New Optically Active *N*-Heterocyclic Carbene Complexes for Hydrogenation: A Tale with an Atropisomeric Twist

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A synthesis of 1,2,4-triazolium salts **1** and **2** from three different, easily varied, components was developed to facilitate access to a diverse set of *N*-heterocyclic carbene complexes. Salts **1** epimerized in the synthesis, so they were not investigated further. A coordinated chlorine atom was retained on reaction of **2** with $[Ir(COD)Cl]_2$, and this resulted in two atropisomeric complexes, **3** and **4**, which were both characterized via X-ray diffraction studies. Neither of these complexes mediated hydrogenation of *E*-1,2-diphenylethene, but both **3** and **4** were reacted with NaBARF to give the chlorine-free complex **5**, which was catalytically active in this reaction.

Introduction

N-Heterocyclic carbenes (NHC) are interesting alternatives for phosphine ligands in asymmetric processes, but their evolution from systems that give relatively poor inductions[1] to ones that give much better enantio-discrimination[2−8] is a relatively difficult process. We suggest two reasons for this. First, the process of making and testing chiral ligands is inherently slow. The second reason is that there is no guiding paradigm. For instance, the notion that favorable C_2-symmetric arrangements[9] of aromatic ligands were favorable for the design of chiral diphosphine ligands inspired efforts in that field for years, but there is no simple equivalent in carbene chemistry. Unfortunately, a credible guiding paradigm probably will not emerge until enough effective ligands are found to contrast against those that are ineffective.

Our group is interested in asymmetric hydrogenations of largely unfunctionalized alkenes.[10] The approaches we have used to address the two issues mentioned above are, crucially, to accelerate the process of ligand screening[11] and development,[12] then to understand the role of the ligand via high-level theoretical calculations.[13−15] Figure 1a summarizes our first, accelerated approach to the design of chiral ligands.[12] We described it in terms of reaction of a library with a library, but it could also be called a "modular"[16−18] or an example of "diversity oriented syntheses".[19,20] The attractive feature of the sequence outlined in Figure 1a is that small libraries of imidazoles and of iodo-oxazolines can be combined to give a relatively large set of ligands. In fact, a library of ligands was prepared using this strategy, and the catalyst **A** (with R^1, R^2 = 2,6-$^{i}Pr_2C_6H_4$, 1-Ada) emerged as the first carbene ligand that was described in the open literature to give enantiomeric excesses of over 98%;[21] prior to that the previous best was 76% ee[22] in *any* asymmetric transformation.

Strategies wherein three libraries are reacted together are potentially more effective for the production of ligands for asymmetric catalysis than approaches like that shown in Figure 1a. Recognizing this, we sought to examine the feasibility of the route shown in Figure 1b to make the 1,2,4-triazolium salts **1** and **2**. In fact, only system **2** was useful for further studies due to facile epimerization of **1**. A representative salt **2** was complexed with iridium using an approach we have used before, but, surprisingly, the atropisomeric, chlorine-containing complexes **3** and **4** were obtained. In one case these were converted to complex **5**, a more typical analogue of Crabtree's catalyst.[23] Complex **5** was active in a representative hydrogenation of a largely unfunctionalized alkene, but **3** and **4** were not. Thus the project did not evolve in the expected way, but did enable us to draw some conclusions and to learn valuable lessons about strategies for accelerated discovery of complexes containing *N*-heterocyclic carbene ligands. The details are given below.

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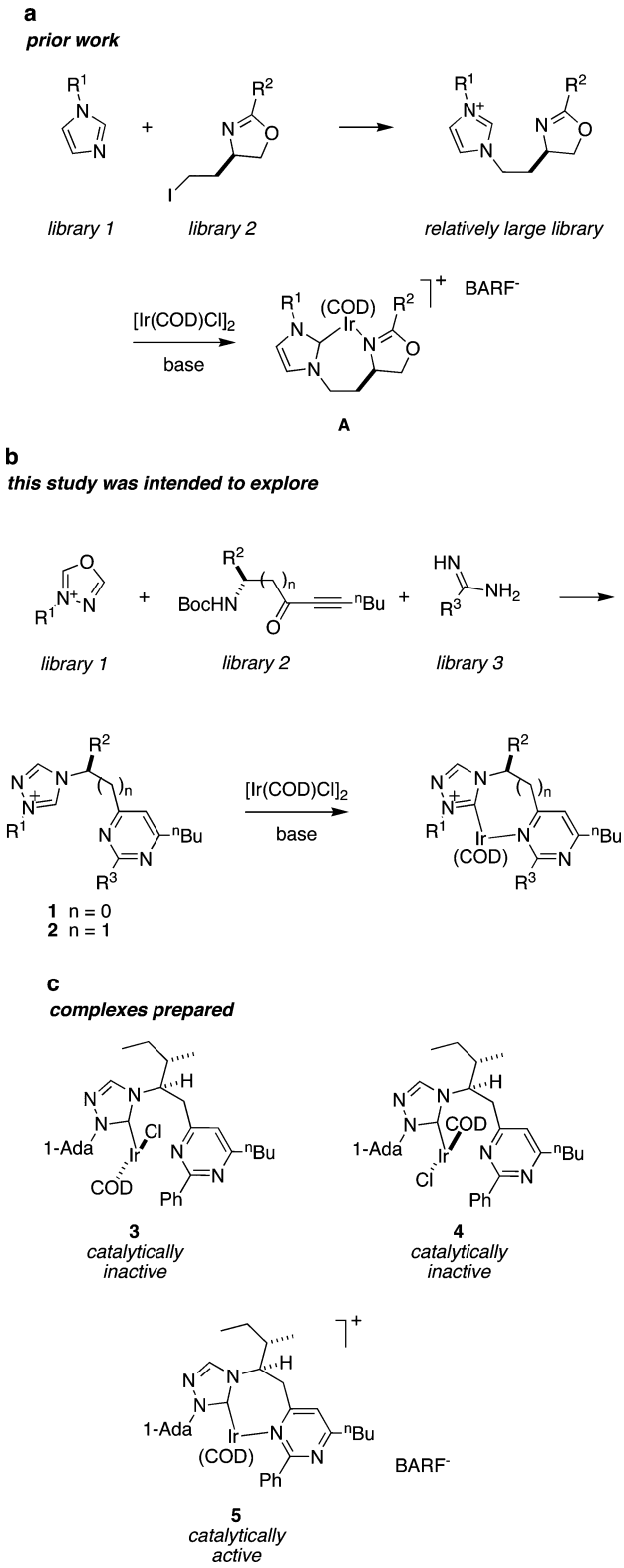
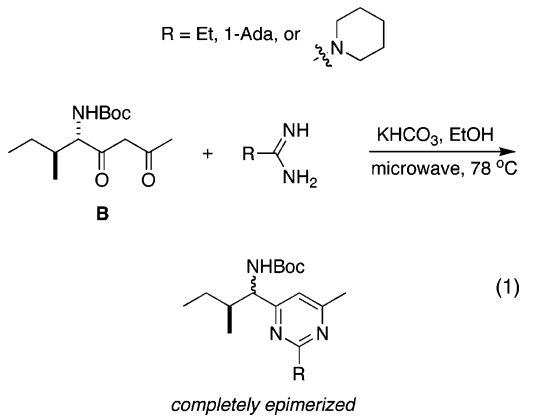


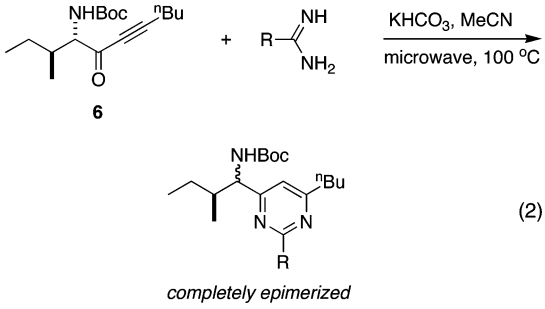
Figure 1. The strategy in **a** could be improved in **b** because a larger set of ligands could be prepared. In **c** complex **5** was prepared and it was active, but the approach was complicated by formation of atropisomeric complexes **3** and **4**.

Results and Discussion

Syntheses of the Ligand Precursors. 1,3-Diketones such as **B** are readily available from amino acids via a literature procedure.[24] We selected isoleucine as a starting point because the stable chirality in the side chain provides an internal marker for epimerization. This turned out to be fortunate because numerous attempts to form pyrimidines by condensation[25] of this dicarbonyl with amidines[26,27] or a guanidine (reaction 1)



gave near complete epimerization of the product. Similarly the ynone **6**, a new compound prepared by modification of a known procedure,[28−30] condensed with the same nucleophiles successfully, but gave epimerized product (reaction 2).



At this stage, plans to prepare the ligand precursors **1** were put aside in favor of the systems for larger chelates, i.e., **2**. Scheme 1 shows how a diazoketone, **C**, a known compound, from isoleucine[24] was subjected to an Arndt−Eistert homologation wherein the ketene intermediate was captured with *N,O*-dimethylhydroxyamine to give the Weinreb amide **7**. This was reacted with the butylacetylide to give ynone **8**, which was then condensed with the three amidines shown. No epimerization was observed in the ^{1}H NMR of the pyrimidines **9** that were isolated. Finally, the *N*-Boc protection was removed and the free amine was condensed[31,32] with *N*-(1-adamanyl)oxadiazolium tetrafluoroborate[33,34] to give the 1,2,4-triazolium salts **2**.

Ligand **2a** was selected as a test case to form the iridium complexes; reaction conditions that we have used extensively before were employed (reaction 3).[18] To our surprise, two

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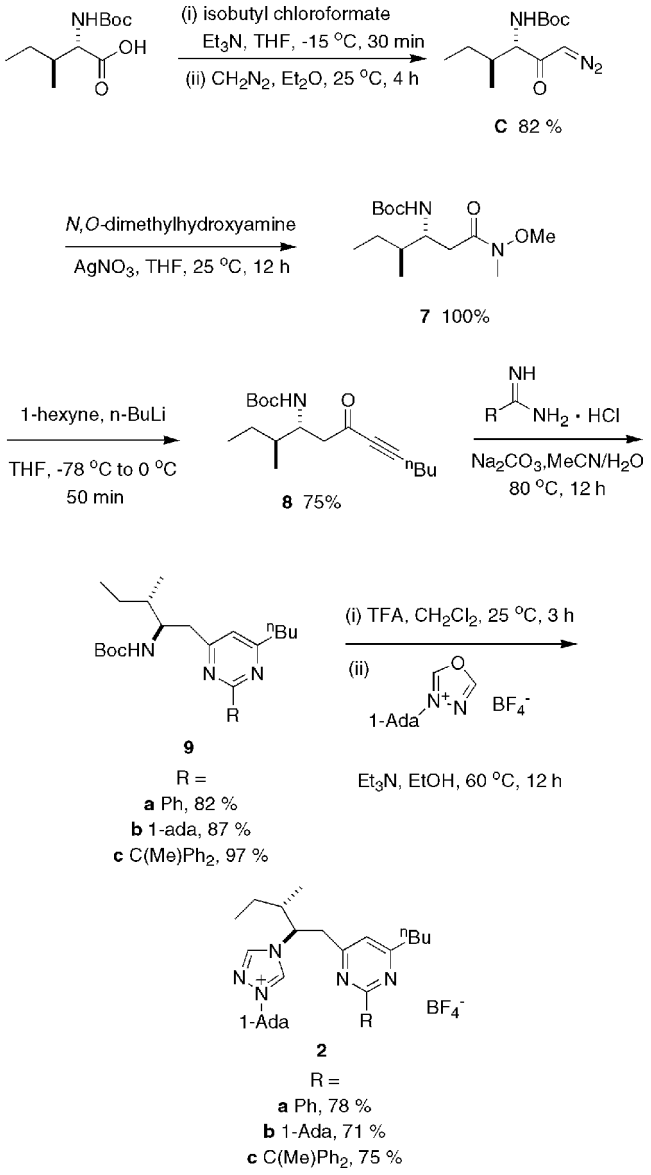
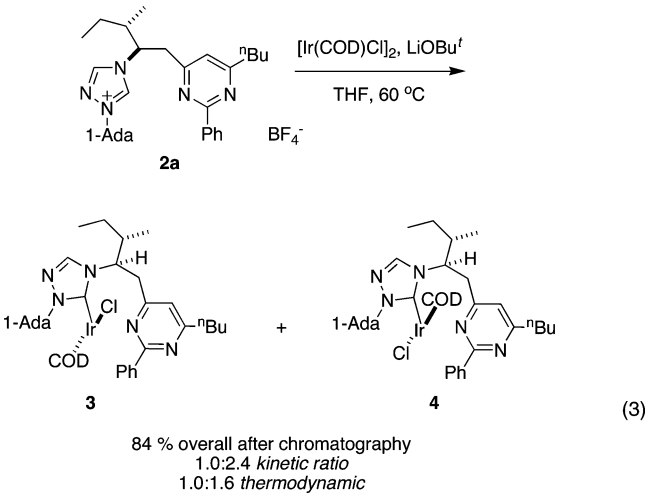
Scheme 1. Syntheses of the 1,2,4-Triazolium Salts 2



isomeric products, **3** and **4**, were formed, and neither had a BF_4^- counterion. Data from $^1H/^{13}C$ NMR and mass spectra (ESI) revealed that these isomers had the same composition. Further, a chlorine atom was shown to be connected to the Ir atom (in mass spectra, both $[M + H]^+$ and $[M - Cl]^+$ were observed in



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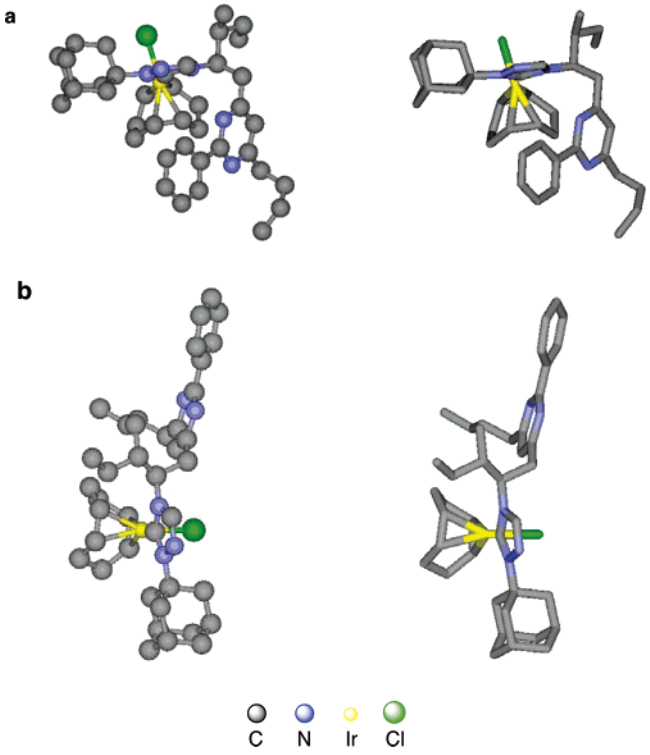
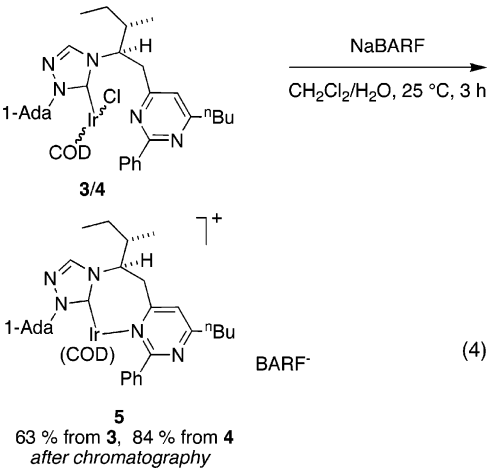


Figure 2. Structures of (a) complex **3** and (b) complex **4**.

almost equal intensity). Single-crystal X-ray data for the two isomers (Figure 2) show these are two atropisomers caused by hindered C−Ir bond rotation. Ligand **2b** formed the corresponding Ir complexes with a ratio of 1:1.6 for the two atropisomers.

Isomers **3** and **4** were stable in THF at room temperature, but heating at 65−70 °C in THF for 10 days gave an equilibrium ratio of 1.0:1.6 (^1H NMR; some decomposition occurred). The equilibrium ratio corresponds to a free energy difference, ΔG, of about 1.3 kJ/mol, but the slow conversion rate indicates a high energy barrier for the C−Ir rotation.

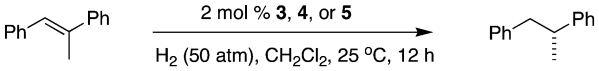
Compounds **3** and **4** reacted with NaBARF to form the same complex **5** in good yields (reaction 4). This product, just as **3** and **4**, can be purified via chromatography and is air- and moisture-stable.



(4)

E-1,2-Diphenylethene tends to be the most popular largely unfunctionalized alkene for testing new ligands, and it is therefore the one used here. Complexes **3** and **4** showed no hydrogenation activity under the conditions indicated in Scheme 2. Complex **5** gave total conversion, but the enantioselectivity was poor.

Scheme 2. Attempted Asymmetric Hydrogenation of *E*-1,2-Diphenylethene



	conversion (%)	ee (%)
3	0	-
4	0	-
5	100	12

Conclusions

In retrospect, there was one obvious potential weakness in the original strategy. Pyrimidines are less effective ligands than pyridines, so it is unsurprising that the synthesis shown in reaction 3 gave chloroiridium complexes. It appears that the chlorine atom is ligated strongly enough to prevent the complexes from being catalytically competent.

Atropisomerism of the chloroiridium complexes is something that could not have been foreseen. Unfortunately, this makes chromatographic isolation of intermediates **3** and **4** tedious, and this alone would make formation of libraries of numerous complexes by this route impractical. The fact that the enantiomeric excess of the product was only 12% for complex **5** is not discouraging. Our previous experience in this area has shown that it is necessary to screen many different substituents before high inductions are obtained. Moreover, the phenyl group here was included for experimental convenience; it would not have been our first choice to obtain high enantioselectivities.

In summary, the exact route shown here did not afford a library of complexes for screening. However, it did teach some important lessons that will assist in devising superior, modified strategies. We intend to publish on these in the near future.

Experimental Section

General Methods. All the chemicals used were purchased from Aldrich, Lancaster, or ACROS and were used without further purification. *n*-Butyllithium (1.6 M in hexanes) was titrated with diphenylacetic acid prior to use. Tetrahydrofuran and ether were distilled from sodium/benzophenone prior to use. Dichloromethane was distilled from calcium hydride. Flash column chromatography was performed using 230−450 mesh silica gel purchased from Sorbent Technology, and the eluants used (typically ethyl acetate, hexanes, dichloromethane, 2-propanol) were ACS reagent grade without further purification.

All NMR spectra were recorded on Varian instruments at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR. NMR chemical shifts are expressed in ppm relative to internal solvent peaks, and coupling constants were measured in Hz.

Boc-L-Isoleucyldiazomethane (C). Triethylamine (2.8 mL, 20 mmol) was added to the solution of L-Boc-Ile-OH (4.62 g, 20 mmol) in 35 mL of THF and 35 mL of ether at −15 °C, followed by isobutyl chloroformate (2.6 mL, 20 mmol). After stirring for 30 min, the resulting solution was warmed to −10 °C, and diazomethane (∼35 mmol in 100 mL of ether, made from Diazald and KOH) was added over 20 min. The solution was stirred for another 4 h while allowing it to warm to 25 °C. The reaction was quenched by dropwise addition of 10 mL of acetic acid/water (1/10, v/v) and then washed with 50 mL of saturated aqueous $NaHCO_3$ solution and brine. After drying with Na_2SO_4, the solvent was removed under vacuum and the yellow residue was recrystallized from 60 mL of hexanes to give the product **C** (4.2 g, 82%) as a yellow crystalline solid. ^{1}H NMR ($CDCl_3$): δ 5.43 (s, 1H), 5.13 (d, J = 8.0 Hz, 1H), 4.09 (b, 1H), 1.78 − 1.88 (m, 1H), 1.42 − 1.52 (m, 1H), 1.44 (s, 9H), 1.07−1.19 (m, 1H), 0.96 (d, J = 7.0 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 194.2, 155.9, 80.1, 62.2, 54.9, 37.9, 28.6, 24.8, 15.9, 11.8. MS (ESI) for $C_{12}H_{22}N_3O_3$: $[M + H]^+$ calcd 256.17, found 256.17.

Boc-L-β-Ile-OH Weinreb Amide (7). Solid $AgNO_3$ (0.19 g, 1.1 mmol) was added to a solution of **C** (0.249 g, 1 mmol) and *N*,*O*-dimethylhydroxyamine (prepared by stirring 2.0 g of its HCl salt and 5.0 g of K_2CO_3 in 1.0 mL of H_2O and 100 mL of THF). The resulting solution was stirred at 25 °C for 12 h, then the solvent was removed *in vacuo*. The residue was dissolved with 20 mL of EtOAc and passed through a silica gel pad to remove the inorganic salts. Removing the solvent gave the corresponding Weinreb amide **7** as a colorless oil with 100% yield. It was used directly for the next step without further purification. ^{1}H NMR ($CDCl_3$): δ 5.26 (d, J = 8.0 Hz, 1H), 3.83 (b, 1H), 3.71 (s, 3H), 3.19 (s, 3H), 2.53−2.72 (m, 2H), 1.66−1.78 (m, 1H), 1.50−1.62 (m, 1H), 1.44 (s, 9H), 1.08−1.18 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H), 0.81 (d, J = 7.0 Hz, 3H). MS (ESI) for $C_{12}H_{28}N_2O_4Li$: $[M + Li]^+$ calcd 295.22, found 295.22.

(3*S*,4*S*)-*N*-Boc-4-Aminododec-7-yn-6-one (8). Compound **7** (0.25 g, 0.9 mmol) was dissolved in 2 mL of THF and cooled to −78 °C. A solution of lithium hexylide (prepared from 0.40 mL of 1-hexyne, 2.0 mL of 1.6 M n-BuLi in hexanes, and 8 mL of THF) was added over 40 min. The resulting solution was stirred at −10 °C and monitored by TLC every 20 min. After all the starting material was consumed (approximately 50 min), the solution was poured into a vigorously stirred mixture of 30 mL of 1 N HCl and 30 mL of ether. The phases were separated and the aqueous phase was extracted with 2 × 40 mL of ether. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Flash column chromatography (EtOAc/hexanes, 1/20, v/v) gave **8** (0.23 g, 75%) as a slightly yellow oil. ^{1}H NMR ($CDCl_3$): δ 4.75 (d, J = 8.5 Hz, 1H), 3.95 (p, J = 7.0 Hz, 1H), 2.56−2.74 (m, 2H), 2.36 (t, J = 7.0 Hz, 2H), 1.66 (m, 1H), 1.56 (p, J = 7.0 Hz, 2H), 1.38−1.50 (m, 3H), 1.41 (s, 9H), 1.03−1.14 (m, 1H), 0.91 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 7.0 Hz, 3H), 0.85 (d, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 186.9, 155.5, 95.7, 81.1, 79.4, 52.0, 47.2, 38.4, 29.9, 28.6, 25.7, 22.2, 18.9, 15.5, 13.7, 11.7. MS (ESI) for $C_{18}H_{32}NO_3$: $[M + H]^+$ calcd 310.24, found 310.23.

Pyrimidine Derivative 9a. Phenylamidine hydrochloride (0.86 g, 5.4 mmol), Na_2CO_3 (1.14 g, 10.8 mmol), and 0.5 mL of H_2O were added into a solution of **8** (1.39 g, 4.5 mmol) in 60 mL of MeCN. The resulting solution was stirred at 80 °C for 12 h before it was cooled to 25 °C. Flash column chromatography (EtOAc/hexanes, 1/10 to 1/5, v/v) gave **9a** (1.52 g, 82% yield) as a white solid. ^{1}H NMR ($CDCl_3$): δ 8.43−8.52 (m, 2H), 7.42−7.53 (m, 3H), 6.97 (s, 1H), 5.36 (d, J = 8.0 Hz, 1H), 3.97 (b, 1H), 3.01 (dd, J = 4.5, 14.0 Hz, 1H), 2.82 (dd, J = 8.5, 14.5 Hz, 1H), 2.79 (t, J = 8.0 Hz, 2H), 1.79 (p, J = 7.5 Hz, 2H), 1.54−1.64 (m, 2H), 1.28−1.52 (m, 3H), 1.36 (s, 9H), 1.14−1.26 (m, 1H), 0.86−1.02 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 171.4, 167.9, 163.9, 155.9, 138.3, 130.6, 128.7, 128.5, 117.9, 79.1, 54.6, 39.1, 38.8, 37.9, 31.1, 28.6, 25.7, 22.7, 15.5, 14.2, 11.9. MS (ESI) for $C_{25}H_{38}N_3O_2$: $[M + H]^+$ calcd 412.30, found 412.30.

Pyrimidine Derivative 9b. A procedure similar to that described for **9a** was used. Compound **8** and the corresponding amidine[35,36] gave **9b** in 87% yield as a white solid. ^{1}H NMR ($CDCl_3$): δ 6.78 (s, 1H), 6.19 (d, J = 8.0 Hz, 1H), 3.78 (b, 1H), 2.86 (dd, J = 4.5, 14.0 Hz, 1H), 2.76 (dd, J = 6.5, 6.5 Hz, 1H), 2.67 (t, J = 8.0 Hz, 2H), 2.00−2.12 (m, 9H), 1.70−1.82 (m, 6H), 1.64−1.74 (m, 2H), 1.49−1.59 (m, 2H), 1.39 (s, 9H), 1.32−1.44 (m, 2H), 1.10−1.20 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H), 0.91 (t, J = 6.0 Hz, 3H), 0.85 (d, J = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 175.5, 170.7, 167.1, 156.0, 125.5, 116.7, 78.8, 54.6, 41.5, 40.9, 40.1, 38.4, 37.8, 37.1, 36.0, 31.1, 29.0, 28.6, 27.3, 25.9, 22.7, 15.3, 14.2, 12.0, impure

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compound, thus 4 more carbon signals than expected. MS (ESI) for $C_{29}H_{48}N_3O_2$: $[M + H]^+$ calcd 470.37, found 470.37.

Pyrimidine Derivative 9c. A procedure similar to that described for **9a** was used. Compound **8** and the corresponding amidine[35,36] gave product **9c** in 97% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.15−7.30 (m, 10H), 6.82 (s, 1H), 5.42 (d, J = 8.5 Hz, 1H), 3.74 (b, 1H), 2.90 (dd, J = 4.0, 15.0 Hz, 1H), 2.77 (dd, J = 6.5, 15.0 Hz, 1H), 2.68 (t, J = 8.0 Hz, 2H), 2.22 (s, 3H), 1.62 − 1.72 (m, 2H), 1.35−1.50 (m, 2H), 1.39 (s, 9H), 1.26−1.38 (m, 2H), 1.00−1.10 (m, 1H), 0.91 (t, J = 7.5 Hz, 3H), 0.85 (t, J = 7.5 Hz, 3H), 0.79 (d, J = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 173.7, 170.6, 167.2, 155.9, 148.9, 148.5, 128.9, 127.9, 127.8, 126.1, 126.0, 117.1, 78.8, 56.9, 54.4, 38.4, 37.8, 37.6, 30.8, 29.4, 28.7, 25.7, 22.5, 15.5, 14.2, 11.7. MS (ESI) for $C_{33}H_{46}N_3O_2$: $[M + H]^+$ calcd 516.36, found 516.36.

NHC Ligand 2a. A solution of **9a** (1.31 g, 3.18 mmol) in 18 mL of CH_2Cl_2 and 16 mL of TFA was stirred at 25 °C for 3 h, then all the solvent was removed by air flow. The dark residue was dissolved in 150 mL of CH_2Cl_2 and was washed with 100 mL of saturated aqueous K_2CO_3 solution. After drying over Na_2SO_4 and removing all the solvent, the brown oil, 1-adamantyloxadizolium tetrafluoroborate salt (synthesized from 1-adamantylhydrazine hydrochloride, which comes from 1-bromoadmantane)[33,34] (1.03 g, 3.5 mmol), and Et_3N (1.3 mL, 9.0 mmol) were dissolved in 20 mL of absolute EtOH. The resulting solution was stirred at 60 °C under nitrogen protection for 12 h. Flash column chromatography (CH_2Cl_2/hexanes/2-propanol, 20/20/1, v/v/v) gave **2a** (1.32 g, 78% yield) as a slightly yellow solid. ^{1}H NMR ($CDCl_3$): δ 9.92 (s, 1H), 8.54 (s, 1H), 8.30−8.58 (m, 2H), 7.42−7.54 (m, 3H), 7.20 (s, 1H), 5.18−5.27 (m, 1H), 3.63 (dd, J = 11.5, 15.5 Hz, 1H), 3.49 (dd, J = 3.5, 15.5 Hz, 1H), 2.79 (t, J = 8.0 Hz, 2H), 2.11−2.32 (m, 5H), 1.91−2.00 (m, 6H), 1.58−1.84 (m, 10 H), 1.34−1.44 (m, 3H), 1.14−1.24 (m, 1H), 1.17 (d, J = 6.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 172.8, 164.4, 163.7, 143.2, 139.8, 137.1, 131.2, 128.9, 128.6, 118.8, 64.7, 64.6, 41.4, 39.2, 38.1, 37.6, 35.4, 31.0, 29.4, 25.7, 22.7, 15.5, 14.1, 11.3. MS (ESI) for $C_{32}H_{44}N_5$: $[M - BF_4]^+$ calcd 498.36, found 498.34.

NHC Ligand 2b. A procedure similar to that described for **2a** was used. Compound **9b** and 1-adamantyloxadizolium tetrafluoroborate salt (0.315 g, 1.08 mmol)[33,34] gave product **2b** (0.41 g, 71% yield) as a slightly yellow solid. ^{1}H NMR ($CDCl_3$): δ 9.94 (s, 1H), 8.46 (s, 1H), 7.05 (s, 1H), 5.04−5.13 (m, 1H), 3.60 (b, 1H), 3.39 (dd, J = 4.0, 17.0 Hz, 1H), 2.68 (t, J = 8.0 Hz, 2H), 2.28 (b, 3H), 2.20−2.24 (m, 10H), 1.91 (s, 6H), 1.70−1.82 (m, 12 H), 1.60−1.70 (m, 2H), 1.28−1.42 (m, 3H), 1.08−1.18 (m, 1H), 1.10 (d, J = 6.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 175.4, 171.1, 163.3, 143.6, 139.4, 117.7, 64.9, 64.89, 41.6, 41.4, 41.0, 39.3, 37.7, 37.4, 36.9, 35.5, 30.9, 29.4, 28.8, 25.8, 22.6, 15.3, 14.1, 11.3. MS (ESI) for $C_{36}H_{54}N_5$: $[M - BF_4]^+$ calcd 556.44, found 556.45.

NHC Ligand 2c. A procedure similar to that described for **2a** was used. Compound **9c** and 1-adamantyloxadizolium tetrafluoroborate salt (0.141 g, 0.48 mmol)[33,34] gave product **2c** (0.206 g, 75% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 9.86 (s, 1H), 7.22−7.34 (m, 6H), 7.14−7.18 (m, 2H), 7.04 (s, 1H), 6.99−7.03 (m, 2H), 6.82 (s, 1H), 4.64−4.72 (m, 1H), 3.63 (dd, J = 10.5, 17.0 Hz, 1H), 3.36 (dd, J = 3.5, 17.0 Hz, 1H), 2.68 (t, J = 7.5 Hz, 2H), 2.24−2.34 (m, 3H), 2.18 (s, 3H), 2.04−2.22 (m, 7H), 1.70−1.84 (m, 6 H), 1.58−1.66 (m, 2H), 1.24−1.34 (m, 3H), 1.12−1.20 (m, 1H), 1.03 (d, J = 7.0 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H), 0.83 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 173.7, 172.1, 163.6, 148.7, 148.2, 144.2, 138.7, 129.4, 128.7, 128.1, 127.9, 126.5, 126.4, 118.0, 64.8, 64.0, 56.9, 41.5, 38.0, 37.8, 37.5, 35.5, 30.9, 29.4, 29.3, 25.7, 22.5, 15.7, 14.1, 10.4. MS (ESI) for $C_{40}H_{52}N_5$: $[M - BF_4]^+$ calcd 602.42, found 602.43.

Ir−NHC Complex 3/4. A dry Schlenk tube was charged with compound **2a** (0.19 g, 0.325 mmol), $[Ir(COD)Cl]_2$ (0.109 g, 0.163 mmol), and lithium *tert*-butoxide (0.039 g, 0.48 mmol). The tube was flushed with N_2 and 12 mL of dry THF was added. The resulting reaction mixture was stirred at 60 °C for 12 h, then cooled to 25 °C. The solvent was removed *in vacuo* and purified by flash column chromatography (ether/hexanes, 1/5 to 1/1, v/v) to give 0.07 g of **3** and 0.17 g of **4** (84% overall yield) as yellow solids. X-ray crystallography grade crystals for both isomers were developed from CH_2Cl_2 and hexanes. Compound **3**: ^{1}H NMR ($CDCl_3$) δ 8.45−8.53 (m, 2H), 7.46−7.55 (m, 3H), 7.24 (s, 1H), 6.78 (s, 1H), 5.64−5.72 (m, 1H), 4.74−4.82 (m, 1H), 4.58−4.67 (m, 1H), 3.95 (dd, J = 6.5, 14.0 Hz, 1H), 3.45 (dd, J = 3.0, 14.0 Hz, 1H), 3.00−3.07 (m, 1H), 2.83−2.90 (m, 1H), 2.67 (t, J = 8.0 Hz, 2H), 2.52−2.64 (m, 6H), 2.16−2.34 (m, 8H), 1.72−1.84 (m, 8H), 1.54−1.72 (m, 4H), 1.44 (d, J = 6.0 Hz, 3H), 1.30−1.42 (m, 3H), 1.02−1.12 (m, 1H), 0.94 (t, J = 7.0 Hz, 3H), 0.93 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 182.1, 171.5, 166.1, 163.6, 139.4, 138.4, 130.6, 128.8, 128.4, 119.4, 83.9, 81.5, 66.4, 62.7, 52.93, 52.91, 44.1, 38.9, 37.8, 36.5, 36.3, 33.6, 33.4, 31.1, 30.2, 30.0, 29.3, 26.6, 22.8, 16.9, 14.2, 12.6. MS (ESI) for $C_{40}H_{55}IrN_5$: $[M - Cl]^+$ calcd 798.41, found 798.36. Compound **4**: ^{1}H NMR ($CDCl_3$) δ 8.39 (s, 1H), 8.16−8.24 (m, 2H), 7.39−7.48 (m, 3H), 6.93 (s, 1H), 5.85−6.02 (m, 1H), 4.58−4.66 (m, 1H), 4.44−4.52 (m, 1H), 3.26 (dd, J = 12.5, 14.5 Hz, 1H), 3.15 (dd, J = 3.5, 14.0 Hz, 1H), 2.74−2.80 (m, 2H), 2.66 − 2.74 (m, 1H), 2.55−2.64 (m, 4H), 2.42−2.50 (m, 3H), 2.24 (b, 3H), 2.06−2.16 (m, 2H), 1.96−2.06 (m, 1H), 1.78−1.90 (m, 1H), 1.69−1.80 (m, 8H), 1.50−1.69 (m, 6H), 1.34−1.44 (m, 2H), 1.24−1.34 (m, 1H), 1.23 (t, J = 7.5 Hz, 3H), 0.92− 1.00 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 182.1, 171.8, 166.8, 164.3, 140.4, 137.8, 130.8, 128.7, 128.5, 117.6, 83.4, 81.3, 64.5, 62.6, 52.4, 52.0, 44.2, 38.9, 37.9, 36.3, 34.8, 33.5, 33.3, 31.1, 30.2, 29.7, 29.1, 28.2, 22.7, 14.2, 13.7, 12.3. MS (ESI) for $C_{40}H_{55}IrN_5$: $[M - Cl]^+$ calcd 798.41, found 798.36.

Ir−NHC Complex 5. NaBARF (0.076 g, 0.086 mmol) was added into a solution of **4** (0.048 g, 0.057 mmol) in 5 mL of CH_2Cl_2, followed by 5 mL of water. The resulting mixture was stirred vigorously at 25 °C for 5 h until the phases were separated and extracted with CH_2Cl_2. Flash column chromatography (CH_2Cl_2/hexanes, 3/1 to 10/1, v/v) gave **5** (0.081 g, 84% yield) as yellow solid. Treatment of **3** gave the same product with 63% yield. ^{1}H NMR ($CDCl_3$): δ 8.38−8.44 (m, 2H), 7.83 (s, 1H), 7.72 (b, 8H), 7.68−7.74 (m, 1H), 7.55−7.60 (m, 2H), 7.53 (b, 4H), 7.26 (s, 1H), 6.00 (dd, J = 12.5, 14.5 Hz, 1H), 4.24−4.32 (m, 1H), 4.08−4.14 (m, 1H), 3.92 (dd, J = 5.0, 14.0 Hz, 1H), 3.77−3.86 (m, 2H), 3.39 − 3.46 (m, 1H), 2.80 (t, J = 8.0 Hz, 2H), 2.63 − 2.71 (m, 3H), 2.30−2.40 (m, 6H), 2.16−2.30 (m, 2H), 1.98−2.30 (m, 2H), 1.76−1.90 (m, 6H), 1.66−1.76 (m, 5H), 1.50−1.60 (m, 1H), 1.40−1.50 (m, 1H), 1.32−1.40 (m, 2H), 1.14−1.22 (m, 2H), 1.13 (d, J = 7.0 Hz, 3H), 0.93 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS): δ 174.7, 172.8, 166.4, 166.3, 161.9 (q), 143.2, 136.2, 135.0, 132.6, 130.0, 128.6, 125.9, 123.7, 119.7, 117.7, 82.9, 82.2, 65.8, 65.0, 63.3, 58.1, 44.3, 43.3, 40.9, 37.5, 35.8, 33.7, 30.8, 30.42, 30.39, 29.5, 27.6, 26.4, 22.6, 14.9, 13.8, 11.5. MS (ESI) for $C_{40}H_{55}IrN_5$: $[M - BARF]^+$ calcd 798.41, found 798.36.

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Supporting Information Available: Detailed experimental data and X-ray crystallographic data for **3** and **4** in CIF format are available free of charge via the Internet at http://pubs.acs.org.

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