are fixed, four chiral complexes are obtained from the reaction mixture, with two pairs of diastereomers being clearly differentiated by NMR spectroscopy and showing a 5:1 molar ratio according to the integrals of the ^1H NMR spectrum of the reaction mixture. Both diastereomers can be easily separated by column chromatography. The $^{13}C\{^1H\}$ NMR spectra of the products reveal that the orthometalation has occurred. The major diastereomer (**2a**) shows the signal of the carbene carbon at 154.2 ppm, while the metalated phenyl carbon appears at 145.0 ppm. The minor product (**2b**) shows a signal at δ 155.1 (carbene carbon) and 142.0 (metalated phenyl carbon). The signals due to the carbene carbon appear in the region of previously reported Cp*Ir(NHC) complexes.[6,7,10,14]

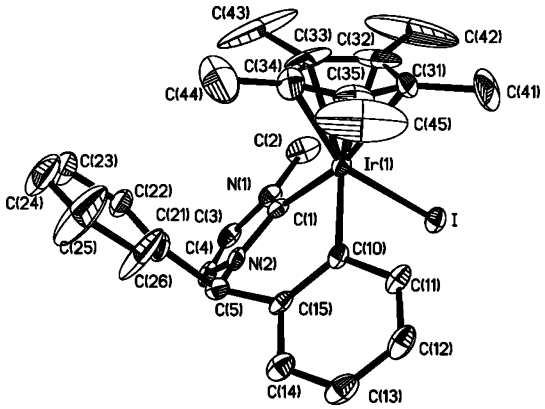


Figure 1. Molecular diagram of compound **2a**. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 1.998(8), Ir(1)−I(2) 2.7263(6), Ir(1)−C(10) 2.048(8), Ir(1)−$Cp^*_{centroid}$ 2.02(18), C(1)−Ir(1)−C(10) 86.2(3), C(1)−Ir(1)−I(2) 86.6(2), C(10)−Ir(1)−I(2) 88.0(2), $Cp^*_{centroid}$−Ir(1)−C(1) 120(6), $Cp^*_{centroid}$−Ir(1)−C(10) 96-(6), $Cp^*_{centroid}$ −Ir(1)−I(2) 153(6). Ellipsoids are at 30% probability.

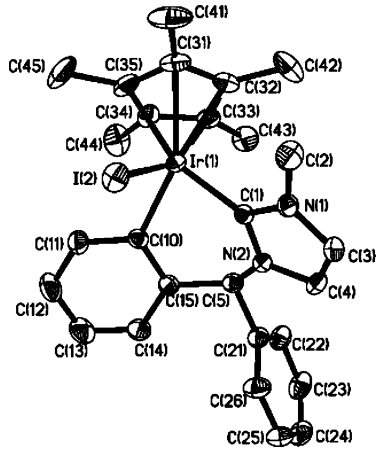


Figure 2. Molecular diagram of compound **2b**. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.001(4), Ir(1)−I(2) 2.7047(3), Ir(1)−C(10) 2.050(4), Ir(1)−$Cp^*_{centroid}$ 1.872(4), C(1)−Ir(1)−C(10) 85.83(15), C(1)−Ir(1)−I(2) 91.84(10), C(10)−Ir(1)−I(2) 87.76(11), $Cp^*_{centroid}$−Ir(1)−C(1) 129.61(2), $Cp^*_{centroid}$−Ir(1)−C(10) 126.90(8), $Cp^*_{centroid}$−Ir(1)−I(2) 122.45(5). Ellipsoids are at 30% probability.

The structures of **2a** and **2b** were confirmed by X-ray diffraction studies. The ORTEP diagrams of **2a** and **2b** are illustrated in Figures 1 and 2, respectively, together with the most representative bond distances and angles. The structures of the two complexes reveal that the orthometalation of one of the phenyl substituents of the carbene ligand has occurred, with the formation of a six-membered iridacycle in a distorted boat conformation. The Cp* ring and an iodine ligand complete the coordination sphere about the Ir center. Both complexes show similar structural parameters in terms of bond distances and angles. The chelate bite angles are 86.2° (**2a**) and 85.8° (**2b**),

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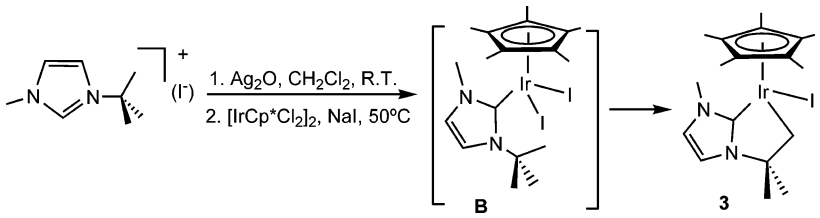
Scheme 3



similar to that shown for our previously reported cyclometalated complex **1** (85.7°).[10] The Ir−$C_{carbene}$ distances of 1.998 (**2a**) and 2.001 Å (**2b**) lie in the expected range for other similar complexes.[6,7,10,14] The Ir−C bond distances for the cyclometalated phenyl ring are 2.048 (**2a**) and 2.050 Å (**2b**).

The most important difference between the structures of **2a** and **2b** lies in the configuration of the carbon of the bridging methylene group of the chelate ligand. Figure 3 shows a lateral view of both complexes, where this different configuration can be more clearly seen. If we attend only to steric factors governing the formation of **2a** and **2b**, we may wrongly predict **2b** to be the more stable species, since the orientation of the phenyl ring suggests a lower steric hindrance about the metal center. The higher stability of **2a** is mainly due to electronic reasons. The orientation of one of the C−H bonds of the methyl groups in the Cp* ring to the centroid of the phenyl ring favors a C−H/π interaction. This low-energy hydrogen-bonding interaction is known to stabilize molecular structures by ca. 1 kcal/mol.[15] Regarding the molecular ratio in which **2a** and **2b** are obtained, we can estimate an energy difference of 0.9 (±0.3) kcal/mol between the two diastereomers.

(b) Aliphatic C−H Activation. In a recent report, Yamaguchi and co-workers reported the alkyl intramolecular C−H activation of the 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene (I^{i-PrMe}) in $Cp^*IrI_2(I^{i-PrMe})$, providing a cyclometalated complex.[7] The cyclometalation in this complex may be favored by the presence of the methyl groups in the 4 and 5 positions of the imidazolylidene, thus increasing the σ-donor character of the ligand and hence favoring the C−H activation process,[10] although the use of a strong base was needed in order to facilitate the process. To verify whether the alkylic C−H activation may have a more general character, we used 1-*tert*-butyl-3-methylimidazolium iodide as a new NHC precursor. The reaction of this imidazolium salt with Ag_2O in CH_2Cl_2 and further addition of $[Cp^*IrCl_2]_2$ provided complex **3**, in which the cyclometalation of the ligand through one of the methyl groups of the *tert*-butyl group has been produced. As we already described for the preparation of complexes **2a** and **2b**, the presence of the monometalated species (**B**, Scheme 3) was not detected under the reaction conditions used, not even when the reaction was carried out at room temperature, thus suggesting that the cyclometalation is a highly favorable process.

The ^{1}H NMR spectrum of **3** showed the signals of the nonequivalent geminal protons of the metalated CH_2 group at

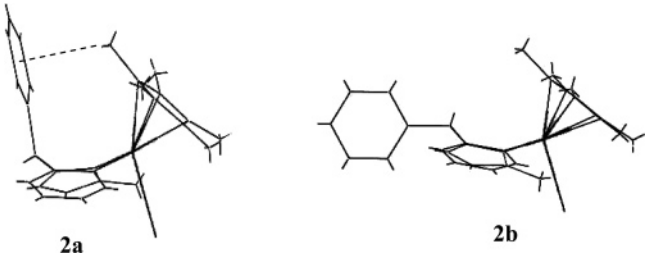
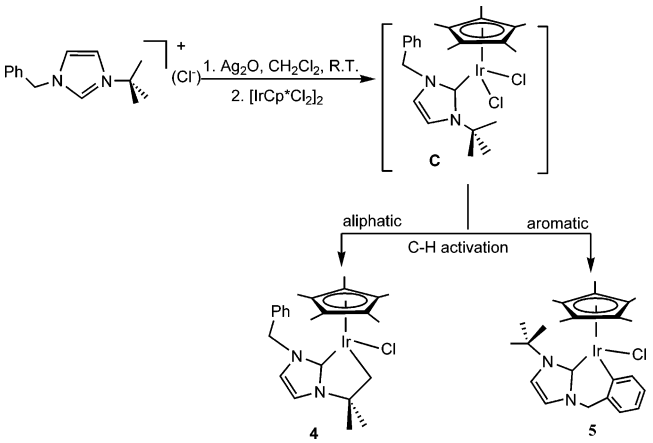


Figure 3. Lateral view of the molecular diagrams of complexes **2a** and **2b**. C−H···$Ph_{centroid}$ distance = 2.871 Å in **2a**.

Scheme 4



3.08 and 2.48 ppm ($^2J_{H-H}$ = 9.9 Hz). The other two methyl groups of the *tert*-butyl group are diastereotopic and appear as two singlets at 1.16 and 1.54 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows the signals due to the carbene carbon at 161.8 ppm and the metalated methylene carbon at 27.5 ppm.

(c) Aromatic vs Aliphatic C−H Activation. The preparation of **2** and **3** under mild reaction conditions suggests that both aromatic and aliphatic intramolecular C−H activation are facile processes in Cp*Ir(NHC) complexes. Previously reported results by us[10] and others[6,7] support the same conclusion. The easy access to imidazolium salts as NHC precursors allows the design of new ligands in which both aliphatic and aromatic C−H activations are possible. This can allow the determination of which of the processes (aliphatic vs aromatic) is the most favorable one for this type of complexes. The preparation of 1-benzyl-3-*tert*-butylimidazolium chloride and its coordination to $[Cp^*IrCl_2]_2$ may lead to cyclometalated complexes in which alkylic and/or aromatic C−H activations can occur (Scheme 4). According to our previous results discussed in the present work, both processes are possible and may be easily produced.

If we were to predict whether **4** or **5** is the reaction product of our process, we should consider that C−H bond activation in aromatic hydrocarbons is favored over aliphatic ones due to kinetic and thermodynamic reasons,[13,16] and this should be playing in favor of the formation of **5**. On the other hand, cyclometalated five-membered rings are generally more stable than six-membered rings, thus favoring the formation of **4**.

The reaction of 1-benzyl-3-*tert*-butylimidazolium chloride with Ag_2O and further addition of $[Cp^*IrCl_2]_2$ selectively proceeded to the cyclometalated species **4**, without any detectable formation of **5**. The monometalated species **C** was not detected under the reaction conditions used, suggesting that the alkylic C−H activation is a readily accessible process. Compound **4** was characterized by NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum shows the signals due to the

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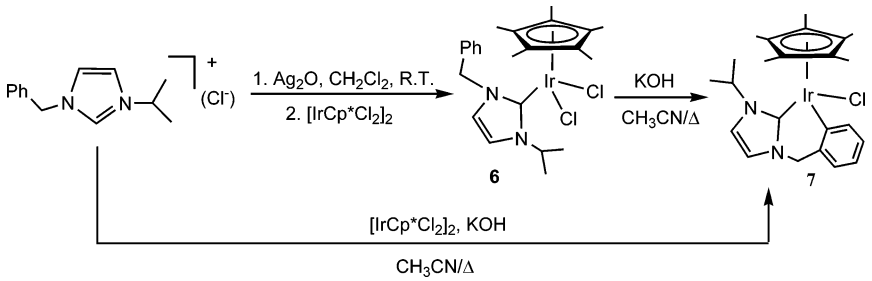
Scheme 5



inequivalent protons in the metalated CH_2 at 3.1 and 2.5 ppm ($^2J_{H-H}$ = 10 Hz). The protons of the *tert*-butyl methyl groups appear at 1.6 and 1.2 ppm. The signals due to the protons of the benzylic CH_2 group are diastereotopic as a consequence of the loss of the symmetry of the ligand upon coordination (δ = 5.5 and 5.1, $^2J_{H-H}$ = 15 Hz). The $^{13}C\{^1H\}$ NMR spectrum confirms that the cyclometalation has occurred, with the most significant signals at 162.3 (carbene carbon) and 27.5 ppm (metalated CH_2).

The molecular structure of **4** was unambiguously confirmed by X-ray diffraction studies (Figure 4). The structure can be regarded as a distorted three-legged piano stool, with a five-membered imidazolylidene-methylene chelating ligand. The Ir−$C_{carbene}$ bond distance is 1.998 Å, in the range of other Cp*Ir(NHC) complexes.[6,7,10,14] The Ir−CH_2 distance of 2.102 Å is similar to the distances shown by other iridium alkyl-cyclometalated species.[2,7] The bite angle of the chelate ligand is 77.2°. All other distances (Cp*$_{centroid}$−Ir, 1.76 Å; Ir−Cl, 2.4066 Å) lie in the expected range.

To check whether the preference of the aliphatic C−H activation over the aromatic one has a general character for this type of complexes, we coordinated 1-benzyl-3-isopropylimidazol-2-ylidene to the Cp*Ir fragment. The monometalated compound **6** (Scheme 5) was obtained by transmetalation of the corresponding silver carbene complex to $[Cp^*IrCl_2]_2$. Complex **6** was highly stable and did not show any tendency to evolve to any of the two possible cyclometalated species. The reaction between 1-benzyl-3-isopropylimidazolium chloride and $[Cp^*IrCl_2]_2$ in refluxing acetonitrile in the presence of KOH afforded the cyclometalated complex **7**, in which aromatic C−H activation has been produced. Alternatively, **7** can be directly obtained by treatment of **6** with KOH in refluxing acetonitrile. Weaker bases such as NaOAc afforded only mixtures of **6** and **7** under reaction conditions similar to those described above, hence not providing full conversion to the cyclometalated product.

The coordination of the imidazolylidene ligand in **6** is confirmed in the $^{13}C\{^1H\}$ NMR spectrum by the presence of a signal at 155.5 ppm due to the carbene carbon. The ^1H NMR spectrum confirms the loss of the 2-fold symmetry of the ligand upon coordination, showing inequivalent signals due to the methyl groups of the isopropyl group (two doublets at 1.49 and 1.35 ppm) and to the protons of the methylene-benzyl group (5.88 and 5.15 ppm, $^2J_{H-H}$ = 15 Hz). The ^1H NMR of **7** shows four signals due to the inequivalent phenyl protons, suggesting that the cyclometalation of the phenyl ring has occurred. The protons of the methylene-benzyl group are diastereotopic, displaying signals at 4.79 and 4.62 ppm ($^2J_{H-H}$ = 14.0 Hz). The $^{13}C\{^1H\}$ NMR spectrum of **7** reveals that the orthometalation has occurred. The signal due to the carbene carbon appears at 155.6 ppm, and that of the metalated phenyl carbon at 145.0 ppm.

Conclusions

We have shown that Cp*Ir(NHC) complexes can undergo facile intramolecular aromatic and aliphatic C−H activations. In the case of the formation of the cyclometalated complexes **2** and **4**, the activation is so fast that we could not even detect the presence of the noncyclometalated intermediate species (**A** and **B**, Schemes 2 and 3, respectively) during the reaction process. When comparing the abilities of the aromatic and aliphatic C−H activations to occur, we observed different results depending on the type of imidazolylidene ligand used. When using 1-benzyl-3-*tert*-butylimidazol-2-ylidene, the reaction yielded the product resulting from the aliphatic C−H activation. This result would make us think that for this type of complexes the alkylic activation is preferred over the aromatic activation. An opposite result was obtained when using 1-benzyl-3-isopropyl-imidazol-2-ylidene, for which the aromatic activation is preferred, although the addition of a strong base and harsher reaction conditions (refluxing CH_3CN) were needed. We find it difficult to justify the reactivity differences between 1-benzyl-3-*tert*-butylimidazol-2-ylidene and 1-benzyl-3-isopropylimidazol-2-ylidene in terms of C−H bond energies or electronic properties of the ligands, since both are qualitatively identical. From a statistical point of view, the activation of the alkylic

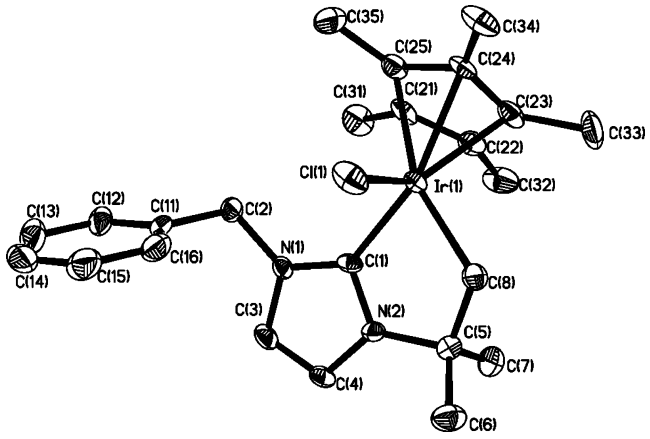


Figure 4. Molecular diagram of compound **4**. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 1.998(6), Ir(1)−Cl(1) 2.4066(16), Ir(1)−C(8) 2.102(6), Ir(1)−Cp*$_{centroid}$ 1.760(19), C(1)−Ir(1)−C(8) 77.2(2), C(1)−Ir(1)−Cl(1) 87.28(15), C(8)−Ir(1)−Cl(1) 87.4(2), Cp*$_{centroid}$−Ir(1)−C(1) 136.3(7), Cp*$_{centroid}$−Ir(1)−C(8) 129.7(6), Cp*$_{centroid}$−Ir(1)−Cl(1) 122.7(6). Ellipsoids are at 30% probability.

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C−H bond in 1-benzyl-3-*tert*-butylimidazol-2-ylidene should be more favorable than in its isopropyl analogue, since the first has nine C−H alkylic bonds compared to six in the latter one, but we also believe that this should not be the main reason to justify the differences in reactivity. In this regard, we believe that steric reasons may be playing an important role. The presence of the *tert*-butyl group in complex **B** (Scheme 3) and **C** (Scheme 4) should provide a structure in which one of the methyl groups is oriented toward the bulky Cp* ring. This steric hindrance may be triggering the alkylic cyclometalation to occur, as the only way to release the steric crowding about the metal. On the other hand, the isopropyl group in complex **6** (Scheme 5) may orientate the C−H bond in the secondary carbon toward the Cp* ring, thus avoiding steric repulsions and favoring the cyclometalation by the aromatic ring. This would imply that, under a situation where sterics is not playing an important role, the aromatic C−H activation is, in fact, favored over the alkylic one.

For the cyclometalation of 1-diphenylmethyl-3-methylimidazolylidene (Scheme 2) a similar effect based on the steric hindrance of the intermediate **A** would explain the fast cyclometalation to provide **2** and also why this intermediate could not be detected. The preference in the formation of the diastereoisomer **2a** is justified by a C−H/π hydrogen-bonding interaction, as depicted in Figure 3.

In conclusion, we have shown how intramolecular aromatic and aliphatic C−H activation can be performed under mild reaction conditions in complexes of the type "Cp*Ir(NHC)". Our results suggest that fine-tuning the steric hindrance of the aliphatic/aromatic fragments is an important tool that can be used for selective aliphatic vs aromatic C−H activation.

Experimental Section

General Procedures. $[Cp^*IrCl_2]_2$,[17] *tert*-butylimidazole, and isopropylimidazole[18] were prepared according to literature procedures. NMR spectra were recorded on a Varian Innova 300 and 500 MHz, using $CDCl_3$, DMSO-d_6, and CD_3CN as solvents. Elemental analyses were carried out in an EA 1108 CHNS-O Carlo Erba analyzer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument, and nitrogen was employed as drying and nebulizing gas. All other reagents were used as received from commercial suppliers.

Synthesis of 1-Diphenylmethylimidazole. To a RB flask was added imidazole (1.00 g, 15 mmol), KOH (1.24 g, 22 mmol), and 5 mL of DMSO. The mixture was stirred at 100 °C for 1 h, and then diphenylmethyl chloride (2.6 mL, 15 mmol) was added. After stirring overnight at 100 °C the reaction mixture was extracted with diethyl ether/H_2O and the organic extracts were collected and dried over Na_2SO_4. Evaporation of the solvent under vacuum gave an oil, which was the desired product. Yield: 2.7 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (s, 1H, NC*H*N), 7.34 (m, 5H, Ph), 7.09 (s, 1H, C*H* imidazole), 6.98 (s, 1H, C*H* imidazole), 5.26 (s, 1H, N−C*H*−Ph_2).

Synthesis of 1-Diphenylmethyl-3-methylimidazolium Iodide. 1-Diphenylmethylimidazole (2.7 g, 12 mmol) was dissolved in 10 mL of acetonitrile, and methyl iodide was added (1.1 mL, 18 mmol). The reaction mixture was refluxed overnight. Evaporation of the solvent under vacuum gave an oil, which, after washing with diethyl ether, was the pure salt. Yield: 3.8 g (85%). ^{1}H NMR (500 MHz, CD_3CN): δ 8.35 (s, 1H, NC*H*N), 7.49 (m, 3H, Ph), 7.45 (s, 1H, C*H* imidazole), 7.33 (s, 1H, C*H* imidazole), 7.29 (m, 2H, Ph), 6.93 (s, 1H, N−C*H*−Ph_2), 3.83 (s, 3H, N−CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.4 (N*C*HN), 136.1 (Ph), 132.6 (Ph), 129.7 (Ph), 128.6 (Ph), 124.0 (*C*H imidazole), 121.9 (*C*H imidazole), 67.4 (N−*C*H−Ph_2), 37. 9 (N−*C*H_3). Anal. Calcd for $C_{17}H_{17}N_2I$: C, 54.27; H, 4.55; N, 7.45. Found: C, 54.18; H, 4.56; N, 7.47. Electrospray MS, cone 35 V, *m*/*z* (fragment): 249.0 $[M]^+$.

Synthesis of 1-*tert*-Butyl-3-methylimidazolium Iodide. Methyl iodide (600 μL, 9.6 mmol) was added to a solution of *tert*-butylimidazole (1.0 g, 8 mmol) in methanol, and the reaction mixture was refluxed overnight. The solvent was evaporated under vacuum and the resulting oil washed with diethyl ether to give the pure imidazolium salt. Yield: 1.8 g (88%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.23 (s, 1H, NC*H*N), 7.99 (s, 1H, C*H* imidazole), 7.75 (s, 1H, C*H* imidazole), 3.84 (s, 3H, N−CH_3), 1.57 (s, 9H, N−C(CH_3)$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 135.0 (N*C*HN), 123.7 (*C*H imidazole), 120.0 (*C*H imidazole), 59.3 (N−*C*(CH_3)$_3$), 35.7 (N−CH_3), 29.0 (N−C(*C*H_3)$_3$). Anal. Calcd for $C_8H_{15}IN_2$: C, 36.11; H, 5.68; N, 10.53. Found: C, 36.19; H, 5.68; N, 10.51. Electrospray MS, cone 30 V, *m*/*z* (fragment): 139.1 $[M]^+$.

Synthesis of 1-Benzyl-3-*tert*-butylimidazolium Chloride. To a RB flask was added *tert*-butylimidazole (1.0 g, 8 mmol) and benzyl chloride (0.9 mL, 8 mmol), and the reaction mixture was stirred at room temperature for 12 h. The desired product was obtained as an oil after washing with ether. Yield: 2.1 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.05 (s, 1H, NC*H*N), 7.52 (s, 2H, C*H* imidazole), 7.34 (m, 5H, Ph), 5.67 (s, 2H, N−CH_2−Ph), 1.70 (s, 9H, N−C(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.8 (N*C*HN), 121.7 (*C*H imidazole), 119.3 (*C*H imidazole), 136.8 (Ph), 133.6 (Ph), 129.4 (Ph), 128.7 (Ph), 60.5 (N−*C*(CH_3)$_3$), 53.4 (N−*C*H_2−Ph), 30.2 (N−(C(*C*H_3)$_3$). Anal. Calcd for $C_{14}H_{19}ClN_2$: C, 67.05; H, 7.64; N, 11.17. Found: C, 67.17; H, 7.61; N, 11.15. Electrospray MS, cone 30 V, *m*/*z* (fragment): 215.3 $[M]^+$.

Synthesis of 1-Benzyl-3-isopropylimidazolium Chloride. To a RB flask was added isopropylimidazole (1.0 g, 9.1 mmol) and benzyl chloride (1.2 mL, 10.9 mmol), and the reaction mixture was stirred at room temperature for 12 h. The desired product was obtained as an oil after washing with diethyl ether. Yield: 1.8 g (85%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.59 (s, 1H, NC*H*N), 7.93 (s, 1H, C*H* imidazole), 7.84 (s, 1H, C*H* imidazole), 7.41 (m, 5H, Ph), 5.44 (s, 2H, N−CH_2−Ph), 4.69 (m, 1H, N−C*H*(CH_3)$_2$), 1.47 (d, 6H, N−CH(CH_3)$_2$). ^{13}C NMR (125 MHz, DMSO-d_6): δ 135.1 (N*C*HN), 134.9 (Ph), 128.9 (Ph), 128.6 (Ph), 128.4 (Ph), 122.5 (*C*H imidazole), 121.0 (*C*H imidazole), 51.8 (N−*C*H_2−Ph), 46.2 (N−*C*H(CH_3)$_2$), 22.3 (N−CH(*C*H_3)$_2$). Anal. Calcd for $C_{13}H_{17}ClN_2$: C, 65.95; H, 7.24; N, 11.83. Found: C, 66.01; H, 7.25; N, 11.83. Electrospray MS, cone 30 V, *m*/*z* (fragment): 201.3 $[M]^+$.

Synthesis of 2. (a) A mixture of $[Cp^*IrCl_2]_2$ (200 mg, 0.25 mmol), 1-diphenylmethyl-3-methylimidazolium iodide (188 mg, 0.5 mmol), and NaOAc (62 mg, 0.75 mmol) in CH_3CN was refluxed overnight in the presence of an excess of NaI. The solution was filtered through Celite, the solvent was evaporated, and the crude solid was purified by column chromatography. The two diastereomeric compounds were separately eluted with hexanes/diethyl ether (9:1) and precipitated in ether to give yellow solids. Yield: **2a**, 252 mg (72%); **2b**, 52 mg (16%). Diastereomeric ratio, 83:17.

(b) Silver oxide (88 mg, 0.38 mmol) was added to a solution of 1-diphenylmethyl-3-methylimidazolium iodide (188 mg, 0.5 mmol) in CH_2Cl_2. The solution was stirred at room temperature for 1 h, and then $[Cp^*IrCl_2]_2$ (200 mg, 0.25 mmol) and an excess of NaI were added. The mixture was stirred at room temperature for 3 h and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. The two diastereomeric compounds were separately eluted with hexanes/diethyl ether (9:1) and precipitated in ether to give yellow solids.

Compound 2a. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, ^3J(H,H) = 7.5 Hz, 1H, Ph), 7.22 (t, ^3J(H,H) = 7.5 Hz, 1H, Ph), 7.20 (d, ^3J(H,H) = 6.5 Hz, 1H, Ph), 7.15 (s, 1H, C*H* imidazole), 7.09 (m,

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Table 1. Crystallographic Data

	2a	2b	4
empirical formula	$C_{27}H_{30}IIrN_2$	$C_{27}H_{30}IIrN_2$	$C_{24}H_{32}ClIrN_2$
mol wt	701.63	701.63	576.17
radiation		Mo Kα (monochr); 0.71073 λ (Å)	
T (K)	273	273	273
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	14.8940(6)	11.3533(9)	9.4872(6)
b (Å)	15.0136(6)	8.4587(6)	21.0737(13)
c (Å)	23.2831(9)	26.431(2)	11.7786(7)
β (deg)	104.5000(10)	98.643(2)	90.959(2)
V (Å^3)	5040.6(3)	2509.5(3)	2354.6(3)
Z	8	4	4
D_{calcd} (g cm^{-3})	1.849	1.857	1.625
μ(Mo Kα) (cm^{-1})	6.539	6.567	5.795
total, unique no. of rflns	41329, 15 243	16 563, 5676	19 535, 7108
R_{int}	0.0986	0.0325	0.0749
no. of params, restrictions	569, 0	286, 0	260, 0
R, R_w	0.0539, 0.0965	0.0262, 0.0512	0.0470, 0.0774
GOF	0.953	1.037	0.992
min., max. resid dens (e Å^{-3})	−1.668, 1.475	−0.973, 0.970	−1.303, 0.966

3H, Ph), 6.94 (s, 1H, C*H* imidazole), 6.91 (t, 1H, Ph), 6.90 (m, 2H, Ph), 6.21 (s, 1H, N−C*H*−Ph$_2$), 3.83 (s, 3H, N−CH_3), 1.38 (s, 15H, C$_5$(CH_3)$_5$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2 (C−Ir carbene), 149.0 (Ph), 145.0 (C−Ir Ph), 138.6 (Ph) 136.8 (Ph), 128.5 (Ph), 127.4 (Ph), 127.0 (Ph), 127.0 (Ph), 126.0 (Ph), 122.8 (Ph), 121.4 (*C*H imidazole), 121.1 (*C*H imidazole), 91.5 (*C*$_5$(CH$_3$)$_5$), 69.8 (N−*C*H−Ph$_2$−), 40.4 (N−*C*H$_3$), 9.4 (C$_5$(*C*H$_3$)$_5$).

Compound 2b. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, ^3J(H,H) = 7.5 Hz, 1H, Ph), 7.50 (m, 3H, Ph), 7.43 (m, 2H, Ph), 6.85 (t, ^3J(H,H) = 7.0 Hz, 1H, Ph), 6.80 (s, 1H, C*H* imidazole), 6.61 (t, ^3J(H,H) = 7.5 Hz, 1H, Ph), 6.39 (s, 1H, C*H* imidazole), 6.38 (d, ^3J(H,H) = 6.5 Hz, 1H, Ph), 5.98 (s, 1H, N−C*H*−Ph$_2$), 3.89 (s, 3H, N−CH_3), 1.81 (s, 15H, C$_5$(CH_3)$_5$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1 (C−Ir carbene), 147.4 (Ph), 142.0 (C−Ir Ph), 141.0 (Ph) 137.9 (Ph), 131.6 (Ph), 129.1 (Ph), 129.1 (Ph), 127.2 (Ph), 125.2 (Ph), 121.5 (Ph), 120.1 (*C*H imidazole), 119.9 (*C*H imidazole), 91.3 (*C*$_5$(CH$_3$)$_5$), 70.2 (N−*C*H−Ph$_2$), 40.4 (N−*C*H$_3$), 10.2 (C$_5$(*C*H$_3$)$_5$). Anal. Calcd for $C_{27}H_{30}IIrN_2$: C, 46.22; H, 4.31; N, 3.99. Found: C, 46.32; H, 4.30; N, 3.99. Electrospray MS, cone 30 V, *m*/*z* (fragment): 575 [Cp*IrL]$^+$.

Synthesis of 3. Silver oxide (88 mg, 0.38 mmol) was added to a solution of 1-*tert*-butyl-3-methylimidazolium iodide (134 mg, 0.50 mmol) in CH_2Cl_2. The solution was stirred at room temperature for 1 h under nitrogen, and then [Cp*IrCl$_2$]$_2$ (200 mg, 0.25 mmol) and an excess of NaI were added. The mixture was stirred at 50 °C for 4 h and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. The pure compound **3** was eluted with CH_2Cl_2/acetone (9:1) and then precipitated in hexanes to give an orange solid. Yield: 204 mg (66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.85 (s, 1H, C*H* imidazole), 6.68 (s, 1H, C*H* imidazole), 3.80 (s, 3H, N−CH_3), 3.08 (d, ^2J(H,H) = 9.9 Hz, 1H, CH_2−Ir), 2.48 (d, ^2J(H,H) = 9.9 Hz, 1H, CH_2−Ir), 1.58 (s, 15H, C$_5$(CH_3)$_5$), 1.54 (s, 3H, N−C(CH_3)$_2$-CH$_2$), 1.16 (s, 3H, N−C(CH_3)$_2$CH$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.8 (C−Ir carbene), 121.1 (*C*H imidazole), 115.9 (*C*H imidazole), 88.5 (*C*$_5$(CH$_3$)$_5$), 65.1 (N−*C*(CH$_3$)$_2$CH$_2$), 36.4 (N−*C*H$_3$), 31.9 (N−C(*C*H$_3$)$_2$CH$_2$), 30.8 (N−C(CH$_3$)$_2$CH$_2$), 27.5 (*C*H$_2$−Ir) 9.7 (C$_5$(*C*H$_3$)$_5$). Anal. Calcd for $C_{18}H_{28}IIrN_2$: C, 36.55; H, 4.77; N, 4.74. Found: C, 36.61; H, 4.76; N, 4.74. Electrospray MS, cone 25 V, *m*/*z* (fragment): 465.2 [Cp*IrL]$^+$.

Synthesis of 4. Silver oxide (88 mg, 0.38 mmol) was added to a solution of 1-benzyl-3-*tert*-butylimidazolium chloride (126 mg, 0.50 mmol) in CH_2Cl_2. The solution was stirred at room temperature for 1 h under nitrogen, and then [Cp*IrCl$_2$]$_2$ (200 mg, 0.25 mmol) was added. The mixture was stirred at 50 °C for 4 h and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. The pure compound **4** was eluted with CH_2Cl_2/acetone (9:1) and then precipitated in hexanes to give a yellow solid. Yield: 210 mg (72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, ^3J(H,H) = 7.5 Hz, 2H, Ph), 7.35 (t, ^3J(H,H) = 7.5 Hz, 2H, Ph), 7.29 (t, ^3J(H,H) = 7.0 Hz, 1H, Ph), 6.68 (s, 1H, C*H* imidazole), 6.61 (s, 1H, C*H* imidazole), 5.55 (d, ^2J(H−H) = 15.0 Hz, N−CH_2−Ph), 5.15 (d, ^2J(H−H) = 15.0 Hz, N−CH_2−Ph), 3.14 (d, ^2J(H−H) = 10.0 Hz, 1H, CH_2−Ir), 2.56 (d, ^2J(H−H) = 10.0 Hz, 1H, CH_2−Ir), 1.77 (s, 15H, C$_5$(CH_3)$_5$), 1.59 (s, 3H, N−C(CH_3)$_2$CH$_2$), 1.20 (s, 3H, N−C(CH_3)$_2$CH$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.3 (C−Ir carbene), 136.7 (Ph), 129.0 (Ph), 128.6 (Ph), 128.1 (Ph), 119.4 (*C*H imidazole), 116.3 (*C*H imidazole), 88.7 (*C*$_5$(CH$_3$)$_5$), 65.1 (N−*C*(CH$_3$)$_2$CH$_2$), 53.8 (N−*C*H$_2$−Ph), 32.2 (N−C(*C*H$_3$)$_2$CH$_2$), 30.8 (N−C(*C*H$_3$)$_2$CH$_2$), 27.5 (*C*H$_2$−Ir), 9.8 (C$_5$(*C*H$_3$)$_5$). Anal. Calcd for $C_{24}H_{32}ClIrN_2$: C, 50.03; H, 5.60; N, 4.86. Found: C, 50.09; H, 5.61; N, 4.85. Electrospray MS, cone 25 V, *m*/*z* (fragment): 541.2 [Cp*IrL]$^+$.

Synthesis of 6. Silver oxide (58 mg, 0.25 mmol) was added to a solution of 1-benzyl-3-isopropylimidazolium chloride (118 mg, 0.50 mmol) in CH_2Cl_2. The solution was stirred at room temperature for 1 h under nitrogen, and then [Cp*IrCl$_2$]$_2$ (200 mg, 0.25 mmol) was added. The mixture was stirred at 50 °C for 4 h and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. The pure compound **6** was eluted with CH_2Cl_2/acetone (9:1) and then precipitated in diethyl ether to give an orange solid. Yield: 450 mg (72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (m, 5H, Ph), 6.89 (s, 1H, C*H* imidazole), 6.63 (s, 1H, C*H* imidazole), 5.88 (d, ^2J(H−H) = 15.0 Hz, 1H, N−CH_2−Ph), 5.26 (m, 1H, N−C*H*(CH$_3$)$_2$), 5.15 (d, ^2J(H−H) = 15.0 Hz, 1H, N−CH_2−Ph), 1.55 (s, 15H, C$_5$(CH_3)$_5$), 1.49 (d, ^3J(H−H) = 6.5 Hz, 3H, N−CH(CH_3)$_2$), 1.35 (d, 3H, ^3J(H−H) = 6.5 Hz, N−CH(CH_3)$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.5 (C−Ir carbene), 136.9 (Ph), 128.7 (Ph), 128.7 (Ph), 128.5 (Ph), 128.0 (Ph), 127.9 (Ph), 122.2 (*C*H imidazole), 118.4 (*C*H imidazole), 88.9 (*C*$_5$-(CH$_3$)$_5$), 54.7 (N−*C*H$_2$−Ph), 51.6 (N−*C*H(CH$_3$)$_2$), 25.3 (N−CH-(*C*H$_3$)$_2$), 25.0 (N−CH(*C*H$_3$)$_2$), 9.2 (C$_5$(*C*H$_3$)$_5$). Anal. Calcd for $C_{23}H_{31}Cl_2IrN_2$: C, 46.15; H, 5.22; N, 4.68. Found: C, 46.15; H, 5.21; N, 4.68. Electrospray MS, cone 20 V, *m*/*z* (fragment): 563.5 [Cp*IrLCl]$^+$.

Synthesis of 7. A mixture of [Cp*IrCl$_2$]$_2$ (100 mg, 0.13 mmol), 1-benzyl-3-isopropylimidazolium chloride (59 mg, 0.25 mmol), and KOH (21 mg, 0.38 mmol) in CH_3CN was refluxed overnight. The solution was filtered through Celite, the solvent was evaporated, and the crude solid was purified by column chromatography. The pure compound **7** was eluted with CH_2Cl_2/diethyl ether (95:5) and precipitated in hexanes to give a yellow solid. Yield: 132 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, ^3J(H−H) = 8.0 Hz, 1H, Ph), 6.97 (m, 2H, Ph), 6.96 (s, 1H, C*H* imidazole), 6.91 (s, 1H,

C*H* imidazole), 6.81 (t, ^3J(H,H) = 7.0 Hz, 1H, Ph), 5.17 (m, 1H, N−C*H*$(CH_3)_2$), 4.79 (d, ^2J(H−H) = 14.0 Hz, 1H, N−CH_2−Ph), 4.62 (d, ^2J(H−H) = 14.0 Hz, 1H, N−CH_2−Ph), 1.66 (s, 15H, C_5-(CH_3)$_5$), 1.50 (d, ^3J(H−H) = 7.0 Hz, 3H, N−CH(CH_3)$_2$), 1.46 (d, ^3J(H−H) = 7.0 Hz, 3H, N−CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6 (C−Ir carbene), 145.0 (C−Ir Ph), 141.5 (Ph), 139.0 (Ph), 127.7 (Ph), 124.2 (Ph), 122.0 (Ph), 120.9 (*C*H imidazole), 116.5 (*C*H imidazole), 90.2 (C_5(CH_3)$_5$), 57.4 (N−*C*H_2−Ph), 51.3 (N−*C*H$(CH_3)_2$), 26.0 (N−CH(*C*H_3)$_2$), 24.5 (N−CH-(*C*H_3)$_2$), 9.6 (C_5(*C*H_3)$_5$). Anal. Calcd for $C_{23}H_{30}ClIrN_2$: C, 49.14; H, 5.38; N, 4.98. Found: C, 49.09; H, 5.38; N, 4.98. Electrospray MS, cone 20 V, *m*/*z* (fragment): 527.5 $[Cp^*IrL]^+$.

X-ray Diffraction Studies. Single crystals of **2a**, **2b**, and **4** were mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 4.0 cm. Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions, and structure refinement are given in Table 1. The diffraction frames were integrated using the SAINT package.[20]

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060343R

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