"Cp*Ir(III)" Complexes with Hemicleaveable Ligands of the Type *N*-Alkenyl Imidazolin-2-ylidene. Reactivity and Catalytic Properties

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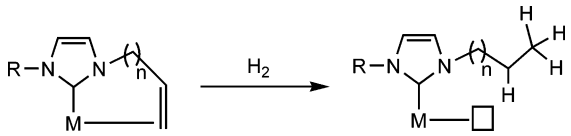
A series of Cp*Ir(III) complexes with *N*-alkenyl imidazole-2-ylidene ligands have been obtained by transmetalation of the previously obtained silver−carbene species. Two structural and electronic parameters have been modified in the preparation of the NHC ligands: (i) the length of the linker between the azole ring and the terminal alkenyl group, and (ii) the nature of the substituents (H, Cl, CH_3) on the backbone of the NHC. Short linkers (*N*-allyl and *N*-butenyl) afford bis-chelating species, while the long linker (*N*-pentenyl) yields the monocoordinated species through the carbene. The structures of four of the new complexes have been characterized by X-ray diffraction. The catalytic activities of the bis-chelating carbene−alkenyl compounds have been tested on the transfer hydrogenation of ketones and imines.

Introduction

During the last three decades, there has been considerable interest in the design of catalytic systems for hydrocarbon C−H bond activation.[1,2] Among the compounds studied, those containing the Cp*Ir(III) fragment have appeared as very versatile systems,[2,3] which have been widely used in catalytic reactions, implying H/D exchange of organic molecules,[4] and in a remarkable recent example, the oxidant-free dehydrogenation of alcohols to yield ketones.[5] We recently introduced N-heterocyclic carbene ligands (NHCs) into the coordination sphere of a series of Cp*Ir(III) complexes, providing species that are highly efficient catalysts for H/D exchange,[6] and also compounds capable of selectively activating intramolecular aliphatic or aromatic C−H bonds.[7]

Cp*Ir(III)(NHC) complexes have been used by Yamaguchi and co-workers in the Oppenhauer-type oxidation of alcohols,[8] and they have also studied the intramolecular C−H bond activation of the carbene ligand.[9]

Scheme 1



The easy access to N-heterocyclic carbenes has allowed the preparation of a large variety of NHC ligands with different types of functionalizations.[10] Allylimidazolylidene ligands have provided complexes that have afforded interesting chemical and structural features to a series of Ir compounds, as recently reported by Hahn and Oro.[11,12] In principle, alkenyl−NHC ligands provide an interesting example of hemilabile coordination, which can have potential applications in homogeneous catalysis. It is easy to imagine that, under certain circumstances, we can force the irreversible decoordination of the alkenyl arm of the ligand, if we irreversibly cleave the M−alkene bond. This irreversible activation can take place by, for example, hydrogenation of the alkenyl group, using any of the known hydrogen sources. Under these conditions we would have an *in situ* generation of a vacant site and the activation of the catalyst in the reaction medium of the catalytic system (Scheme 1).

Taking all this into account, we now report the synthesis of a series of NHC−alkenyl ligands that we have coordinated to the Cp*Ir(III) fragment. The structural and chemical properties of the compounds obtained are discussed on the basis of the length of the linker (*n*, Scheme 1) between the azole ring and the alkene and also in view of the nature of the substituents on the backbone of the azole ring. The catalytic activities of the compounds obtained have been examined in the transfer

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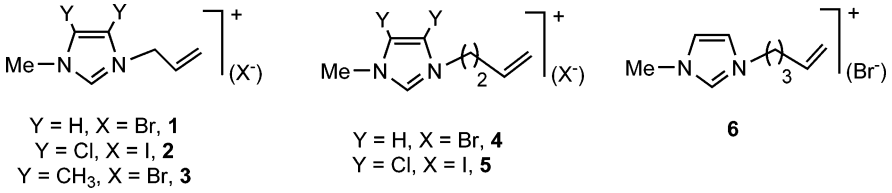
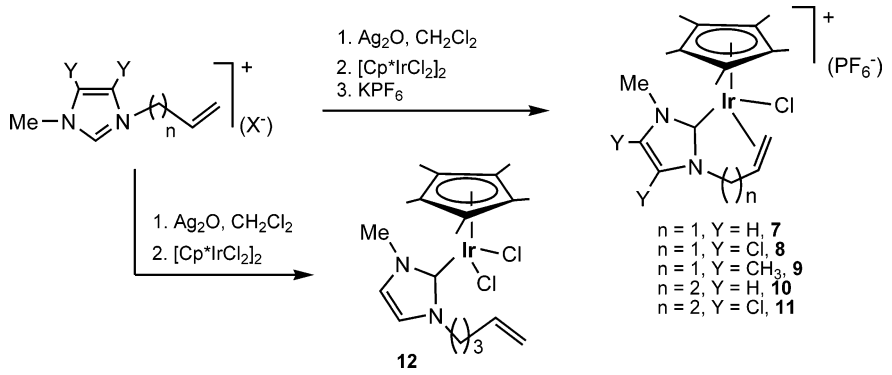
Scheme 2



Scheme 3



hydrogenation of ketones and imines, where very high efficiencies have been observed.

Results and Discussion

A series of alkenylimidazolium halides have been prepared. In the preparation of these ligand precursors, we intended to modify the length of the linker between the azole ring and the alkenyl fragment and the nature of the substituents on the backbone of the azole ring. In this sense, the six precursors depicted in Scheme 2 were prepared (see Experimental Section for details about synthesis).

The coordination of the NHC precursors **1**−**6** to $[Cp^*IrCl_2]_2$ was performed by transmetalation of the previously obtained silver carbenes in CH_2Cl_2 at room temperature. For the reactions using the allyl- (propenyl) and butenylimidazolium salts (**1**−**5**), the reaction proceeded to the carbene−alkenyl-chelating species (Scheme 3, compounds **7**−**11**). Only the use of the pentenylimidazolium salt **6** afforded a neutral compound in which the carbene ligand remained monocoordinated, with the alkene arm out of the coordination sphere of the metal center (**12**, Scheme 3). All our attempts to afford the chelation of the alkene group in compound **12** (increasing the reaction temperature or addition of silver salts to generate a coordination vacant site by removal of one of the Cl ligands) were unsuccessful.

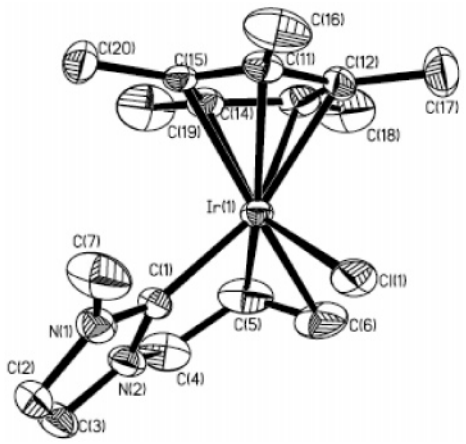


Figure 1. Molecular diagram of compound **7**. Hydrogen atoms and anion (PF_6^-) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.012(6), Ir(1)−Cl(1) 2.4213(19), Ir(1)−$Cp^*_{centroid}$ 1.869, Ir(1)−$alkene_{midpoint}$ 2.068, C(5)−C(6) 1.409(18), C(1)−Ir(1)−Cl(1) 88.1(2), C(1)−Ir(1)−C(5) 77.1(3), C(1)−Ir(1)−C(6) 88.7(4). Ellipsoids are at 30% probability.

Compounds **7**−**12** were characterized by spectroscopic techniques and elemental analyses. The chelating mode of the ligands in compounds **7**−**11** is clearly seen in the NMR spectra. The most significant features of the ^{1}H NMR spectra of compounds **7**−**11** are the signals due to the coordinated alkenyls, appearing at lower frequencies than the same protons in the ligand precursors, thus suggesting their coordination. For example, the signals due to the allylic CH and CH_2 resonances in the imidazolium salt **1** appear at 6.04, and 5.50 ppm, and at 5.18, 3.89, and 3.60 ppm for **7**, respectively. Also, the signals due to the protons of the methylene groups in the allylic (compounds **7**−**9**) and butenyl (**10**, **11**) fragments appear as diastereotopic as a consequence of their loss of symmetry upon coordination. The ^{13}C NMR spectra of these complexes also reflect the metal shielding in the signals due to the alkenic carbons, which also appear at lower δ values than the corresponding precursors. The ^{13}C NMR spectra also show the characteristic signals due to the $C_{carbene}$ atoms, ranging from 138 to 147 ppm, in the region of previously reported Cp*Ir(NHC) complexes.[6−9,13]

For the pentenylimidazolylidene complex **12**, the NMR spectra reflect that the alkene remains unbound. The resonances due to the alkenic protons appear in the same region as in the starting imidazolium precursor **6**. The ^{13}C NMR spectrum shows the signal due to the $C_{carbene}$ at δ 156.3 and the resonances due to the alkenic carbons appear at δ 137.8 and 115.2.

The molecular structures of compounds **7**−**10** were confirmed by single-crystal X-ray diffraction studies (Figures 1−4, respectively). The molecular diagrams of compounds **7**−**9** are qualitatively similar and confirm the chelating coordination of the NHC ligand by the carbene and the allyl fragment. A Cp* ring and a chlorine ligand complete the coordination sphere in all three cases. The most important consequence of the substitution of the H atoms in the imidazole-2-ylidene backbone by Cl or CH_3 groups is the modification of the Ir−$C_{carbene}$ distance (**7**, H, 2.012 Å; **8**, Cl, 1.92 Å; **9**, CH_3, 2.029 Å), this being

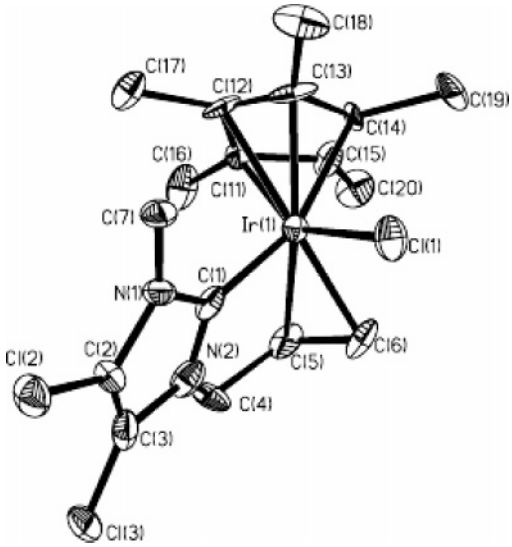


Figure 2. Molecular diagram of compound **8.** Hydrogen atoms, anion (PF_6^-), and crystallization solvent (CH_3OH) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 1.92(2), Ir(1)−Cl(1) 2.441(8), Ir(1)−Cp*$_{centroid}$ 1.869, Ir(1)−alkene$_{midpoint}$ 2.077, C(5)−C(6) 1.43(3), C(1)−Ir(1)−Cl(1) 86.1(9), C(1)−Ir(1)−C(5) 76.9(10), C(1)−Ir(1)−C(6) 89.1(10). Ellipsoids are at 30% probability.

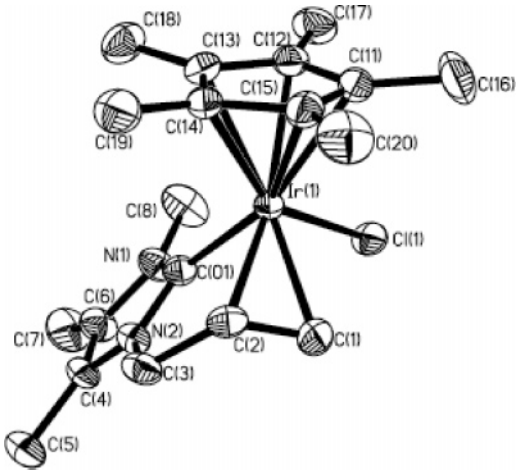


Figure 3. Molecular diagram of compound **9.** Hydrogen atoms, anion (PF_6^-), and crystallization solvent (H_2O) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−C(01) 2.029(8), Ir(1)−Cl(6) 2.410(2), Ir(1)−Cp*$_{centroid}$ 1.864, Ir(1)−alkene$_{midpoint}$ 2.064, C(1)−C(2) 1.385(12), C(1)−Ir(1)−Cl(6) 82.9(3), C(01)−Ir(1)−C(1) 88.8(3), C(01)−Ir(1)−C(2) 77.1(3). Ellipsoids are at 30% probability.

shorter as the electron-attracting character of the substituent increases. The Ir−alkene$_{midpoint}$ distance does not seem to be influenced by the nature of the substituent on the NHC backbone, showing distances in the range 2.064−2.077 Å, but the alkene C−C distances vary in the order **8** > **7** > **9** (**7**, H, 1.409 Å; **8**, Cl, 1.43 Å; **9**, CH_3, 1.385 Å).

The molecular diagram of compound **10** is shown in Figure 4. The structure confirms the chelating coordination of the alkenylimidazolylidene ligand by the carbene and the alkenyl group. The Ir−C$_{carbene}$ distance is 2.055 Å, similar to that shown by **7** and in the range of other Cp*Ir(III)NHC complexes.[6−9,13] The Ir−alkene$_{midpoint}$ distance is 2.105 Å, slightly longer than

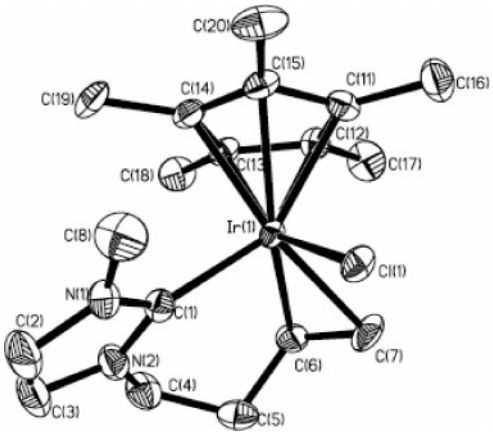


Figure 4. Molecular diagram of compound **10.** Hydrogen atoms, anion (PF_6^-), and crystallization solvent (CH_2Cl_2) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.055(6), Ir(1)−Cl(1) 2.4659(12), Ir(1)−Cp*$_{centroid}$ 1.869, Ir(1)−alkene$_{midpoint}$ 2.105, C(6)−C(7) 1.390(9), C(1)−Ir(1)−Cl(1) 90.72(17), C(1)−Ir(1)−C(6) 86.7(2), C(1)−Ir(1)−C(7) 105.7(3). Ellipsoids are at 30% probability.

Table 1. Selected Results of the Catalytic Transfer Hydrogenation of Ketones Using 7−11[a]

entry	substrate	catalyst	yield, %	time, h
1	cyclohexanone	**7**	>99	0.5
2		**8**	>99	0.5
3		**9**	90	0.5
4		**10**	>99	0.5
5		**11**	91	0.5
6	2-butanone	**7**	85	5
7		**8**	56	5
8		**9**	36	5
9		**10**	>99	5
10		**11**	89	5

[a] Reaction conditions: S/C/KOH 100:1:50 with 0.1 M substrate in 10 mL of *i*-PrOH at reflux temperature. Yields were determined by ^{1}H NMR spectroscopy.

Table 2. Catalytic Results of the Transfer Hydrogenation of Ketones and Imines with Catalyst 10[a]

entry	substrate	catalyst (mol %)	yield, %	time/h
1	cyclohexanone	1	>99	0.5
2		0.1	>99	5
3	2-butanone	1	>99	5
4	benzophenone	1	>99	5
5	acetophenone	1	>99	3
6		0.1	70	19
7	*N*-benzylideneaniline	1	>99	9

[a] Reaction conditions: S/KOH 100:50 with 0.1 M substrate in 10 mL of *i*-PrOH at reflux temperature. Yields were determined by ^{1}H NMR spectroscopy.

the same distance in the allylic compounds **7**−**9**. The C−C bond distance of the alkenyl group is 1.39 Å, similar to that shown by **7**.

Complexes **7**−**11** catalyzed the hydrogenation of the C═O groups of ketones via hydrogen transfer from *i*-PrOH/KOH at 80 °C.[14] For a first screening of the catalytic performances of the compounds, we decided to check the reduction of two alkylic ketones, namely, cyclohexanone and 2-butanone, which were converted to the corresponding alcohols in quantitative yields (Table 1). The reactions were slow at room temperature, but proceeded at very good rates at 80 °C, affording almost

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Scheme 4

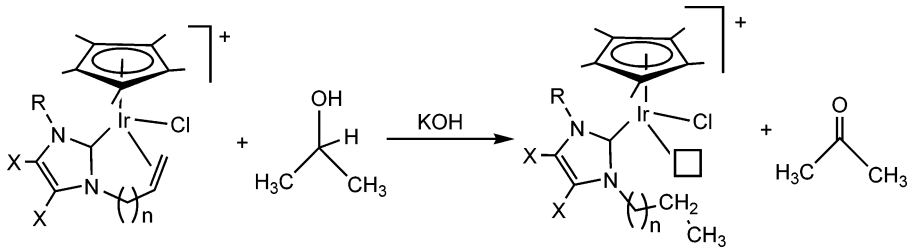

Table 3. Crystallographic Data

	7	8	9	10
empirical formula	$C_{17}H_{25}ClF_6IrN_2P$	$[C_{17}H_{23}Cl_3F_6IrN_2P]_2(CH_3OH)$	$C_{19}H_{29}ClF_6IrN_2(H_2O)$	$C_{18}H_{27}ClF_6IrN_2P(CH_2Cl_2)$
mol wt	630.01	1429.83	674.06	728.96
radiation		Mo K_α (monochr); 0.71073 λ (Å)		
T (K)	273	273	273	293
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	P_1	$P2_1/n$	$P2_1/n$
a (Å)	12.2517(7)	8.6793(5)	12.2199(10)	12.7251(7)
b (Å)	13.3636(7)	11.7118(7)	14.7477(12)	14.1698(8)
c (Å)	13.6072(7)	11.8520(7)	14.6193(12)	14.1577(8)
α (deg)	90	84.1110(10)	90	90
β (deg)	103.6250(10)	79.7980(10)	104.305(2)	100.3240(10)
γ (deg)	90	84.9930(10)	90	90
V (Å^3)	2165.2(2)	1176.51(12)	2552.9(4)	2511.5(2)
Z	4	1	4	4
D_{calcd} (g cm^{-3})	1.933	2.018	1.754	1.928
μ(Mo Kα) (cm^{-1})	6.419	6.141	5.453	5.754
total, unique no. of rflns	14 069, 6270	8825, 7417	18 373, 6345	20 122, 7399
R_{int}	0.0487	0.0241	0.0526	0.0298
no. of params, restrictions	259, 0	556, 3	276, 0	289, 0
R, R_w	0.0550, 0.1568	0.0363, 0.1207	0.0500, 0.1330	0.0394, 0.1149
GOF	1.043	1.102	1.094	1.065
min., max. resid dens (e Å^{-3})	−1.705, 3.008	−1.204, 2.665	−1.350, 1.345	−1.448, 2.219

quantitative yields in 30 min, in the case of cyclohexanone, with catalyst loadings of 1 mol %. For the two substrates used, the imidazolylidene complex **10** showed the best catalytic performances (Table 1, entries 4 and 9), probably due to the higher lability of the coordinated alkene. For the chloro- and methyl-substituted imidazolylidene complexes **8** and **9** and complex **11** the catalytic activities are lower than that shown for the H-substituted compounds **7** and **10**, although we cannot infer a clear relation between the electronic character of the NHC ligand and the catalytic performance of the related catalyst.

Compound **10** was tested in the hydrogen transfer of a wider series of ketones and of *N*-benzylideneaniline (Table 2). The catalyst showed quantitative conversions to the corresponding hydrogenated species using catalyst loadings of 1 mol % under refluxing *i*-PrOH, thus illustrating the wide scope of application of the catalyst in the hydrogenation of aromatic and aliphatic ketones and also imines. Catalyst loadings of 0.1 mol % also afforded high conversions of acetophenone and 2-butanone.

The fact that the bis-chelating compounds **7**−**11** show high catalytic activity in the transfer hydrogenation of ketones and imines contrasts with the negligible catalytic performances shown by other bis-chelating Cp*Ir(III)(NHC) complexes reported by us,[7] thus implying that the blocking of the two coordination vacant sites by the chelating ligand prevents any catalytic activity. In the case of the catalysts **7**−**11**, the catalytic activity of the complexes may be explained by the irreversible cleavage of the Ir−alkene bond in the reaction medium. As shown in Scheme 4, in the first step of the reaction, the hydrogenation of the *N*-alkenyl fragment would be produced, thus generating a coordination vacant site that explained the catalytic activity of the system. In order to support this point, we tried to obtain the hydrogenated products of **7**−**11** by reacting these complexes with KOH in refluxing *i*-PrOH, but in all cases we obtained decomposition products that we were unable to characterize. Our suggested activation of the catalyst is supported by previous results described by Hahn and co-workers, who observed a similar intramolecular hydrogenation of the alkenic fragment of a ligand for a related alkenylbenzimidazolylidene complex of Ir(I) in MeOH in the presence of a base.[12]

Conclusions

We have prepared a series of Cp*Ir(III) compounds with a series of *N*-alkenylimidazole-2-ylidene ligands in which the nature of the substituents on the NHC backbone and the length of the linker between the azole ring and the alkenyl fragment are modified. The reactivity of such ligands toward coordination on the Cp*Ir fragment was studied, showing that short *N*-alkenyl fragments allow the formation of the carbene−alkenyl bis-chelating compounds (**7**−**10**), while the *N*-pentenylimidazole-2-ylidene yields a compound where the ligand is monocoordinated through the carbene−carbon atom (**12**). The crystal structures of four of the complexes reported (**7**−**10**) have been described.

The catalytic activity of the bis-chelating carbene−alkenyl complexes **7**−**11** has been tested on the transfer hydrogenation to ketones and imines, showing high activity in all cases. We have proposed a preactivation step in which the catalyst irreversibly generates a coordination vacant site by hydrogenation of the coordinated alkene, generating an *N*-alkyl fragment. This process would imply that the NHC−alkenyl ligands may be considered as a new type of hemicleavable ligands, with

potential catalytic applications that are worth exploring. Further studies on the catalytic implications of this type of system are underway.

Experimental Section

General Procedures. $[Cp^*IrCl_2]_2$,[15] 3-methyl-1-propenylimidazolium bromide,[16] and 1,4,5-trimethylimidazole[17] 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 acetone-d_6 as solvents. Elemental analyses were carried out in an EuroEA3000 Eurovector analyzer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. All other reagents were used as received from commercial suppliers.

Synthesis of 1-Propenyl-4,5-dichloroimidazole. To a round-bottom (RB) flask were added 4,5-dichloroimidazole (2.0 g, 14 mmol), KOH (1.2 g, 21 mmol), and DMSO. The mixture was stirred at room temperature for 1 h, and then 3-bromo-1-propene (1.2 mL, 14 mmol) was added. After heating at 100 °C overnight 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 a crude oil, which was purified by column chromatography. The desired product was obtained as a yellow oil after elution with a mixture of hexanes/ethyl acetate (9:1) and evaporation of the solvents under vacuum. Yield: 1.4 g (56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (s, 1H, NC*H*N), 5.83 (m, 1H, $NCH_2CH{=}CH_2$), 5.25 (d, ^3J(H,H) = 10.2 Hz, 1H, $NCH_2CH{=}CH$*Htrans*), 5.08 (d, ^3J(H,H) = 17.1 Hz, 1H, $NCH_2CH{=}CH$*Hcis*), 4.45 (d, ^3J(H,H) = 5.4 Hz, 2H, $NCH_2CH{=}CH_2$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 135.9 (N*C*HN), 132.4 ($NCH_2CH{=}CH_2$), 124.4 (*C*−Cl imidazole), 117.7 ($NCH_2CH{=}CH_2$), 112.2 (*C*−Cl imidazole), 47.6 ($NCH_2CH{=}CH_2$).

Synthesis of 3-Methyl-1-propenyl-4,5-dichloroimidazolium Iodide, 2. Methyl iodide (211 μL, 3.4 mmol) was added to a solution of 1-propenyl-4,5-dichloroimidazole (0.5 g, 2.8 mmol) in acetonitryle, and the mixture was refluxed for 24 h. After evaporation of the solvents under vacuum, the pure salt was precipitated in diethyl ether as a light brown solid. Yield: 0.6 g (63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.64 (s, 1H, NC*H*N), 6.10 (m, 1H, $NCH_2CH{=}CH_2$), 5.57 (d, ^3J(H,H) = 17.0 Hz, 1H, $NCH_2CH{=}CH$*Hcis*), 5.53 (d, ^3J(H,H) = 10.0 Hz, 1H, $NCH_2CH{=}CH$*Htrans*), 5.01 (d, ^3J(H,H) = 6.5 Hz, 2H, $NCH_2CH{=}CH_2$), 4.07 (s, 3H, NCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.8 (N*C*HN), 127.9 ($NCH_2CH{=}CH_2$), 123.6 ($NCH_2CH{=}CH_2$), 120.1 (*C*−Cl imidazole), 119.1 (*C*−Cl imidazole), 51.3 ($NCH_2CH{=}CH_2$), 36.1 (NCH_3). Electrospray MS cone 20 V. *m*/*z* (fragment): 191.0 $[L]^+$

Synthesis of 1-Methyl-3-propenyl-4,5-dimethylimidazolium Bromide, 3. 1,4,5-Trimethylimidazole (0.5 mg, 4.8) and 3-bromo-1-propene (0.5 mL, 5.8 mmol) were stirred at room temperature for 4 h. The resulting brown oil was washed with diethyl ether and dried under vacuum. Yield: 0.8 g (74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.95 (s, 1H, NC*H*N), 5.90 (m, 1H, $NCH_2CH{=}CH_2$), 5.29 (d, ^3J(H,H) = 10.5 Hz, 1H, $NCH_2CH{=}CH$*Htrans*), 5.18 (d, ^3J(H,H) = 17.0 Hz, 1H, $NCH_2CH{=}CH$*Hcis*), 4.82 (d, ^3J(H,H) = 6.0 Hz, 2H, $NCH_2CH{=}CH_2$), 3.85 (s, 3H, NCH_3), 2.18 (s, 3H, C−CH_3 imidazole), 2.16 (s, 3H, C−CH_3 imidazole). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.8 (N*C*HN), 130.2 ($NCH_2CH{=}CH_2$), 127.3 (*C*−CH_3 imidazole), 126.7 (*C*−CH_3 imidazole), 120.5 ($NCH_2CH{=}CH_2$), 49.5 ($NCH_2CH{=}CH_2$), 34.1 (NCH_3), 8.6 (C−*C*H_3 imidazole), 8.5 (C−*C*H_3 imidazole). Electrospray MS cone 20 V. *m*/*z* (fragment): 151.4 $[L]^+$

Synthesis of 1-Butenyl-3-methylimidazolium Bromide, 4. 1-Methylimidazole (1.0 mL, 13 mmol) and 4-bromo-1-butene (1.3 mL, 13 mmol) were stirred at room temperature for 48 h. The resulting brown oil was washed with diethyl ether and dried under vacuum to give the pure salt. Yield: 2.9 g (100%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.22 (s, 1H, NC*H*N), 7.76 (s, 1H, C*H* imidazole), 7.68 (s, 1H, C*H* imidazole), 5.68 (m, 1H, $N(CH_2)_2CH{=}CH_2$), 4.97 (m, 2H, $N(CH_2)_2CH{=}CH_2$), 4.21 (t, ^3J(H,H) = 6.9 Hz, 2H, $NCH_2CH_2CH{=}CH_2$), 3.79 (s, 3H, NCH_3), 2.49 (q, ^3J(H,H) = 6.6 Hz, 2H, $NCH_2CH_2CH{=}CH_2$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 136.5 (N*C*HN), 133.5 ($N(CH_2)_2CH{=}CH_2$), 123.4 (*C*H imidazole), 122.2 (*C*H imidazole), 118.2 ($N(CH_2)_2CH{=}CH_2$), 47.8 ($NCH_2CH_2CH{=}CH_2$), 35.7 (NCH_3), 33.5 ($NCH_2CH_2CH{=}CH_2$). Electrospray MS cone 20 V. *m*/*z* (fragment): 137.4 $[L]^+$.

Synthesis of 1-Butenyl-4,5-dichloroimidazole. To a RB flask were added 4,5-dichloroimidazole (2.0 g, 14 mmol), KOH (1.2 g, 21 mmol), and DMSO. The mixture was stirred at room temperature for 1 h, and then 4-bromo-1-butene (1.4 mL, 14 mmol) was added. After heating at 100 °C overnight 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 a crude oil, which was purified by column chromatography. The desired product was obtained as a yellow oil after elution with a mixture of hexanes/ethylacetate (9:1) and evaporation of the solvents under vacuum. Yield: 1.3 g (49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (s, 1H, NC*H*N), 5.68 (m, 1H, $N(CH_2)_2CH{=}CH_2$), 5.09 (d, ^3J(H,H) = 7.2 Hz, 1H, $N(CH_2)_2CH{=}CH$*Htrans*), 5.04 (d, ^3J(H,H) = 16.5 Hz, 1H, $N(CH_2)_2CH{=}CH$*Hcis*), 3.94 (t, ^3J(H,H) = 7.0 Hz, 2H, $NCH_2CH_2CH{=}CH_2$), 2.47 (q, ^3J(H,H) = 6.9 Hz, 2H, $NCH_2CH_2CH{=}CH_2$).

Synthesis of 1-Butenyl-3-methyl-4,5-dichloroimidazolium Iodide, 5. Methyl iodide (332 μL, 5.3 mmol) was added to a solution of 1-butenyl-4,5-dichloroimidazole (0.8 g, 4.5 mmol) in acetonitryle. The mixture was refluxed overnight. After evaporation of the solvents under vacuum, the pure salt was precipitated in a mixture of dichlorometane/diethyl ether as a light brown solid. Yield: 1.3 g (87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.82 (s, 1H, NC*H*N), 5.87 (m, 1H, $N(CH_2)_2CH{=}CH_2$), 5.19 (m, 2H, $NCH_2CH{=}CH_2$), 4.48 (t, ^3J(H,H) = 7.2 Hz, 2H, $NCH_2CH_2CH{=}CH_2$), 4.07 (s, 3H, NCH_3), 2.78 (q, ^3J(H,H) = 6.9 Hz, 2H, $NCH_2CH_2CH{=}CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.1 (N*C*HN), 131.7 ($N(CH_2)_2CH{=}CH_2$), 120.1 ($N(CH_2)_2CH{=}CH_2$), 119.9 (*C*−Cl imidazole), 119.0 (*C*−Cl imidazole), 48.5 ($NCH_2CH_2CH{=}CH_2$), 36.0 (NCH_3), 33.2 ($NCH_2CH_2CH{=}CH_2$). Electrospray MS cone 20 V. *m*/*z* (fragment): 205.0 $[L]^+$

Synthesis of 1-Methyl-3-pentenylimidazolium Bromide, 6. 1-Methylimidazole (0.5 mL, 6.25 mmol) and 5-bromo-1-pentene (0.7 mL, 6.25 mmol) were stirred at room temperature for 48 h. The resulting oil was washed with diethyl ether and dried under vacuum to give the pure salt. Yield: 1.5 g (100%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.32 (s, 1H, NC*H*N), 7.85 (s, 1H, C*H* imidazole), 7.77 (s, 1H, C*H* imidazole), 5.79 (m, 1H, $N(CH_2)_3CH{=}CH_2$), 5.00 (m, 2H, $N(CH_2)_3CH{=}CH_2$), 4.19 (t, ^3J(H,H) = 7.0 Hz, 2H, $NCH_2(CH_2)_2CH{=}CH_2$), 3.87 (s, 3H, NCH_3), 2.02 (q, ^3J(H,H) = 6.6 Hz, 2H, $N(CH_2)_2CH_2CH{=}CH_2$), 1.92 (q, ^3J(H,H) = 6.6 Hz, 2H, $NCH_2CH_2CH_2CH{=}CH_2$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 137.0 (N*C*HN), 136.5 ($N(CH_2)_3CH{=}CH_2$), 123.5 (*C*H imidazole), 122.2 (*C*H imidazole), 115.6 ($N(CH_2)_3CH{=}CH_2$), 48.2 ($NCH_2(CH_2)_2CH{=}CH_2$), 35.7 (NCH_3), 29.5 ($N(CH_2)_2CH_2CH{=}CH_2$), 28.4 ($NCH_2CH_2CH_2CH{=}CH_2$). Electrospray MS cone 20 V. *m*/*z* (fragment): 151.4 $[L]^+$

Synthesis of 7. Silver oxide (58 mg, 0.25 mmol) was added to a solution of 3-methyl-1-propenylimidazolium bromide (102 mg, 0.50 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) was added. The mixture was stirred at room temperature overnight and then filtered through Celite. The solvent was evaporated and the crude

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(16) Chen, W. Z.; Liu, F. H. *J. Organomet. Chem.* **2003**, *673*, 5.

(17) Arduengo, A. J. U.S. Patent 6 177 575, 2001.

solid purified by column chromatography. After addition of KPF_6, the pure compound **7** was eluted with acetone. After precipitation of the excess of KPF_6 in CH_2Cl_2, compound **7** was precipitated in a mixture of CH_2Cl_2/diethyl ether to give a yellow solid. Yield: 170 mg (54%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.45 (s, 1H, C*H* imidazole), 7.41 (s, 1H, C*H* imidazole), 5.18 (m, 1H, $NCH_2CH{=}CH_2$), 4.42 (dd, ^2J(H,H) = 13.0, ^3J(H,H) = 6.0 Hz, 1H, $NCHHCH{=}CH_2$), 4.00 (d, ^2J(H,H) = 13.5, 1H, $NCHHCH{=}CH_2$), 3.89 (d, ^3J(H,H) = 8.0 Hz, 1H, $NCH_2CH{=}CH$*Htrans*), 3.66 (s, 3H, NCH_3), 3.60 (d, ^3J(H,H) = 12.5 Hz, 1H, $NCH_2CH{=}CH$*Hcis*), 1.81 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 144.1 (*C*−Ir), 123.7 (*C*H imidazole), 118.9 (*C*H imidazole), 100.1 ($C_5(CH_3)_5$), 72.5 ($NCH_2CH{=}CH_2$), 53.9 ($NCH_2CH{=}CH_2$), 45.6 ($NCH_2CH{=}CH_2$), 34.4 (NCH_3), 6.9 ($C_5(CH_3)_5$). Anal. Calcd for $[C_{17}H_{25}ClF_6IrN_2P]\cdot CH_3OH$: C, 32.65; H, 4.41; N, 4.23. Found: C, 32.75; H, 4.40; N, 4.24. Electrospray MS cone 25V. *m*/*z* (fragment): 485.3 $[Cp^*IrLCl]^+$

Synthesis of 8. Silver oxide (29 mg, 0.125 mmol) was added to a solution of 3-methyl-1-propenyl-4,5-dicholoroimidazolium iodide (80 mg, 0.25 mmol) in CH_2Cl_2. The solution was stirred at room temperature for 1 h, and then $[Cp^*IrCl_2]_2$ (100 mg, 0.125 mmol) was added. The mixture was stirred at room temperature overnight and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. After addition of KPF_6, the pure compound **8** was eluted with CH_2Cl_2/acetone (4:6). After precipitation of the excess of KPF_6 in CH_2Cl_2, compound **8** was precipitated in a mixture of CH_2Cl_2/diethyl ether to give a yellow solid. Yield: 86 mg (49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.07 (m, 1H, $NCH_2CH{=}CH_2$), 4.59 (dd, ^2J(H,H) = 13.5, ^3J(H,H) = 6.0 Hz, 1H, $NCHHCH{=}CH_2$), 3.99 (d, ^2J(H,H) = 13.2, 1H, $NCHHCH{=}CH_2$), 3.83 (d, ^3J(H,H) = 12.6 Hz, 1H, $NCH_2CH{=}CH$*Hcis*), 3.75 (d, ^3J(H,H) = 8.4 Hz, 1H, $NCH_2CH{=}CH$*Htrans*), 3.67 (s, 3H, NCH_3), 1.89 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 145.0 (*C*−Ir), 117.4 (*C*−Cl imidazole), 116.4 (*C*−Cl imidazole), 102.7 ($C_5(CH_3)_5$), 73.0 ($NCH_2CH{=}CH_2$), 56.4 ($NCH_2CH{=}CH_2$), 47.7 ($NCH_2CH{=}CH_2$), 35.5 (NCH_3), 8.7 ($C_5(CH_3)_5$). Anal. Calcd for $[C_{17}H_{23}Cl_3F_6IrN_2P]\cdot CH_3OH$: C, 29.58; H, 3.72; N, 3.83. Found: C, 29.66; H, 3.72; N, 3.84. Electrospray MS cone 25V. *m*/*z* (fragment): 552.9 $[Cp^*IrLCl]^+$

Synthesis of 9. Silver oxide (58 mg, 0.25 mmol) was added to a solution of 1-methyl-3-propenyl-4,5-dimethylimidazolium bromide (115 mg, 0.50 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) was added. The mixture was stirred at room temperature overnight and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. After addition of KPF_6, the pure compound **9** was eluted with a mixture of dichloromethane/acetone (1:1). After precipitation of the excess of KPF_6 in CH_2Cl_2, compound **9** was precipitated in diethyl ether to give a yellow solid. Yield: 167 mg (51%). ^{1}H NMR (500 MHz, acetone-d_6): δ 5.21 (m, 1H, $NCH_2CH{=}CH_2$), 4.55 (dd, ^2J(H,H) = 12.8, ^3J(H,H) = 6.5 Hz, 1H, $NCHHCH{=}CH_2$), 4.10 (d, ^2J(H,H) = 12.4, 1H, $NCHHCH{=}CH_2$), 3.90 (d, ^3J(H,H) = 8.2 Hz, 1H, $NCH_2CH{=}CH$*Htrans*), 3.76 (d, ^3J(H,H) = 12.4 Hz, 1H, $NCH_2CH{=}CH$*Hcis*), 3.67 (s, 3H, NCH_3), 2.24 (s, 6H, C−CH_3), 1.93 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.8 (*C*−Ir), 127.5 (*C*−CH_3 imidazole), 125.0 (*C*−CH_3 imidazole), 101.9 ($C_5(CH_3)_5$), 71.8 ($NCH_2CH{=}CH_2$), 55.20 ($NCH_2CH{=}CH_2$), 45.5 ($NCH_2CH{=}CH_2$), 33.6 (NCH_3), 9.4 (C−CH_3 imidazole), 8.4 ($C_5(CH_3)_5$). Anal. Calcd for $[C_{19}H_{29}ClF_6IrN_2P]\cdot CH_3OH$: C, 34.81; H, 4.82; N, 4.06. Found: C, 34.88; H, 4.83; N, 4.04. Electrospray MS cone 20 V. *m*/*z* (fragment): 513.2 $[Cp^*IrLCl]^+$

Synthesis of 10. Silver oxide (58 mg, 0.25 mmol) was added to a solution of 1-butenyl-3-methylimidazolium bromide (109 mg, 0.50 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) was added. The mixture was stirred at room temperature overnight and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. After addition of KPF_6, the pure compound **10** was eluted with acetone. After precipitation of the excess of KPF_6 in CH_2Cl_2, compound **10** was precipitated in diethyl ether to give a yellow solid. Yield: 200 mg (62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (s, 1H, C*H* imidazole), 6.96 (s, 1H, C*H* imidazole), 4.43 (m, 1H, $N(CH_2)_2CH{=}CH_2$), 4.13 (d, ^2J(H,H) = 13.2 Hz, 1H, $NCHHCH_2CH{=}CH_2$), 3.76 (d, ^3J(H,H) = 7.3 Hz, 1H, $N(CH_2)_2CH{=}CH$*Htrans*), 3.68 (t, *J*(H,H) = 13.0 Hz, 1H, $NCHHCH_2CH{=}CH_2$), 3.62 (s, 3H, NCH_3), 3.51 (d, ^3J(H,H) = 13.2 Hz, 1H, $N(CH_2)_2CH{=}CH$*Hcis*), 2.90 (d, ^2J(H,H) = 13.7 Hz, 1H, $NCH_2CHHCH{=}CH_2$), 1.43 (s, 15H, $C_5(CH_3)_5$), 1.06 (q, *J*(H,H) = 12.7 Hz, 1H, $NCH_2CHHCH{=}CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9 (*C*−Ir), 125.1 (*C*H imidazole), 124.5 (*C*H imidazole), 101.2 ($C_5(CH_3)_5$), 70.1 ($N(CH_2)_2CH{=}CH_2$), 62.9 ($N(CH_2)_2CH{=}CH_2$), 51.4 ($NCH_2CH_2CH{=}CH_2$), 38.6 ($NCH_2CH_2CH{=}CH_2$), 31.9 (NCH_3), 8.4 ($C_5(CH_3)_5$). Anal. Calcd for $[C_{18}H_{27}ClF_6IrN_2P]\cdot(CH_3OH)_2$: C, 33.92; H, 4.98; N, 3.96. Found: C, 34.01; H, 4.98; N, 3.97. Electrospray MS cone 25V. *m*/*z* (fragment): 499.3 $[Cp^*IrLCl]^+$

Synthesis of 11. Silver oxide (29 mg, 0.125 mmol) was added to a solution of 1-butenyl-3-methyl-4,5-dichloroimidazolium iodide (83 mg, 0.25 mmol) in CH_2Cl_2. The solution was stirred at room temperature for 1 h, and then $[Cp^*IrCl_2]_2$ (100 mg, 0.125 mmol) was added. The mixture was stirred at room temperature overnight and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. After addition of KPF_6, the pure compound **11** was eluted with CH_2Cl_2/acetone (1:1). After precipitation of the excess of KPF_6 in CH_2Cl_2, compound **11** was precipitated in a mixture of CH_2Cl_2/hexanes to give a yellow solid. Yield: 130 mg (73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.77 (m, 1H, $N(CH_2)_2CH{=}CH_2$), 4.60 (d, ^2J(H,H) = 12.5 Hz, 1H, $NCHHCH_2CH{=}CH_2$), 3.97 (d, ^3J(H,H) = 8.5 Hz, 1H, $N(CH_2)_2CH{=}CH$*Htrans*), 3.84 (s, 3H, N−CH_3), 3.80 (t, 1H, *J*(H,H) = 13.0 Hz, $NCHHCH_2CH{=}CH_2$), 3.80 (d, ^3J(H,H) = 13.0 Hz, 1H, $N(CH_2)_2CH{=}CH$*Hcis*), 3.25 (d, ^2J(H,H) = 14.5 Hz, 1H, $NCH_2CHHCH{=}CH_2$), 1.68 (s, 15H, $C_5(CH_3)_5$), 1.27 (q, *J*(H,H) = 12.0 Hz, 1H, $NCH_2CHHCH{=}CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.7 (*C*−Ir), 120.0 (*C*−Cl imidazole), 118.42 (*C*−Cl imidazole), 101.7 ($C_5(CH_3)_5$), 71.0 ($N(CH_2)_2CH{=}CH_2$), 63.5 ($N(CH_2)_2CH{=}CH_2$), 48.8 ($NCH_2CH_2CH{=}CH_2$), 37.3 (NCH_3), 31.5 ($NCH_2CH_2CH{=}CH_2$), 8.3 ($C_5(CH_3)_5$). Anal. Calcd for $[C_{18}H_{25}Cl_3F_6IrN_2P]\cdot Et_2O$: C, 33.57; H, 4.48; N, 3.56. Found: C, 33.44; H, 4.48; N, 3.57. Electrospray MS cone 25V. *m*/*z* (fragment): 567.1 $[Cp^*IrLCl]^+$

Synthesis of 12. Silver oxide (58 mg, 0.25 mmol) was added to a solution of 1-methyl-3-pentenylimidazolium bromide (115 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) was added. The mixture was stirred at room temperature overnight and then filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography. The pure compound **12** was eluted with CH_2Cl_2/diethyl ether (95:5) and precipitated in diethyl ether to give an orange solid. Yield: 82 mg (28%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (s, 1H, C*H* imidazole), 6.93 (s, 1H, C*H* imidazole), 5.83 (m, 1H, $N(CH_2)_3CH{=}CH_2$), 5.04 (d, ^3J(H,H) = 17.2 Hz, 1H, $N(CH_2)_3CH{=}CH$*Hcis*), 4.96 (d, ^3J(H,H) = 10.0 Hz, 1H, $NCH_2CH{=}CH$*Htrans*), 4.63 (m, 1H, $NCHH(CH_2)_2CH{=}CH_2$), 3.92 (s, 3H, NCH_3), 3.76 (m, 1H, $NCHH(CH_2)_2CH{=}CH_2$), 2.14 (m, 3H, $NCH_2(CH_2)_2CH{=}CH_2$), 1.78 (m, 1H, $NCH_2(CH_2)_2CH{=}CH_2$), 1.56 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3 (*C*−Ir), 137.8 ($N(CH_2)_3CH{=}CH_2$), 123.6 (*C*H imidazole), 121.07 (*C*H imidazole), 115.2 ($N(CH_2)_3CH{=}CH_2$), 88.7 ($C_5(CH_3)_5$), 50.4 ($NCH_2(CH_2)_2CH{=}CH_2$), 38.6 (NCH_3), 31.1 ($NCH_2(CH_2)_2CH{=}CH_2$), 30.9 ($NCH_2(CH_2)_2CH{=}CH_2$), 9.1 ($C_5(CH_3)_5$). Anal. Calcd for $C_{19}H_{29}Cl_2IrN_2$: C, 41.60; H, 5.33; N, 5.11. Found: C,

41.67; H, 5.34; N, 5.09. Electrospray MS cone 25V. *m*/*z* (fragment): 513.3 $[Cp^*IrLCl]^+$

X-Ray Diffraction Studies. Single crystals of **7**, **8**, **9**, and **10** 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 ($\lambda = 0.71073$ 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 structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package.[18] 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 3. The diffraction frames were integrated using the SAINT package.[19]

Hydrogen Transfer Catalysis. General Procedure. A mixture of the substrate (1 mmol), KOH (0.5 mmol), and catalyst (0.01 mmol or 0.001 mmol) was refluxed in 10 mL of *i*-PrOH. Aliquots were extracted from the reaction vessels and added to an NMR tube containing 0.5 mL of $CDCl_3$. Yields were determined by ^1H NMR spectroscopy.

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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

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(18) Sheldrick, G. M. *SHELXTL*, version 6.1; Bruker AXS, Inc.: Madison, WI, 2000.

(19) *SAINT*, Bruker Analytical X-ray System, version 5.0. ed.; Madison, WI, 1998.