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Shvo's Catalyst and [IrCp*Cl_2(amidine)] Effectively Catalyze the Formation of Tertiary Amines from the Reaction of Primary Alcohols and Ammonium Salts

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Abstract: The reaction of (pentamethylcyclopentadienyl)iridium dichloride dimer, [IrCp*Cl_2]$_2$, with bis(2,4,6-trimethylphenyl)formamidine allows the preparation of two new [IrCp*Cl_2(amidine)] and [IrCp*Cl(amidinate)] complexes, which have been fully characterized. Both complexes have been tested in the β-alkylation of 1-phenylethanol with primary alcohols, and in the formation of tertiary amines from the reaction of ammonium salts with primary alcohols, and the results have been compared with those shown by Shvo's catalyst. Our studies demonstrate that both [IrCp*Cl_2(amidine)] and Shvo's catalyst are very efficient in both catalytic processes. The high activity of the Ir-amidine complex may be attributed to the presence of the NH group in the amidine ligand.

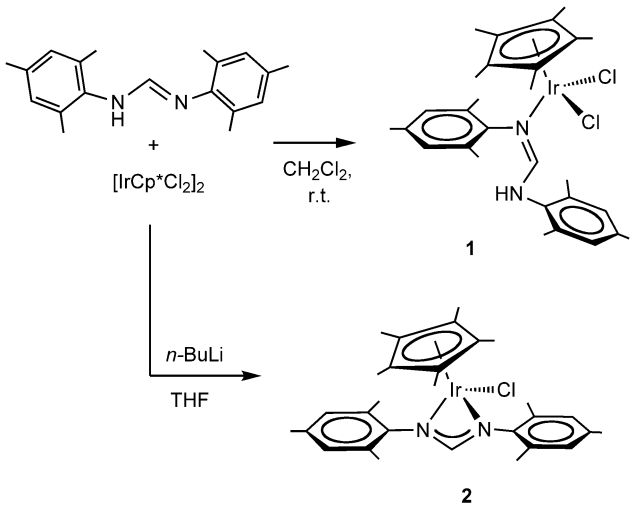
Keywords: alcohols; β-alkylation; ammonia; homogeneous catalysis; iridium

Introduction

Although ammonia has rarely been used as substrate for homogeneously catalyzed transformations, some recently developed catalysts have allowed the preparation of nitrogen-containing compounds from this inexpensive nitrogen source.[1] The alkylation of ammonia with alcohols is normally catalyzed by heterogeneous catalysts requiring high pressures and temperatures,[2] although a number of such processes catalyzed by soluble transition metal complexes are now known.[3] For example, Fujita and co-workers recently described that [IrCp*Cl_2]$_2$ catalyzes the alkylation of ammonium acetate with benzylic alcohols,[3c] and that [IrCp*$(NH_3)_3$]$^{2+}$ is able to alkylate aqueous ammonia with primary and secondary alcohols.[4] Additionally, Milstein described the alkylation of pressurized ammonia with primary alcohols using a ruthenium PNP pincer complex.[3b] In all these reactions, the selectivity on the product obtained is one of the main goals to achieve, since imines can be obtained together with primary, secondary or tertiary amines. Nitriles can also be obtained from the homogeneously catalyzed reaction of alcohols and ammonia.[5]

On the other hand, the ubiquitous Shvo's catalyst [(η^5-C_5Ph_4O)$_2$$HRu_2H(CO)_4$] is very active in all kinds of transfer hydrogenations to alkenes, alkynes, carbonyl groups and imines from alcohols and other dihydrogen sources.[6] In general, this catalyst is unique because the mechanism that explains its activity involves simultaneous transfer of separate hydrogen atoms from (or to) the metal and the ligand, thus providing one clear example of a metal-ligand bifunctional catalyst.

We have recently been interested in the study of C–N and C–C bond formation processes implying alcohols and amines, mostly using 'IrCp*(NHC)' (NHC = N-heterocyclic carbene) type complexes.[7] In all these reactions, the oxidation of the alcohol plays an important role in the initial steps of the reaction,[8] and the presence of cooperating ligands is known to improve the catalytic efficiency, through a metal-ligand bifunctional catalysis.[9] Specifically, Fujita and co-workers elegantly showed that the acceptorless oxidation of alcohols by 'IrCp*' complexes may be facilitated by the presence of 2-hydroxipyridine, on a 'ligand-promoted dehydrogenation'.[10] Based on these principles, we now report the preparation of two new 'IrCp*' complexes with a bis(2,4,6-trimethylphenyl)-



Scheme 1. Synthesis of complexes **1** and **2**.

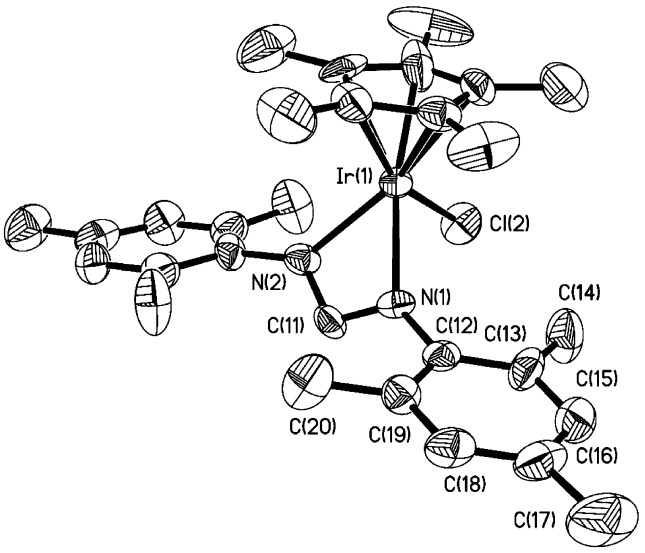


Figure 1. Molecular diagram of complex **1**. Selected bond distances (Å) and angles (°): Ir(1)–N(1) 2.126(3), Ir(1)–Cl(1) 2.4199(10), Ir(1)–Cl(2) 2.4113(10), N(1)–C(11) 1.290 (4), N(2)–C(11) 1.334 (5); Cl(1)–Ir(1)–Cl(2) 89.47(4), N(1)–Ir(1)–Cl(1) 84.73(8), N(2)–Ir(1)–Cl(2) 85.22(8).

formamidine ligand, which have been used in several C–C and C–N bond forming reactions. The complex with the monocoordinated amidine (**1**, as will be labelled later on) is highly active in the formation of tertiary amines from the reaction of primary alcohols with solutions of ammonia.

Results and Discussion

The reaction of bis(2,4,6-trimethylphenyl)formamidine with [IrCp*Cl$_2$]$_2$ at room temperature affords the formamidine-Ir(III) complex **1** (Scheme 1). The complex was characterized by the usual spectroscopic techniques and gave satisfactory elemental analysis. As a diagnostic of the monodentate coordination of the ligand, the ^{1}H NMR spectrum shows two doublets ($^3J_{H,H}$ = 13 Hz) due to the CH (8.1 ppm) and NH (5.8 ppm) groups at the imine. This is one of the very few examples in which an amidine ligand is monodentate,[11] and the only Ir complex with this type of coordination that has been reported to date. When the reaction between the same two reactants is carried out in THF in the presence of *n*-BuLi, the formamidate complex **2** is obtained.

The molecular structures of complexes **1** and **2** were determined by means of X-ray diffractommetry. The molecular diagram of **1** is shown in Figure 1. The molecule consists of an Ir(III) center in a pseudo-three-legged piano-stool environment, with one Cp*, two chlorides and one amidine ligand completing the coordination sphere. The Ir–N bond distance is 2.126 Å, and the mesityl group bound to N(1) is pointing out of the metal coordination sphere, in a quasi-parallel orientation with respect to the Cp* plane.

The molecular structure of compound **2** (Figure 2), consists of an Ir(III) centre with one Cp*, one chloride and an amidinate ligand in a chelating form. The two Ir–N distances are virtually identical (2.140 and 2.149 Å), and the same happens with the two N–C bonds (1.292 and 1.332 Å), which gives a highly sym-

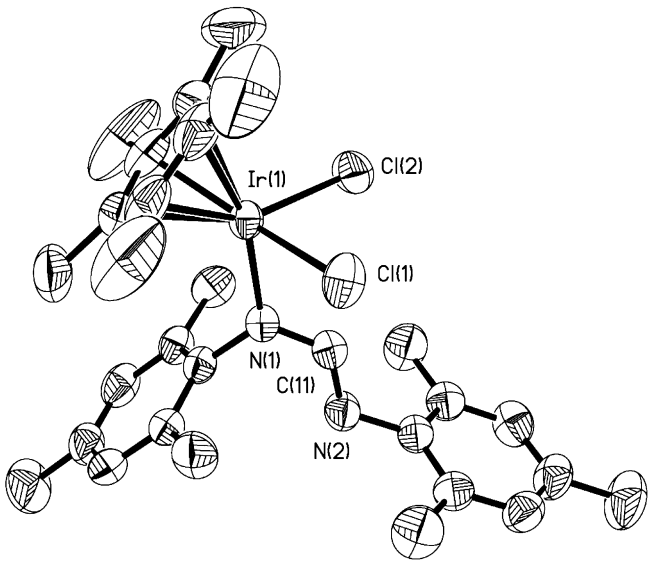


Figure 2. Molecular diagram of complex **2**. Selected bond distances (Å) and angles (°): Ir(1)–N(1) 2.140(7), Ir(1)–N(2) 2.149(8), Ir(1)–Cl(2) 2.391(2), N(1)–C(11) 1.292(11), N(2)–C(11) 1.332(11); N(1)–Ir(1)–Cl(2) 89.6(2), N(2)–Ir(1)–Cl(2) 89.0(2), N(1)–Ir(1)–N(2) 60.4(3).

metric chelating coordination form. The chelate bite-angle is 60.4°, based on the N(1)–Ir(1)–N(2) angle.

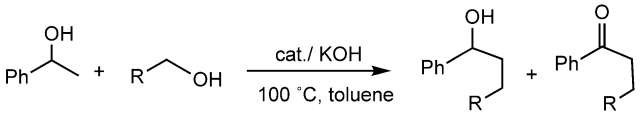
Compounds **1** and **2** were first tested in the β-alkylation of 1-phenylethanol with primary alcohols. We decided to start by studying this model reaction, because we wanted to test the capabilities of our two catalysts in a general borrowing-hydrogen process, prior to the study of the activation of the more challenging substrate, ammonia, which we will discuss later. In both reactions the oxidation of the alcohol to an aldehyde/ketone is needed prior to the C–C or C–N bond formation. The β-alkylation of secondary alcohols is believed to involve oxidation of both alcohols to form a ketone and an aldehyde, which then undergo an aldol condensation giving an α,β-unsaturated ketone, which is further reduced to give the saturated alcohol.[8a,12] The reactions were carried out in toluene at 100 °C under aerobic conditions, using catalyst loadings of 1 or 0.1 mol%. We performed the reactions trying to achieve the maximum atomic efficiency, so we used a molar ratio of 1:1 between the primary and secondary alcohols, except in the cases shown in Table 1 (entries 3, 7, 11 and 15). As can be seen from the data shown in Table 1, **1** is far more efficient than **2** (compare entries 1/2, 5/6, 9/10 and 13/14), both in terms of conversions to the final products and selectivity toward the corresponding β-alkylated alcohols. Catalyst **1** is also active at a catalyst loading of 0.1 mol%, especially when benzyl alcohol and 4-chlorobenzyl alcohol were used, although longer reaction times were needed (24 h). These data compare well with the catalytic outcomes shown by other previously reported catalysts based on 'IrCp*(NHC)' reported by Crabtree[13] and us,[7c,d] and Ru(η^6-arene)(NHC)'[14] complexes. Remarkably, the *in situ* preparation of **1**, resulted in a much lower activity than that shown by the preformed catalyst (compare entries 1 and 17).

In order to test the catalytic versatility of **1** and **2**, we decided to test their activities in the alkylation of ammonium salts with primary alcohols. Ammonia is one of the most desirable substrates for the formation of nitrogen-containing organic molecules, despite its lack of reactivity in most catalytic reactions.[15] We first made a catalyst screening by comparing the activity of $[IrCp^*Cl_2]_2$, our newly reported compounds **1** and **2**, and the ubiquitous Shvo's catalyst.

As can be seen from the data shown in Table 2, both **1** and Shvo's catalyst afford excellent catalytic outcomes for the reactions carried out using NH_4OAc and $NaHCO_3$, especially when we compare these data with those provided by $[IrCp^*Cl_2]_2$ and **2** under the same reaction conditions. As previously reported by Fujita and co-workers,[3c] all catalysts exhibited excellent activities when the ammonium/alcohol ratio was increased from 3 to 3.6, even when the catalyst loading was reduced to 0.5 mol%. Both Shvo's catalyst and **1** were also tested in the alkylation of NH_4Cl, for which they provided very similar activity. Remarkably, **1** was moderately active in the alkylation of an aqueous solution of NH_3 (entry 14), an observation that will probably deserve further incoming studies. For the reactions carried out in the absence of an extra amount of base, Shvo's and **1** afforded excellent yields to the final product (entries 6 and 11) while $[IrCp^*Cl_2]_2$ and **2** provided moderate-low outcomes (entries 3 and 8, respectively).

Taking all these data into account, we decided to widen the catalytic scope of **1** and Shvo's catalyst by studying their activity with a variety of primary alcohols. Compound **2** was also tested in some selected reactions for comparative purposes. The results are summarized in Table 3. As can be seen from the data shown, both **1** and Shvo's catalyst afford excellent yields for the coupling of several ammonium salts with a wide set of primary alcohols, including benzylic and alkylic alcohols. Catalyst **2** is less active than the other two catalysts under study. In general, catalyst **1** affords excellent yields when benzylic alcohols are used, but its activity is moderate-high when alkylic

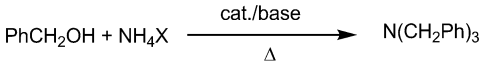
Table 1. β-Alkylation of 1-phenylethanol with primary alcohols.[a]



Entry	Cat. (mol%)	R	*t* [h]	Alcohol [%][b]	Ketone [%][b]
1	**1** (1)	Ph	3	90	9
2	**2** (1)	Ph	3	72	23
3[c]	**1** (1)	Ph	8	75	0
4	**1** (0.1)	Ph	24	65	0
5	**1** (1)	*n*-Pr	6	62	25
6	**2** (1)	*n*-Pr	6	61	15
7[c]	**1** (1)	*n*-Pr	8	91	8
8	**1** (0.1)	*n*-Pr	24	10	0
9	**1** (1)	3-ClC_6H_4	6	93	4
10	**2** (1)	3-ClC_6H_4	6	60	7
11[c]	**1** (1)	3-ClC_6H_4	8	40	0
12	**1** (0.1)	3-ClC_6H_4	24	40	0
13	**1** (1)	4-ClC_6H_4	3	91	8
14	**2** (1)	4-ClC_6H_4	3	62	7
15[c]	**1** (1)	4-ClC_6H_4	3	80	0
16	**1** (0.1)	4-ClC_6H_4	24	80	0
17[d]	**1** (1)	Ph	3	37	0

[a] *Reaction conditions:* 1-phenylethanol (1 mmol), primary alcohol (1 mmol), KOH (1 mmol), and 1 (or 0.1) mol% of catalyst in 0.3 mL of toluene at 100 °C.
[b] Yields determined by ^1H NMR.
[c] Primary alcohol (2 mmol).
[d] *In situ* preparation of **1** by addition of 0.5 mol% of $[IrCp^*Cl_2]_2$ and 1 mol% of dimesitylformamidine.

Table 2. Alkylation of ammonium salts with benzyl alcohol.[a]

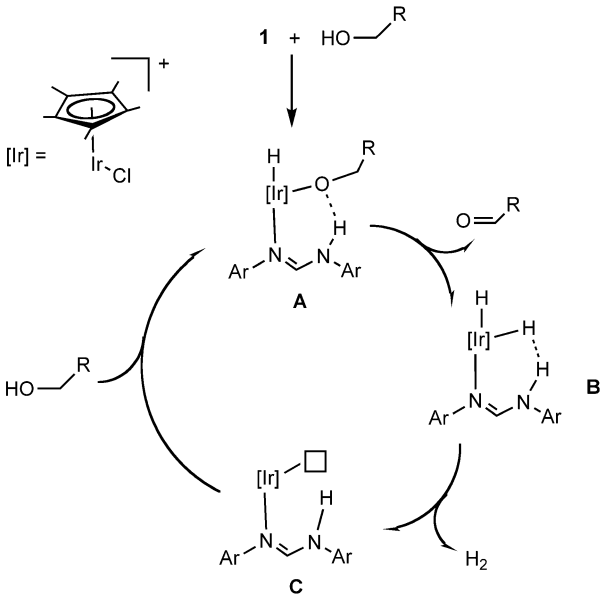


Entry	Cat.	Load (mol%)	X	Base	Alcohol/NH_4^+	*T* [°C]	Yield [%]
1	$[IrCp^*Cl_2]_2$	3	OAc	$NaHCO_3$	3	110	72
2	$[IrCp^*Cl_2]_2$	0.5	OAc	$NaHCO_3$	3.6	130	87
3	$[IrCp^*Cl_2]_2$	0.5	OAc	–	3.6	130	44
4	**1**	3	OAc	$NaHCO_3$	3	110	97
5	**1**	0.5	OAc	$NaHCO_3$	3.6	130	99
6	**1**	0.5	OAc	–	3.6	130	97
7	**2**	3	OAc	$NaHCO_3$	3	110	98
8	**2**	0.5	OAc	–	3.6	130	60
9	Shvo's	3	OAc	$NaHCO_3$	3	110	97
10	Shvo's	0.5	OAc	$NaHCO_3$	3.6	130	99
11	Shvo's	0.5	OAc	–	3.6	130	99
12	**1**	3	Cl	$NaHCO_3$	3	110	51
13	**2**	3	Cl	$NaHCO_3$	3	110	18
14[b]	**1**	3	OH	–	3	110	44
15[c]	**1**	5	Cl	KOH	3.6	130	99
16[c]	Shvo's	5	Cl	KOH	3.6	130	99

[a] *Reaction conditions:* benzylalcohol (3 or 3.6 mmol), ammonium source (1 mmol), $NaHCO_3$ (3 mol%) and 0.5, 3 or 5 mol% of catalyst at 110 or 130 °C for 17 h. Yields determined by GC, using anisole as internal standard.
[b] NH_4OH, 30% in H_2O.
[c] $t = 39$ h; 1 mmol of KOH.

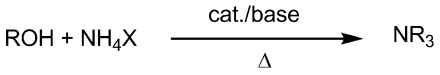
primary alcohols are utilized. The activity of the ruthenium catalyst is higher in most of the cases, thus illustrating the wide applicability of this exceptional catalyst. The reactions are very selective to the formation of the tertiary amines, except those where cyclohexanol is used, that selectively renders dicyclohexylamine (entries 26–30). Catalyst **1** is more selective than Shvo's catalyst in the production of the tertiary amine when 3-chlorobenzyl alcohol is used (compare entries 9 and 10; Shvo's catalyst produces the secondary and primary amines in a 1/1 ratio).

We believe that the presence of the NH group on the amidine ligand of the catalyst **1** is increasing the catalytic activity compared to the activity shown by $[IrCp^*Cl_2]_2$. This '*NH effect*' may facilitate the dehydrogenation of the primary alcohol to aldehyde in the first steps of the catalytic cycle,[3c] in a similar way to that previously shown by Noyori's group for the reverse reaction implying the hydrogenation of ketones.[9d,16] However, we believe that the NH bond does not deprotonate during the process, because this would imply the formation of the chelated species **2**, which – as we have shown – displays a much lower catalytic activity than **1**, so its participation in the process can be discarded. In fact, the conversion of **1** into **2**, needs the addition of a very strong base, such a *n*-BuLi, so the formation of this species under the reaction conditions is rather unlikely. Based on our previously proposed mechanism for the dehydrogenation of alcohols performed by 'IrCp*(NHC)' complexes, we believe that the amidine ligand may stabilize the Ir(V) transition states (**A** and **B**, Scheme 2) through a hydrogen bond between the NH and the oxygen of the alkoxide ligand in **A** and a NH···HIr dihydrogen bond[17] in **B**. As previously proposed by Fujita and Yamaguchi,[3c,4] once the aldehyde has been formed, its reaction with ammonia would facilitate the forma-



Scheme 2. Dehydrogenation of alcohols catalyzed by **1**

Table 3. Alkylation of ammonium salts with primary alcohols.[a]



Entry	Cat. (mol%)	X	R	Base	*t* [h]	Yield [%]
1	**1** (1)	OAc	4-Cl-benzyl	–	17	76
2	**2** (1)	OAc	4-Cl-benzyl	–	17	73
3	Shvo's (1)	OAc	4-Cl-benzyl	–	17	99
4	**1** (5)	Cl	4-Cl-benzyl	KOH	39	67
5	Shvo's (5)	Cl	4-Cl-benzyl	KOH	39	99
6	**1** (1)	OAc	3-Cl-benzyl	–	17	45[c]
7	**2** (1)	OAc	3-Cl-benzyl	–	17	20
8	Shvo's (1)	OAc	3-Cl-benzyl	–	17	66
9	**1** (5)	Cl	3-Cl-benzyl	KOH	39	87
10	Shvo's (5)	Cl	3-Cl-benzyl	KOH	39	90[c]
11	**1** (1)	OAc	4-Me-benzyl	–	17	99
12	**2** (1)	OAc	4-Me-benzyl	–	17	70
13	Shvo's (1)	OAc	4-Me-benzyl	–	17	99
14	**1** (5)	Cl	4-Me-benzyl	KOH	39	99
15	Shvo's (5)	Cl	4-Me-benzyl	KOH	39	99
16	**1** (1)	OAc	*n*-hexyl	–	17	51
17[b]	**1** (3)	OAc	*n*-hexyl	–	17	90
18[b]	Shvo's (3)	OAc	*n*-hexyl	–	17	99
19[b]	**1** (5)	Cl	*n*-hexyl	KOH	39	95
20[b]	Shvo's (5)	Cl	*n*-hexyl	KOH	39	99
21	**1** (1)	OAc	*n*-butyl	–	17	15
22[b]	**1** (3)	OAc	*n*-butyl	–	17	37
23[b]	Shvo's (3)	OAc	*n*-butyl	–	17	93
24[b]	**1** (5)	Cl	*n*-butyl	KOH	39	26
25[b]	Shvo's (5)	Cl	*n*-butyl	KOH	39	99
26	**1** (1)	OAc	cyclohexyl	–	17	51[d]
27[b]	**1** (3)	OAc	cyclohexyl	–	17	78[d]
28[b]	Shvo's (3)	OAc	cyclohexyl	–	17	99[d]
29[b]	**1** (5)	Cl	cyclohexyl	KOH	39	66[d]
30[b]	Shvo's (5)	Cl	cyclohexyl	KOH	39	99[d]

[a] *Reaction conditions:* alcohol (3.6 mmol), NH_4X (1 mmol), at 130 °C. Yields determined by GC, using anisole as internal standard.
[b] 6 mmol of alcohol and 1 mmol of NH_4X, at 140 °C.
[c] Yield as a mixture in a ratio 1/1 trisalkylamine:bisalkylamine.
[d] Only bisalkylamine is observed.

tion of the corresponding primary imine, which is then reduced to the corresponding amine by the primary alcohol, in a metal-mediated transfer hydrogenation process. Subsequent alkylations of the resulting primary amine, afford the final tertiary amine.

In order to prove that catalyst **1** is able to oxidize primary alcohols under hydrogen-acceptorless conditions, we performed a reaction of benzyl alcohol in refluxing toluene in the presence of **1** (5 mol%) and Cs_2CO_3. After 15 h we observed a 65% yield of benzaldehyde, although the conversion of the alcohol was complete.

Conclusions

In summary, we have described two effective catalytic systems for the selective synthesis of tertiary amines by multialkylation of ammonium salts, in the absence of solvent. The two catalysts (Shvo's and **1**) add to the list of the very few metal complexes active in this type of reaction and clearly improve the catalytic outcomes of previously reported systems.[3c] We have also added a new extraordinary useful catalytic application of the ubiquitous Shvo's catalyst.

Experimental Section

General Comments

All manipulations were carried out using standard Schlenk techniques. Solvents were purified using an MBraun SPS solvent system (THF, CH_2Cl_2, hexane). Deuterated solvents were used as received (Merk and Aldrich) without further purification. NMR spectra were recorded on Varian Innova 300 and 500 MHz spectrometers, using C_6D_6 and $CDCl_3$ (Merk). 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. A gas chromatograph GC-2020 (Shimadzu) equipped with an FID and a Teknokroma (TRB-5MS, 30 m × 0.25 mm × 0.25 μm) column. Bis(2,4,6-trimethylphenyl)formamidine[18] and $[IrCp^*Cl_2]_2$[19] were prepared according to literature procedures. All other reagents are commercially available and were used as received.

Synthesis of Compound 1

$[IrCp^*Cl_2]_2$ (100 mg, 0.126 mmol) and bis(2,4,6-trimethylphenyl)formamidine (70 mg, 0.250 mmol) were stirred at room temperature under nitrogen in dry CH_2Cl_2 (10 mL) for 2 h. After evaporation of the solvent under vacuum, the remaining solid obtained was washed with hexane (3 × 5 mL). Compound **1** was obtained as a crystalline orange solid by precipitation from CH_2Cl_2/hexane; yield: 153 mg (90%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of **1** in $CHCl_3$. Analysis for $C_{29}H_{39}N_2IrCl_2$ [found (calculated)]: C 51.47 (51.32), H 5.70 (5.79), N 4.22 (4.13); ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta = 8.08$ (d, $^3J_{H,H} = 13$ Hz, 1H, C*H*), 7.00 (s, 2H, CH_{Mes}), 6.77 (s, 2H, CH_{Mes}), 5.75 (d, $^3J_{H,H} = 12$ Hz, 1H, N*H*) , 2.34 (s, 3H, CH_3), 2.31 (s, 6H, CH_3), 2.19 (s, 3H, CH_3), 2.16 (s, 6H, CH_3), 1.29 [s, 15H, C_5-(CH_3)$_5$]; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 303 K): $\delta = 160.8$ (s, *C*H), 140.4 (s, C_{Mes}), 136.8 (s, C_{Mes}), 136.4 (s, C_{Mes}), 133.9 (s, C_{Mes}), 133.2 (s, C_{Mes}), 132.7 (s, C_{Mes}), 129.6 (s, *C*H$_{Mes}$), 129.4 (s, *C*H$_{Mes}$), 85.6 [s, C_5(CH$_3$)$_5$], 21.0 (s, *C*H$_3$), 20.9 (s, *C*H$_3$), 19.1 (s, *C*H$_3$), 17.8 (s, *C*H$_3$), 8.6 [s, C_5(*C*H$_3$)$_5$]; electrospray MS: $m/z = 634.4$ $[M-Cl]^+$.

Synthesis of Compound 2

Bis(2,4,6-trimethylphenyl)formamidine (70 mg, 0.250 mmol) was dissolved in dry THF under nitrogen and cooled to 0 °C.

n-BuLi (120 μL, 2.5 M in hexanes) was added, and the solution was stirred for 10 min. The resulting yellow solution was cannuled into a Schlenk tube with ([IrCp*Cl$_2$]$_2$ (100 mg, 0.126 mmol) in dry THF (10 mL). The resulting solution was stirred for 10 min at 0 °C and then for 2 h at room temperature. After evaporation of the solvent under vacuum, the remaining solid obtained was extracted with benzene. After evaporation of the benzene, the solid obtained was washed with hexanes, affording compound **2** as a yellow solid; yield: 113 mg (70%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of **2** in benzene. Analysis for $C_{29}H_{38}N_2IrCl$ [found (calculated)]: C 54.11 (54.23), H 6.00 (5.96), N 4.28 (4.36); ^{1}H NMR (300 MHz, C_6D_6, 303 K): $\delta = 9.16$ (s, 1H, C*H*), 6.83 (s, 4H, CH_{Mes}), 2.57 (s, 12H, CH_3), 2.17 (s, 6H, CH_3), 1.26 [s, 15H, $C_5(CH_3)_5$]; ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 303 K): $\delta = 167.6$ (s, *C*H), 140.4 (s, C_{Mes}), 134.2 (s, C_{Mes}), 133.1 (s, C_{Mes}), 129.6 (s, CH_{Mes}), 83.2 [s, $C_5(CH_3)_5$], 21.8 (s, CH_3), 20.9 (s, CH_3), 9.0 [s, $C_5(CH_3)_5$].

Dehydrogenation of Benzyl Alcohol

A mixture of benzyl alcohol (0.4 mmol), catalyst **1** (5 mol%) and Cs_2CO_3 (20 mol%) was refluxed in toluene (1 mL) for 15 h. The reaction mixture was analyzed by ^{1}H NMR spectroscopy using anisole as internal standard.

β-Alkylation of 1-Phenylethanol with Primary Alcohols: Standard Prodecure

A mixture of primary alcohol (1 or 2 mmol), 1-phenylethanol (1 mmol), KOH (1 mmol) and catalyst (1 or 0.1 mol%), was stirred at 100 °C in 0.3 mL of toluene, under aerobic conditions, in a sealed tube. Yields were determined by ^{1}H NMR using anisole as internal standard and $CDCl_3$ as deuterated solvent. The signals due to reagents and products were taken from the literature.[20]

N-Alkylation of Ammonium: Standard Procedure

Under an inert atmosphere, a mixture of ammonium source (1 mmol of ammonium salt), alcohol (3 or 3.6 mmol) and catalyst (1 mol%) was stirred at 130 °C in a sealed tube. Then, aqueous NaOH (2.0 M, 10 mL) was added to the reaction mixture, and the product was extracted with dichloromethane (30 mL). Yields were determined by GC using anisole as internal standard. All products were isolated by column chromatography and characterized by ^{1}H and ^{13}C spectroscopy. The confirmation of the nature of the products was performed by comparison with the commercial available products or literature data.[3c]

X-Ray Diffraction Studies

Crystals for X-ray diffraction of **1** and **2** were obtained by slow diffusion of hexane into a concentrated solution of the compound in $CHCl_3$. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda =$ 0.71073 Å). The diffraction frames were integrated using the SAINT package.[21] 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 refined using SHELXTL 6.1 software package.[22] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were assigned to ideal positions and refined using a rigid model. CCDC 804268 (**1**) and CCDC 813587 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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