First Cp*-Functionalized N-Heterocyclic Carbene and Its Coordination to Iridium. Study of the Catalytic Properties

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A new pentamethylcyclopentadienyl-functionalized N-heterocyclic carbene ligand (Cp*-NHC^{Me}) has been prepared and coordinated to iridium upon reaction with $[Ir(\mu\text{-Cl})(cod)]_2$. The chiral Ir complex is obtained as a racemic mixture of the two possible enantiomers, and its crystal structure is described. The new compound shows high catalytic activity toward transfer hydrogenation, β-alkylation of secondary alcohols with primary alcohols, and amination of primary alcohols.

Introduction

Since the first use of N-heterocyclic carbenes (NHCs) in the design of homogeneous catalysts[1] there has been an increasing effort in the design of new NHC-containing ligands with different topologies.[2] Now, we can find in the literature a large number of examples in which NHCs are incorporated to chelating,[3] pincer,[4] and chiral[5] architectures, but still, the search for new coordination modes and more effective NHC-containing catalysts is far from having reached its climax. Probably one of the main reasons that NHCs are becoming so popular is that they both provide improved catalysts[6] and the possibilities for topological modifications are almost infinite, just by applying very simple synthetic procedures.

C−H activation processes constitute one of the most important challenges in homogeneous catalysis.[7] Since the pioneering works by Bergman and co-workers in the use of "Cp*Ir(PMe_3)" systems in the activation of alkyl and aryl C−H bonds,[8] there has been an increasing number of works in which similar complexes with NHCs instead of phosphines have been used in many types of C−H activation processes. NHCs have clear advantages over phosphines, because they are more strongly bound to the iridium atom (providing a high thermal stability of the complexes), and are more basic,[9] thus enhancing their effectiveness toward C−H activation.[10] Several "Cp*Ir(NHC)" complexes were first described by Herrmann[11] and then by Yamaguchi and Fujita, who used them in the Oppenauer-type oxidation of alcohols.[12] We focused our attention on C−H activation processes such as the deuteration of organic molecules.[13] The mechanistic aspects regarding the intramolecular activation of aliphatic and aromatic C−H bonds were studied by us,[14–16] as well as by Yamaguchi, Fujita, and co-workers.[17] The high versatility of the "Cp*Ir(NHC)" complexes was pushed

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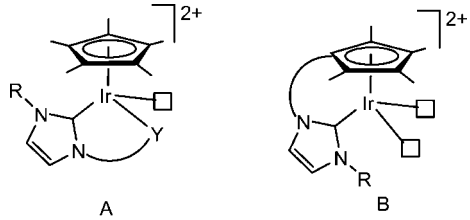
Scheme 1



a step forward when it was recently used as an efficient catalyst for the racemization of secondary alcohols.[18]

The introduction of chelating NHC ligands to the coordination sphere of a metal catalyst has some interesting consequences because it can increase its thermal stability[3,4] and favor the rigidity required for the preparation of effective asymmetric catalysts when a chiral center is present.[5] In the case of the "Cp*Ir" complexes, the introduction of chelating ligands has an important drawback, since it leaves the complex with only one possible vacant coordination site (three are occupied by the Cp* ligand, and two by the bis-chelating ligand), thus reducing the activity of the catalyst, as we have observed (Scheme 1, A).[13] An alternative way of preparing chelating architectures would be the preparation of suitable Cp* ligands with pendant NHCs, thus affording systems in which the chelation does not consume an "extra" coordination site (Scheme 1, B). Related systems with indenyl-, fluorenyl-functionalized NHCs[19] and also a bridged cyclopentadienyl-imidazolylidene ligand[20] recently have been coordinated to early transition metals, and to nickel.[21]

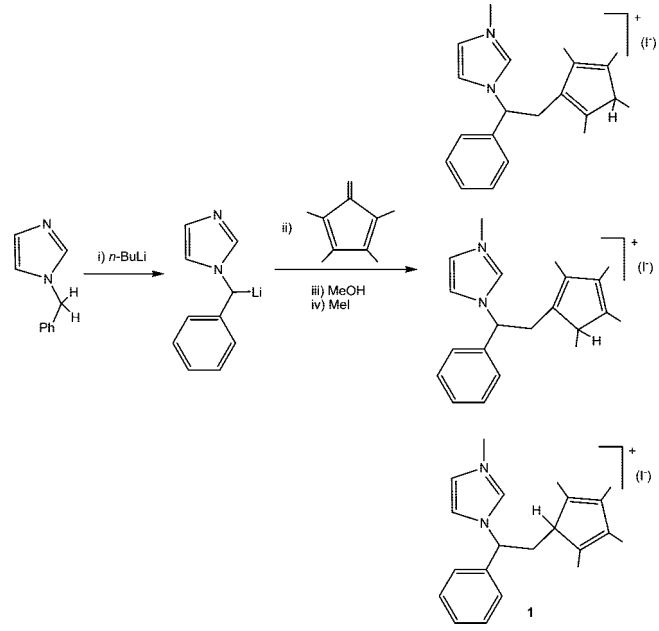
In this paper we describe the preparation of a new pentamethylcyclopentadienyl-imidazolylidene chelating ligand with a chiral bridge and its coordination to iridium. The catalytic activity of this new complex has been studied in a wide set of reactions, showing high efficiency in hydrogen transfer to ketones, β-alkylation of secondary alcohols with primary alcohols, and N-alkylation of amines with alcohols.

Results and Discussion

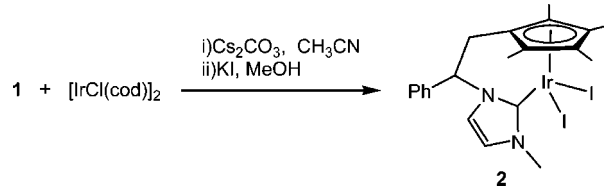
The imidazolium pro-ligand Cp*-NHC^{Me}, **1**, was obtained as shown in Scheme 2 by deprotonation at the methylene group of benzylimidazole with *n*-BuLi,[22] followed by reaction with tetramethylfulvene and treatment with MeOH. Subsequent reaction with MeI in acetone affords **1** as a mixture of tautomers that results from the different position of the double bonds in the cyclopentadienyl ring. The product was isolated as a pale yellow slightly hygroscopic powder and was characterized by analytical and spectroscopic methods. The ^{1}H and ^{13}C NMR spectra of **1** showed very complicated sets of signals that were difficult to accurately assign, although we were able to establish some assignment based on the bidimensional spectra and obtained its satisfactory elemental analysis.

Reaction of **1** with [Ir(μ-Cl)(cod)]$_2$ (cod = 1,5-cyclooctadiene) in the presence of $Cs_2CO_3$and acetonitrile at 50 °C, followed by treatment of the resulting residue (obtained after removing all volatiles from the reaction mixture) with KI in MeOH under reflux, afforded the desired complex **2** in high yield (ca. 70%) as a racemic mixture of the two possible enantiomers (Scheme 3).

Scheme 2



Scheme 3



Compound **2** was characterized by means of NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum shows the two doublets at 6.6 and 6.3 ppm, due to the protons of the imidazolilydene ring. The asymmetry of the coordinated ligand is displayed by the inequivalence of the methyl groups at the cyclopentadienyl ring, as seen by the appeareance of four distinctive signals (δ 2.13, 2.12, 1.99, and 1.79). The ^{13}C NMR spectrum confirms that coordination of both the NHC and the Cp ring have occurred. The signal at 146 ppm, indicative of a Ir$-$C$_{carbene}$, is in the region of previously reported Cp*Ir(NHC) complexes.[12–17] In this case five different signals due to the five carbons of the cyclopentadienyl ring are clearly observed, confirming the asymmetry of the system.

Crystals of **2** suitable for X-ray diffraction were obtained from concentrated THF/ether solutions, and allowed to unambiguously confirm the structure of the complex. Figure 1 shows the molecular structure of **2** with the most representative distances and angles. The structure shows that the cyclopentadienyl-NHC ligand is chelating the iridium atom, and two iodine ligands complete the coordination sphere about the metal. The Ir$-$C$_{carbene}$ distance of 2.044 Å lies in the expected range.[12–17] The Ir$-$C$_{Cp*}$ distances differ depending on their relative orientation with respect to the pendant NHC substituent. The two Cp* carbons trans to the NHC ligand display a larger Ir$-$C distance than that shown for the other three carbon atoms (compare 2.28 and 2.29 Å with 2.12–2.16 Å, respectively) as a consequence of the trans influence of the NHC ligand. The

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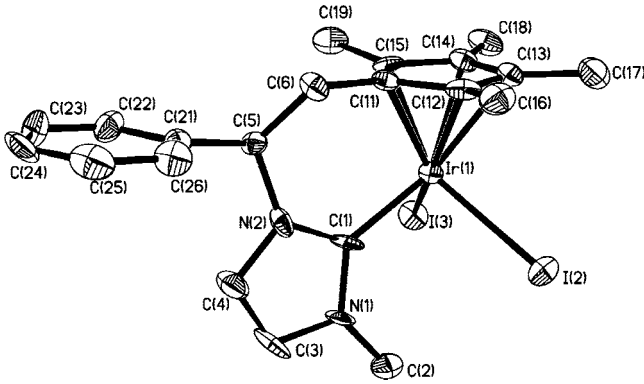


Figure 1. Molecular diagram of compound **2**. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.044(11), Ir(1)−I(2) 2.7205(10), Ir(1)−I(3) 2.7143(9), Ir(1)−C(11) 2.116(11), Ir(1)−C(12) 2.159(11), Ir(1)−C(13) 2.297(11), Ir(1)−C(14) 2.286(11), Ir(1)−C(15) 2.167(10), C(1)−Ir(1)−I(2) 94.7(4), C(1)−Ir(1)−I(3) 91.1(3), I(3)−Ir(1)−I(2) 96.13(3), N(1)−C(1)−Ir(1) 128.3(9), N(2)−C(1)−Ir(1) 126.2(8).

Table 1. Catalytic Transfer Hydrogenation[a]

entry	catalyst	substrate	% cat.	*t* (h)	TON	% yield
1	**2**	acetophenone	0.1	5.5	990	>99
2	**2**	cyclohexanone	0.1	2.5	870	87
3	**2**	cyclohexanone	0.1	4.5	990	>99
4	**2**	cyclohexanone	0.01	20	9900	>99
5	**2**	benzophenone	0.1	2	130	13
6	**2**	benzophenone	0.1	8	990	>99
7	$[Cp^*IrCl_2]_2$	cyclohexanone	0.1	2.5	50	5
8	$[Cp^*IrCl_2]_2$	cyclohexanone	0.1	17	970	97
9	$[Cp^*IrCl_2]_2$	benzophenone	0.1	2	30	3
10	$[Cp^*IrCl_2]_2$	benzophenone	0.1	17	270	27

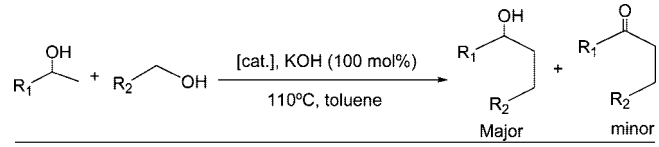
[a] 2 mmol of ketone, KOH (10 mL, 0.2 M in i-PrOH). Temperature: 80 °C. Yields determined by ^{1}H NMR spectroscopy.

difference in the exocyclic and endocyclic angles N(1)−C(1)−Ir(1) and N(2)−C(1)−Ir(1) is small (2.1°) as a consequence of the low strain produced by the C2 tethered functionality.

Preliminary studies of the catalytic activity of **2** were performed to explore its potential applications in the functionalization of organic molecules. Since we wanted to prove the catalytic versatility of our compound, the following model reactions were studied: transfer hydrogenation between ketones and alcohols and alkylation of secondary alcohols and amines with primary alcohols.

Compound **2** catalyzed the hydrogenation of C═O groups of ketones via hydrogen transfer from *i*-PrOH/KOH at 80 °C, as shown in Table 1. The three ketones chosen for this reaction were acetophenone, cyclohexanone, and benzophenone, so that we could have a clear idea about the activity of our compound in the reduction of both aliphatic and aromatic substrates. As observed, the introduction of the NHC ligand has a very positive effect on the enhancement of the catalytic activities of the catalyst compared to the activities shown by $[Cp^*IrCl_2]_2$ (compare entries 1–6 with 7–10, Table 1). Catalyst loadings of 0.1 mol % afforded full conversions to the corresponding alcohols in times ranging from 3 to 5 h. A catalyst loading as low as 10^{-2} mol % was used in the reduction of cyclohexanone, achieving full conversions, despite longer reaction times being needed (20 h). These results were similar to those shown by our previously reported Cp*Ir complexes with alkenyl-functionalized NHCs.[16] As we have previously reported, the fact that **2** shows high catalytic activity in the transfer hydrogenation of ketones contrasts with the negligible performances shown by other bis-chelating Cp*Ir(III)(NHC) complexes reported by us,[14] thus implying that the blocking of the two coordination vacant sites by the chelating ligand prevents any catalytic activity.

Table 2. β-Alkylation of Secondary Alcohols with Primary Alcohols[a]



entry	catalyst	R1	R2	*t* (h)	% conv	% alcohol	% ketone
1	**2**	Ph	Ph	6	91	100	0
2	**2**	Ph	Ph	9	>95	100	0
3	**2**	Ph	4-Cl(C_6H_4)	6	87	100	0
4	**2**	Ph	4-Cl(C_6H_4)	9	100	50	50
5	**2**	Ph	Pr	3	100	80	20
6	**2**	Ph	Pr	6	100	50	50
7	$[Cp^*IrCl_2]_2$	Ph	Ph	9	68	100	0
8	$[Cp^*IrCl_2]_2$	Ph	Pr	3	89	64	36
9	$[Cp^*IrCl_2]_2$	Ph	Pr	6	93	54	46

[a] 1 mmol of primary and secondary alcohol, 1 mmol (100 mol%) of KOH, 0.3 mL of toluene, 1 mol % cat. Temperature: 110 °C. Conversions determined by ^{1}H NMR spectroscopy.

The catalytic β-alkylation of secondary alcohols with primary alcohols has important beneficial implications compared to the traditional multistep processes, especially considering the economical benefits that a high-yielding one-pot procedure implies, together with the use of an environmental friendly process. Despite these obvious implications, we found in the literature just a few examples of such reactions with Ru[23,24] and Ir[25] catalysts. The reactions were performed with 1-phenylethanol as the secondary alcohol and three different primary alcohols. A fixed catalyst loading of 1 mol % was used in the presence of KOH in toluene at a temperature of 110 °C. Table 2 shows the catalytic results for this process. Again, under the same reaction conditions **2** shows improved catalytic activities compared to $[Cp^*IrCl_2]_2$ (compare entries 1–6 with 7–9, Table 2). As observed, short reaction times in the range of 3–9 h were enough for achieving the full conversion of the reactants to the desired products. To our knowledge, compound **2** is the most efficient catalyst for this reaction, if we take into account the short reaction times needed for the completion of the process, and the low catalyst loading used. It is noteworthy to point out that the selectivity of the process clearly depends on the reaction times. For short reaction times, a high selectivity is obtained in the formation of the final alcohol, which is obtained as the only product in some of the experiments (entries 1–3, Table 2). Longer reaction times favor the dehydrogenation of the final alcohol to the corresponding ketone, as observed from the comparison of the data shown in entries 3–4 and 5–6 in Table 2. This dehydrogenation process is not so strange if we take into account the previous work by Fujita, Yamaguchi, and coworkers in which a Cp*Ir complex is used for the dehydrogenation of alcohols in an "oxidant-free" environment.[26] In their complex, a 2-hydroxypyridine ligand is used in the "ligand promoted dehydrogenation". In our case, such a system is not present, so a different mechanism may be operating. To solve this question, further studies on this oxidant-free dehydrogenation of alcohols are currently underway in our laboratories.

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Table 3. N-Alkylation of Aniline with Alcohols[a]

entry	catalyst	alcohol	base	*t* (h)	% yield
1	**2**	benzyl alcohol	KOH[b]	9	54
2	**2**	benzyl alcohol	KOH	25	67
3	**2**	benzyl alcohol	KOH	45	76
4	**2**	benzyl alcohol	KO^{t}Bu	16	85
5	**2**	1-butanol	KO^{t}Bu	16	47
6	**2**	1-butanol	KO^{t}Bu	24	55
7	$[Cp^*IrCl_2]_2$	benzyl alcohol	KOH	13	36
8	$[Cp^*IrCl_2]_2$	benzyl alcohol	KO^{t}Bu	16	60
9	$[Cp^*IrCl_2]_2$	1-butanol	KO^{t}Bu	16	29

[a] 2 mmol of aniline and alcohol, 2 mmol (100 mol %) of base, 0.3 mL of toluene, 0.75 mol % cat. Temperature: 110 °C. Conversions determined by ^{1}H NMR spectroscopy. [b] 50 mol % of base and 2.5 mol % of catalyst.

The metal-mediated alkylation of amines with primary alcohols is an important fundamental reaction in synthetic organic chemistry that has shown an increasing interest in the preparation of molecules with pharmaceutical applications. Typically, the reaction consists of the coupling of a primary or secondary amine with a primary alcohol to provide the corresponding final alkylated amine. For this reaction, only a few examples describing Ru[27] and Ir[28] catalysts have been reported. The reactions were performed with use of aniline and a set of two different alcohols (Table 3), with a fixed catalyst loading of 0.75 mol %, in the presence of a base (KOH or KO^{t}Bu). The conversions were only moderate, but comparable to the results provided by other Ir catalysts,[28] and higher than those obtained by $[Cp^*IrCl_2]_2$ under the same reaction conditions (compare entries 1–6 with 7–9, Table 3).

Conclusions

We have reported a new pathway for the synthesis of pentamethylcyclopentadienyl-functionalized N-heterocyclic carbene ligand that allows the preparation of an unprecedented Cp*-NHC^{Me} chelating compound of Ir in high yield. Having a chiral carbon center in the linker between the Cp* and imidazole rings, the ligand has a high interest in the design of catalysts for asymmetric catalysis, although in our case we just reported the racemic mixture of all compounds described.

Compound **2** is a versatile catalyst in a wide set of reactions implying C−H activations. We have shown the activity of **2** toward transfer hydrogenation, β-alkylation of secondary alcohols with primary alcohols, and amination of primary alcohols. The design of the asymmetric versions of these reactions is one of the most attractive features that are now being explored in our groups. We are currently performing methods for the preparation of enantiomerically pure compounds containing our Cp*-NHC ligand, and the study of their catalytic activity in asymmetric processes.

Experimental Section

All reactions were carried out under inert atmosphere. When required, solvents were dried via standard techniques.

NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer with $CDCl_3$ (Cambridge Isotope Laboratories, Inc.) as solvent. Elemental analyses were performed in our laboratories at ITQB. 1,2,3,4-Tetramethylfulvene,[29] $[Ir(\mu\text{-Cl})(cod)]_2$,[30] and $[Cp*IrCl_2]_2$[31] were synthesized according to literature procedures. All other reagents are commercially available and were used as received.

Synthesis of Cp*-NHC^{Me}I, 1. An hexane solution of *n*-BuLi (7.6 mL of 1.6 M in hexane, 12.15 mmol) was added dropwise to a solution of benzylimidazole (1.6 g, 10.12 mmol) in dried THF (25 mL) at −60 °C. After the solution was stirred for 20 min, tetramethylfulvene was added, and the reaction mixture was allowed to reach room temperature and stirred for 1 h. Methanol was then added, and the volatiles were evaporated. The crude oil was purified by flash chromatography (hexane/ethyl acetate, 1:4) affording a yellow oil of Cp*-NHC^{Me} (2.5 g, 85%). Iodomethane (376 mL, 6 mmol) was added to a solution of Cp*-NHC^{Me} (353 mg, 1.2 mmol) in 5 mL of methanol. The reaction was stirred at room temperature for 12 h and all the volatiles were evaporated affording a yellow solid that was washed several times with dried diethyl ether to yield the title compound **1** in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.2–9.2 (s, 1H, N═C*H*—N), 7.75–6.76 (m, 7H, Ph*H*, N—C*H*═C*H*—N), 5.75–4.9 (m, 1H, Ph—C*H*(Im)—CH_2—Cp*), 4.0–3.8 (s, 3H, N—CH_3), 3.44–2.4 (m, 3H, Ph—CH(Im)—CH_2—Cp*, Cp**H*), 1.74–1.35 (s, 9H, C═C(CH_3)—C), 1.0–0.8 (d, 3H, C—CH(CH_3)—C). Anal. Calcd for $C_{21}H_{27}IN_2$: C, 58.07; H, 6.27; N 6.45. Found: C, 58.46; H, 6.45; N, 6.13.

Synthesis of [Cp*-NHC^{Me}]IrI$_2$, 2. A mixture of Cs_2CO_3 (1.75 g, 4.95 mmol), $[Ir(\mu\text{-Cl})(cod)]_2$ (166 mg, 0.25 mmol), and **1** (215 mg, 0.5 mmol) in acetonirile (15 mL) was heated to 50 °C for 4 h. After cooling to room temperature, the reaction mixture was filtered, the filtrate was evaporated to drynesss, and KI (415 mg, 2.5 mmol) and methanol were added to the residue. After being refluxed overnight, the reaction mixture was allowed to cool to room temperature and the solvent was removed under vacuum and the remaining solid was purified by flash chromatography (CH_2Cl_2) affording the desired complex **2** as a red solid. Yield: 255 mg, 68%. Crystals of **2** suitable for X-ray crystallography were obtained from concentrated THF/ether solutions. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (br, 3H, PhH), 7.36 (br, 2H, PhH), 6.65 (d, 1H, $^3J_{H\text{-}H}$ = 1.6 Hz, CH_3—N—C*H*═CH—N), 6.29 (d, 1H, $^3J_{H\text{-}H}$ =1.6 Hz, CH_3—N—CH═C*H*—N), 5.07 (dd, 1H, $^3J_{H\text{-}H}$ = 3.2 Hz, $^3J_{H\text{-}H}$ = 11.4 Hz, Ph—C*H*(Im)—CH_2—Cp*), 4.07 (s, 3H, N—CH_3), 2.68 (m, 2H, Ph—CH(Im)—CH_2—Cp*), 2.13 (s, 3H, Cp*—CH_3), 2.12 (s, 3H, Cp*—CH_3), 1.99 (s, 3H, Cp*—CH_3), 1.79 (s, 3H, Cp*—CH_3). $\{^1H\}^{13}C$ NMR (100 MHz, $CDCl_3$) δ 146 (*C*—Ir), 138 (C_{phenyl}), 130 (CH_{phenyl}), 123 (CH_3—N—C*H*═CH—N), 120 (CH_3—N—CH═*C*H—N), 104 (C_{Cp}), 103 (C_{Cp}), 84 (C_{Cp}), 83 (C_{Cp}), 80 (C_{Cp}), 65 (Ph—C*H*(Im)—CH_2—Cp*), 46 (N—*C*H_3), 29 (Ph—CH(Im)—*C*H_2—Cp*), 12 (*C*H_{3Cp}), 11 (*C*H_{3Cp}), 10 (*C*H_{3Cp}). Anal. Calcd for $C_{21}H_{25}I_2N_2Ir$: C, 33.57; H, 3.35; N 3.73. Found: C, 33.28; H, 3.28; N, 3.22.

β-Alkylation of Secondary Alcohols with Primary Alcohols: Standard Procedure. The reaction was carried out withsecondary alcohol (1 mmol), primary alcohol (1 mmol), 1 mol % of catalyst, and base, KOH (1 mmol) in toluene (0.3 mL) at 110 °C. The reaction was monitored by ^{1}H NMR spectroscopy by introducing aliquots of the reacting solution inside an NMR tube with 0.5 mL of $CDCl_3$. The evolution was determined by integration.

N-Alkylation of Amines with Alcohols: Standard Procedure. A mixture of the amine (2.0 mmol), alcohol (2.0 mmol), catalyst (0.75 mol %), toluene (0.3 mL), and KO^{t}Bu (2.0 mmol) was placed in a Schlenk with a Teflon screw tap and the mixture was stirred and heated to 110 °C. The reaction was monitored by ^{1}H NMR spectroscopy by introducing aliquots of the reacting solution inside an NMR tube with 0.5 mL of $CDCl_3$. The evolution was determined by integration.

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Hydrogen Transfer: Standard Procedure. A mixture of the ketone (2 mmol), KOH (10 mL, 0.2 M in *i*-PrOH), and catalyst (1 mL, 0.002 M in CH_2Cl_2) was refluxed. The reaction was monitored by ^1H NMR spectroscopy by introducing aliquots of the reacting solution inside an NMR tube with 0.5 mL of $CDCl_3$. The evolution was determined by integration.

X-ray Diffraction Studies. Single crystals of **2** 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 was refined using the SHELXTL 6.1 software package.[32] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined by using a riding model. The diffraction frames were integrated with use of the SAINT package.[33]

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X-ray Crystal Structure Data. $C_{21}H_{25}I_2IrN_2$, monoclinic, space group $P2(1)/n$, a = 9.5338(10) Å, b = 11.0406(12) Å, c = 21.147(2) Å, β = 99.593(3)°, V = 2194.8(4) Å^3, Z = 4, ρ_{calcd} = 2.274 g cm^{-3}, crystal dimensions 0.3 × 0.2 × 0.1 mm^3; Mo Kα radiation, 273(2) K; 11944 reflections, 3736 independent; (μ = 8.904 mm^{-1}); refinement (on F^2) with SHELXTL (version 6.1), 240 parameters, 0 restraints, R_1 = 0.0430 ($I > 2\sigma$) and wR_2 (all data) = 0.0799, GOF = 1.042.

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Supporting Information Available: Crystallographic data for **2** in the form of CIF files and NMR spectra of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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