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N-Heterocyclic Carbenes

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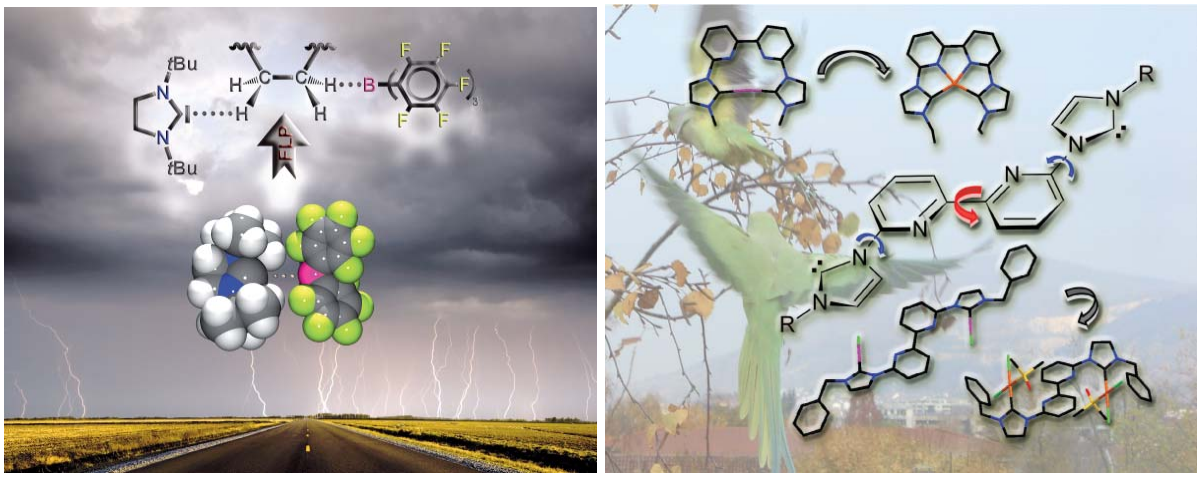

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Easy preparation of Cp*-functionalized N-heterocyclic carbenes and their coordination to rhodium and iridium†

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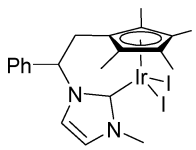
A simple high-yielding method for the preparation of a tetramethylcyclopentadienyl-NHC ligand is described. This ligand has been successfully coordinated to Rh and Ir. A related Cp*-NHC ligand with a -CH_2CMePh- linker between the Cp* and the NHC is also described, together with its coordination to Rh and Ir. This latter ligand, affords the *ortho*cyclometallation of the phenyl ring yielding a constrained structure in which the ligand is tridentate. All the complexes have been fully characterized and their crystal structures are described. Preliminary catalytic results on the β-alkylation of secondary alcohols and N-alkylation of aniline with primary alcohols are also reported.

Introduction

The easy access to N-heterocyclic carbenes and their potential application in a large number of homogeneously-catalyzed processes, has led to a rapid development in the design of an almost unlimited number of NHC-containing architectures. NHCs are known to be compatible with a wide set of functionalities, including pyridines, alcohols, phosphines, arenes, aryls, ethers, oxazolines, amines and other donor groups.[1] Among these NHC-based ligands, those containing η^6-arene-η^1-carbene,[2] η^5-indenyl-η^1-carbene[3] or η^5-cyclopentadienyl-η^1-carbene[4] are limited to a very few recent examples, despite their obvious interest in the preparation of stable and rigid molecules.

After the pioneering studies by Bergman and co-workers on the application of Cp*Ir(phosphine) complexes in C-H activation processes,[5,6] several works appeared showing that the replacement of the phosphine by NHC ligands, may sometimes result in an enhancement of the catalytic activities.[7–9] An early approach to more stable 'Cp*Ir(phosphine)' complexes consisted of the preparation of complexes bearing chelating cyclopentadienyl-phosphine ligands,[6] an idea that was also applied by us to obtain a Cp*Ir(III)-related complex that contained the first chelating tetramethylcyclopentadienyl-NHC ligand, in which the Cp* ring and the NHC were connected by a -CH_2CHPh- linker (A, Scheme 1).[4]

Compound A proved to be an excellent catalyst for a number of reactions implying hydrogen-borrowing processes,[4] a fact that confirmed the applicability of the tethered ligand. In order to extend the use of Cp*-NHC ligands to other metals and widen the scope of their catalytic applications, we thought that the multistep and low-yielding procedure to the preparation of the ligand in A, could be an inconvenient that needed to be addressed. Here we report a new synthetic method that allows one to easily prepare an η-(tetramethylcyclopentadienyl)-NHC ligand and simplifies the multistep process needed for the preparation of our previously described ligand. Together with the description of the new synthetic protocols, we have described the intramolecular C-H activation processes that allows the preparation of the tethered η^5-Cp*-NHC metal complexes, one of which shows an unusual rigid tridentate coordination form. The preliminary catalytic applications of the new complexes are also described.

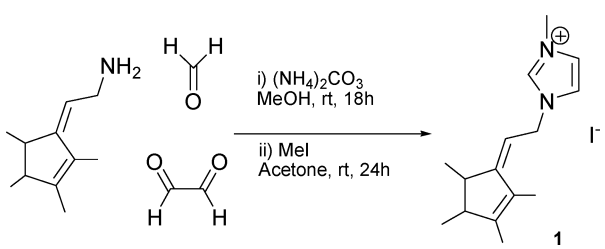


A

Scheme 1

Results and discussion

The salt **1** was prepared by a one-pot synthesis route,[10] starting from the easily accessible 2-(2,3,4,5-tetramethylcyclopentadienyl)-ethylamine,[11] glyoxal and formaldehyde, yielding 2-(2,3,4,5-tetramethylcyclopentadienyl)ethylimidazole, that further reacts with MeI to provide the imidazolium iodide **1** with an overall yield of *ca.* 66% (Scheme 2).



1

Scheme 2 Synthesis of **1**.

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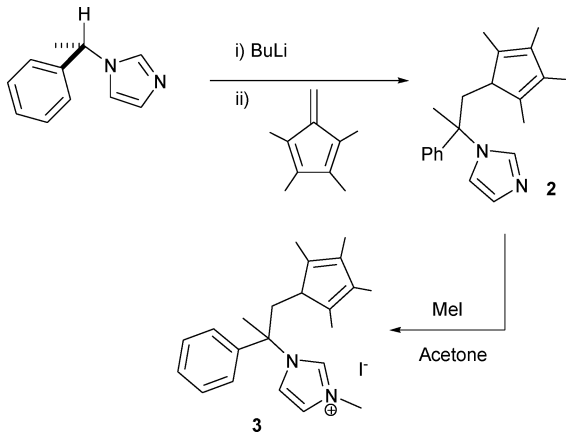
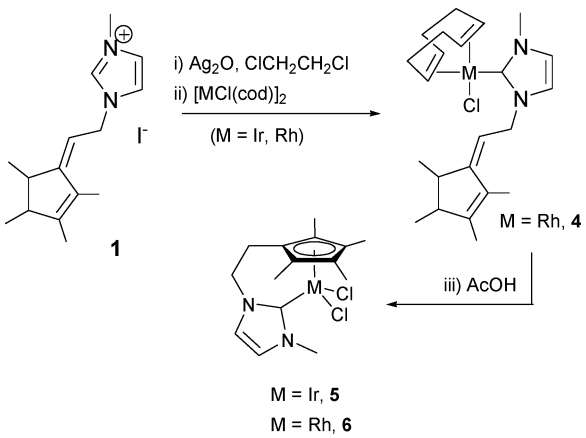
† Electronic supplementary information (ESI) available: Ortep diagram of compound **6**. CCDC reference numbers 717566–717569. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901195a

In an attempt to obtain an enantiomerically pure chiral Cp*-NHC ligand, we prepared the imidazolium salt **3** starting from *S*-1-(phenylethyl)imidazole as depicted in Scheme 3.[4] However, we observed that the final imidazolium-proligand **3** is a racemate, probably as a consequence of the deprotonation of *S*-1-(phenylethyl)imidazole with BuLi, which affords the racemic mixture of the imidazolyl intermediate **2**.



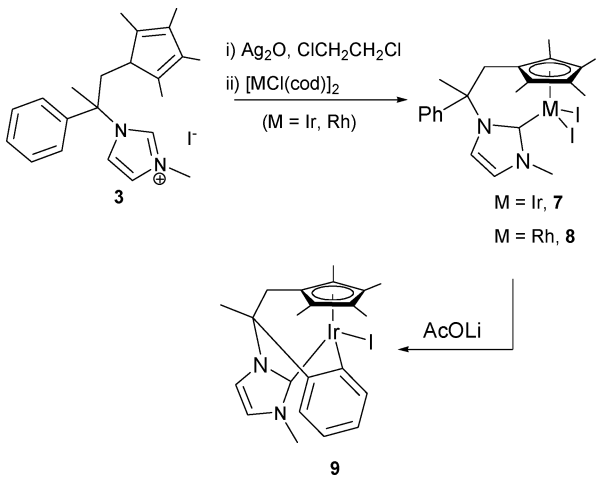
Scheme 3 Synthesis of **3**.

Both **1** and **3** served as useful Cp*-NHC chelating precursors for the preparation of Rh and Ir complexes. The reaction of **1** with $[MCl(cod)]_2$ (M = Rh, Ir) was performed *via* the transmetallation of the *in situ* pre-formed Ag-NHC complex to the rhodium and iridium precursors. The first step of this process affords M(I) species with the monometalated carbene and with uncoordinated tetramethylcyclopentadienyl moiety. For the Rh complex, we have isolated the corresponding Rh(I) intermediate **4**, which was characterized by mass spectrometry (molecular peak at 441 ([Cp*-NHC)Rh(cod)]$^+$) and NMR spectroscopy (Scheme 4). Both ^{13}C and ^1H NMR spectra showed that the isolated species consisted of two isomers that we were unable to separate. Although we could not achieve clean NMR spectra for a detailed characterization, we clearly observed that the ^{13}C NMR spectrum shows two doublets at 182 and 178 ppm, with a $^1J_{Rh\text{-}C}$ value of 51 Hz, both suggesting that **4** is a mixture of two pseudosquare-planar Rh(I) species. The nature of the two isomers may be ascribed to the restricted rotation of the NHC ligand about the Rh-C bond due to the steric interaction with the cyclooctadiene ligand, providing two distinctive rotamers. Further addition of acetic acid facilitates the C-H activation of the cyclopentadienyl and its η^5-coordination to the metal, affording the final M(III) species (compounds **5** and **6**, Scheme 4). In this reaction, together with the CH activation of the pentacyclic fragment, the second step of the reaction implies the metal-mediated isomerization of the exocyclic double bond of the linker chain, to form the final η^5-cyclopentadienyl part of the ligand.



Scheme 4 Coordination of **1** to Ir and Rh.

The coordination of **3** to $[MCl(cod)]_2$ (M = Rh, Ir) was performed *via* the transmetallation of the *in situ* pre-formed Ag-NHC complex to the rhodium or iridium fragments. Further addition of acetic acid and KI completes the reaction to the final M(III) species with the coordination of the chelating Cp*-NHC ligand and formation of compounds **7** and **8** (Scheme 5). The reaction of the iridium complex **7** with LiOAc in methanol, affords the *ortho*cyclometallation of the phenyl ring to form compound **9** in almost quantitative yield, as shown in Scheme 5. Although we have observed this type of aromatic CH activation for related Cp*Ir(NHC) complexes,[9,12] the formation of this rigid terdentate coordination is unprecedented.



Scheme 5 Coordination of **3** to Ir and Rh.

The identity of all complexes was established by analytical and spectroscopic methods. The ^1H NMR of **5** and **6** showed the characteristic signals due to the protons of the imidazolylidene ring. The twofold symmetry of the azole ring is confirmed by the equivalence of the two pairs of methyl groups, showing two distinctive signals. The ^{13}C NMR spectra show the signals due to the M-$C_{carbene}$, at δ 150 (**5**) and 166 (**6**, $^1J_{Rh\text{-}C} = 55.7$ Hz), confirming the coordination of the NHC.

The ^1H NMR of **7** and **8** showed the two doublets due to the protons of the imidazolylidene ligand, and the four distinctive signals of the inequivalent methyl groups at the cyclopentadienyl ring, as a consequence of the asymmetry of the ligand. The ^{13}C NMR confirms that the coordination of both the Cp* ring and the NHC have occurred. Compound **7** shows a signal at 148 ppm, indicative of a Ir-$C_{carbene}$ and in the region of previously reported Cp*Ir(NHC) complexes.[4,8,12–15] The signal due to the metallated carbene in **8** appears as a doublet at 167 ppm ($^1J_{C\text{-}Rh} = 59.0$ Hz). For both, **7** and **8**, five different signals assigned to the five carbons

of the cyclopentadienyl ring are clearly observed, confirming the asymmetry of the system.

The ^{13}C NMR spectrum of **9** confirms that the cyclometallation of the phenyl ring has occurred. A signal at 159 ppm is due to the Ir-C_{phenyl}, while the signal due to the metallated carbene carbon appears at 147 ppm.

The molecular structures of complexes **5**, **6**, **8** and **9** were confirmed by X-ray diffraction methods. Fig. 1, 2, and 3 show the molecular diagrams of complexes **5**, **8** and **9**, respectively. The Ortep diagram of compound **6** can be seen in the ESI† of this manuscript. Compounds **5** (Fig. 1) and **6** (ESI) are isostructural, with the only difference that **5** contains an Ir center and **6** is Rh. Both structures show that the η-(tetramethylcyclopentadienyl)-NHC ligand is chelating the metal atom, and two chlorine ligands complete the coordination sphere about the metal. The M-$C_{carbene}$ distance is 2.041 (**5**, M = Ir) and 2.033 (**6**, M = Rh). All other distances and angles are unexceptional and compare well with related compounds reported in this and other previously published studies.[4,12–14]

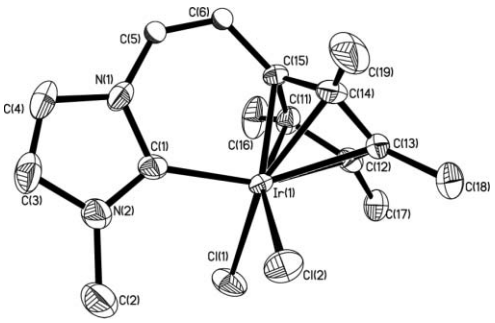


Fig. 1 Ortep diagram of compound **5**, with ellipsoids representing 30% probability. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are: Ir(1)-C(1), 2.041(12); Ir(1)-Cl(1), 2.406(4); Ir(1)-Cl(2), 2.404(3); Ir(1)-C(15), 2.089(11); Ir(1)-C(11), 2.137(11); Ir(1)-C(14), 2.133(13); Ir(1)-C(13), 2.242(11); Ir(1)-C(12) 2.261(10), C(1)-Ir(1)-Cl(1), 92.3(3); C(1)-Ir(1)-Cl(2) 89.2(3), Cl(1)-Ir(1)-Cl(2), 91.82 (16).

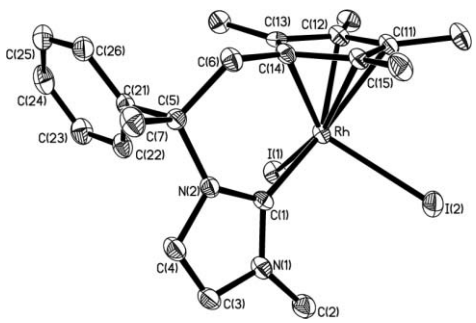


Fig. 2 Ortep diagram of compound **8**, with ellipsoids representing 30% probability. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are: Rh-C(1), 2.045(6); Rh-C(14), 2.104(7); Rh-C(15) 2.141(7); Rh-C(13), 2.181(7); Rh-C(12) 2.266(7); Rh-C(11) 2.279(6); Rh-I(2), 2.7088(18); Rh-I(1), 2.7088(19); C(1)-Rh-I(1) 89.69(18); C(1)-Rh-I(2) 97.5(2); I(2)-Rh-I(1) 97.86(8).

The molecular structure of **8** (Fig. 2) shows that the η-(tetramethylcyclopentadienyl)-NHC ligand is chelating the rhodium atom, and two iodine ligands complete the coordination sphere about the metal. The Rh-$C_{carbene}$ distance is 2.045 Å.

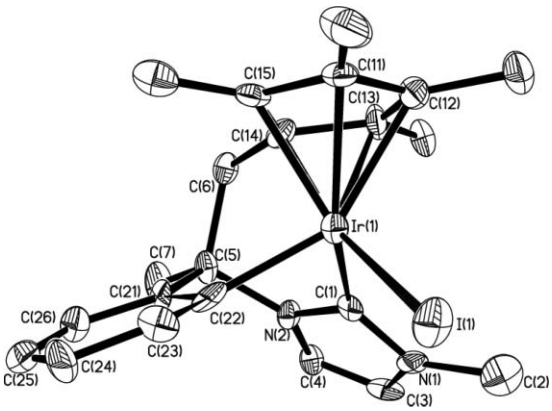


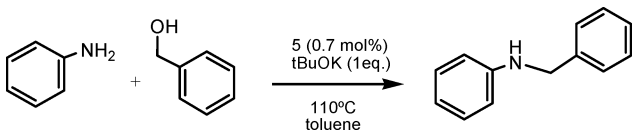
Fig. 3 Ortep diagram of compound **9**, with ellipsoids representing 30% probability. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are: Ir(1)-C(1) 1.951(17), Ir(1)-C(22) 2.074(18), Ir(1)-C(14) 2.073(17), Ir(1)-C(15) 2.239(18), Ir(1)-C(13) 2.24(2), Ir(1)-C(11) 2.259(18), Ir(1)-C(12) 2.238(19), Ir(1)-I(1) 2.6985(17), C(1)-Ir(1)-C(22) 83.2(7), C(1)-Ir(1)-I(1) 102.8(6), C(22)-Ir(1)-I(1) 96.2(5).

The two Cp* carbons *trans* to the NHC ligand display a larger Ir-C distance, than that shown for the three other carbon atoms (compare 2.27 and 2.28, with 2.10–2.18 Å, respectively as a consequence of the *trans* influence of the NHC ligand. This effect is also observed for all the rest of the structures that we have determined in this work, and also in other examples published before.[4]

The molecular structure of **9** (Fig. 3), shows that the phenyl substituent at the C(5) atom of the NHC-Cp* linker has *ortho*metalated, thus forming a structure with a tridentate coordination of the ligand. The Ir-$C_{carbene}$ distance is 1.95 Å, a little shorter than the similar distances shown by the Ir compounds obtained in this work and other similar complexes reported in the literature,[4] although similar to other Cp*Ir-NHC species with *ortho*metalated phenyl rings that we have reported previously.[12,14] The Ir-C bond distance for the cyclometalated phenyl ring is 2.07 Å. The $C_{carbene}$-Ir-C_{phenyl} bite angle is 83.2°.

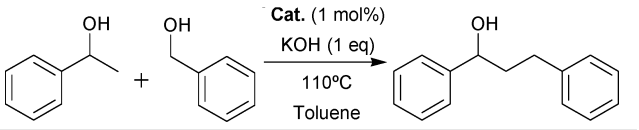
In order to test catalytic applicability of the complexes obtained, we decided to perform a preliminary set of tests using complex **5**. For this purpose, we studied its activity toward hydrogen transfer and β-alkylation of secondary alcohols with primary alcohols, using 2-phenylethanol and benzylic alcohol. As shown in Table 1, the results that we obtained compare well with our previously published results when we used A.[4]

Catalyst **5** was also an excellent catalyst in the alkylation of amines with primary alcohols (Scheme 6), a reaction for which A and other Cp*Ir(NHC)[16] complexes have also shown a good catalytic activity. In the case of **5**, yields on the final product of up to 93% were achieved, with a low catalyst loading of 0.7 mol% for the reaction between aniline and benzylic alcohol.



Scheme 6 Alkylation of aniline with benzylalcohol.

Table 1 Catalytic β-alkylation of secondary alcohols using **5** and A



Catalyst	Time (h)	Conversion (%)
5	3	70
5	6	80
5	24	>99
A	3	70
A	6	90
A	24	>99

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

Conclusions

In this work we have described a convenient and high-yielding method for the preparation of a precursor of a Cp*-NHC ligand with the simple -CH_2CH_2- linker between the Cp* and the NHC ring. This precursor can be easily coordinated to Rh and Ir by transmetallation from the corresponding preformed Ag-NHC complex. We also described the preparation of another Cp*-NHC ligand precursor with a -CH_2CMePh- linker, which was also coordinated to Rh and Ir. Both, the synthetic procedures to the ligand precursor, and the metallation methodologies to the (Cp*-NHC)M complexes constitute valuable protocols that can be extended to the preparation of complexes with other transition metals.

The preliminary studies on the catalytic activity of the Ir complex **5**, shows that this species displays a good activity in the alkylation of secondary alcohols and amines with benzylic alcohol. Further studies in order to widen the catalytic applications of these species, and also in the preparation of enantiomerically pure chiral catalysts of this type, are underway.

Experimental

Materials and methods

NMR spectra were recorded on a Bruker Advance III 400 MHz and a Varian Innova 500 MHz spectrometers using $CDCl_3$ as solvent. Elemental analyses were performed in our laboratories at ITQB. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quattro LC instrument. 1,2,3,4-Tetramethylfulvene,[17] *S*-1-(phenylethyl)imidazole[18], 2-(2,3,4,5-tetramethylcyclopentadienyl)ethylamine,[11] were synthesized according to literature procedures. All other reagents are commercially available and were used as received.

X-Ray diffraction studies

Single crystals of **5**, **6** (ESI†), **8**, and **9** 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 structure was solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package.[19] All non-hydrogen were refined anisotropically, except C(5) and C(6) in compound **5**, that were refined isotropically. These two atoms are probably disordered and cause several problems in the refinement, like the fact that the distances around them, C(5)-C(6) and C(6)-C(15) are shorter than expected. Hydrogen atoms were assigned to ideal positions and refined using a riding model. The diffraction frames were integrated using the SAINT package.[20] Crystals from compound **9** diffracted very poorly. During the integration process, reflections showing negative intensities were omitted. Because of this, some reflections were missed and the completeness was lower than usual.

Synthesis of Cp*-CH_2-CH_2-NHC^{Me}I, 1

An aqueous solution of formaldehyde (190 μL of 33% wt in water, 2.53 mmol) was added dropwise to neat 2-(2,3,4,5-tetramethylcyclopentadienyl)ethylamine (418 mg, 2.53 mmol) at 0 °C. The mixture was stirred until completely formation of a white solid (10–15 min.). Then, ammonium carbonate (121.6 mg, 1.27 mmol), an aqueous solution of glyoxal (290 μL of 40 % wt in water, 2.53 mmol) and 5–10 mL of methanol were subsequently added and the mixture stirred at room temperature overnight. Then, the reaction mixture was treated with brine and extracted with hexane. The organic layer was dried over sodium sulfate anhydrous and evaporated to dryness. The remaining crude brown oil was redissolved in acetone, and iodomethane (720 μL, 11.6 mmol) was added. Stirring was continued for 24 h at room temperature. The solvent was removed under vacuum to yield **1** (600 mg, 66%) as a yellow solid. The product was washed several times with diethyl ether and dried under vacuum. δ_H (400 MHz, $CDCl_3$) 9.87 (1H, br s, CH_{imid}), 7.47 (1 H, br s, CH_{imid}), 7.28 (1 H, br s, CH_{imid}), 5.18 (1 H, t, $^3J_{H\text{-}H} = 7.7$ Hz, CH_{linker}), 4.97 (2 H, d, $^3J_{H\text{-}H} = 7.7$ Hz, $CH_{2\,linker}$), 4.10 (3H, s, N-CH_3), 2.45 (1H, q, $^3J_{H\text{-}H} = 7.2$ Hz, CH_{Cp^*}), 2.10 (1 H, q, $^3J_{H\text{-}H} = 7.0$ Hz, CH_{Cp^*}), 1.73 (3 H, s, $CH_{3\,Cp^*}$), 1.63 (3 H, s, $CH_{3\,Cp^*}$), 1.04 (3 H, d, $^3J_{H\text{-}H} = 7.2$ Hz, $CH_{3\,Cp^*}$), 0.99 (3H, d, $^3J_{H\text{-}H} = 7.0$ Hz, $CH_{3\,Cp^*}$); δ_C (100 MHz, $CDCl_3$) 161.7 (C_{Cp^*}), 150.3 (C_{Cp^*}), 136.6 (CH_{Imid}), 130.1 (C_{Cp^*}), 123.6 (CH_{Imid}), 121.3(CH_{Imid}), 104.7 (CH_{linker}), 51.5 (CH_{Cp^*}), 49.0 ($CH_{2\,linker}$), 42.41 (CH_{Cp^*}), 37.38 (N-CH_3), 22.2 ($CH_{3\,Cp^*}$), 19.33 ($CH_{3\,Cp^*}$), 13.40 ($CH_{3\,Cp^*}$), 10.33 ($CH_{3\,Cp^*}$); *m/z* (Electrospray) 231.1 $[M - I]^+$.

Synthesis of Cp*-CH_2-CPhMe-NHC, 2

An hexane solution of *n*-BuLi (4 mL of 1.6 M in hexane, 6.4 mmol) was added dropwise to a solution of *S*-1-(phenylethyl)imidazole (990 mg, 5.75 mmol) in dried THF (25 mL) at –90 °C. After stirring for 30 minutes, tetramethylfulvene was added, and the reaction mixture was allowed to reach room temperature and stirred for one hour. Methanol was then added and the volatiles were removed under vacuum. The crude oil was purified by flash chromatography (hexane/ethyl acetate, 1:4) affording compound **2** (750 mg, 43%) as a yellow oil. δ_H (400 MHz, $CDCl_3$): 7.45 (1 H, br s, CH_{imid}), 7.28–7.08 (5 H, m, CH_{Ph}), 7.00 (1 H, br s, CH_{imid}), 6.78 (1 H, br s, CH_{imid}), 3.30 (1 H, d, $^2J_{H\text{-}H} = 14.0$ Hz, $CH_{2\,linker}$), 2.93 (1 H, d, $^2J_{H\text{-}H} = 14.0$ Hz, $CH_{2\,linker}$), 1.71-16.4 (15 H, m, $CH_{3\,linker}$ + $CH_{3\,Cp^*}$),

0.70 (3 H, d, $^3J_{H\text{-}H}$ = 7.6 Hz, $CH_{3\,Cp^*}$); δ_H (100 MHz, $CDCl_3$) 146.8 (C_{Phenyl}), 141.6 (C_{Cp^*}), 140.3 (C_{Cp^*}), 136.3 (C_{imid}-H), 136.0 (C_{Cp^*}), 133.3 (C_{Cp^*}), 129.0 (C_{imid}-H), 128.7 (C_{Phenyl}-H), 127.6 (C_{Phenyl}-H), 125.5 (C_{Phenyl}-H), 118.6 (C_{imid}-H), 64.1 (C_{linker}), 49.7 (C_{Cp^*}-H), 37.1 (C_{linker}-H_2), 28.4 (C_{linker}-CH_3), 15.4 (C_{Cp^*}-CH_3), 12.3 (C_{Cp^*}-CH_3), 11.4 (C_{Cp^*}-CH_3), 11.2 (C_{Cp^*}-CH_3).

Synthesis of Cp*-CH_2-CPhMe-NHC^{Me}I, 3

Iodomethane (780 μL, 12.5 mmol) was added to a solution of **2** (750 mg, 2.5 mmol) in methanol (5 mL). The reaction was stirred at room temperature for 12 hours and all the volatiles were evaporated affording a yellow solid, which was washed several times with dried diethyl ether to yield compound **3** in quantitative yield. (Found: C, 58.46; H, 6.69; N, 6.29. Calc for $C_{22}H_{29}IN_2$: C, 58.93; H, 6.25; N 6.52%); δ_H(400 MHz, $CDCl_3$) 9.96 (1 H, br s, CH_{imid}), 7.53 (1 H, br s, CH_{imid}), 7.39–7.22 (5 H, m, CH_{Ph}), 6.89 (1 H, br s, CH_{imid}), 4.19 (3 H, s, N-CH_3), 3.35 (1 H, d, $^2J_{H\text{-}H}$ = 14.2 Hz, $CH_{2\,linker}$), 3.13 (1 H, d, $^2J_{H\text{-}H}$ = 14.2 Hz, $CH_{2\,linker}$), 1.70 (3 H, s, $CH_{3\,Cp^*}$), 1.68 (3 H, s, $CH_{3\,Cp^*}$), 1.52 (3 H, s, $CH_{3\,Cp^*}$), 1.19 (3H, s, $CH_{3\,linker}$), 0.84 (3 H, d, $^3J_{H\text{-}H}$ = 7.4 Hz, $CH_{3\,Cp^*}$); δ_C (100 MHz, $CDCl_3$) 142.7 (C_{Cp^*}), 142.0 (C_{Cp^*}), 141.4 (C_{Phenyl}), 136.8 (C_{imid}-H), 134.1 (C_{Cp^*}), 132.9 (C_{Cp^*}), 129.2 (C_{Phenyl}-H), 128.8 (C_{Phenyl}-H), 125.8 (C_{Phenyl}-H), 123.7 (C_{imid}-H), 120.9 (C_{imid}-H), 69.1 (C_{linker}), 50.0(C_{Cp^*}-H), 37.6 (N-CH_3), 36.8 (C_{linker}-H_2), 28.4 (C_{linker}-CH_3), 15.3 (C_{Cp^*}-CH_3), 12.0 (C_{Cp^*}-CH_3), 11.8 (C_{Cp^*}-CH_3), 11.0 (C_{Cp^*}-CH_3).

Synthesis of [Cp*-CH_2-CH_2-NHC^{Me}]RhCl(cod), 4

To a solution of **1** (100 mg, 0.28 mmol) in 1,2-dichloroethane (10 mL), Ag_2O (180 mg, 0.78 mmol) was added at room temperature. After refluxing for 1 h, [Rh(μ-Cl)(cod)]$_2$ (70 mg, 0.14 mmol) was added. The reaction mixture was refluxed for half an hour, then filtered over Celite and evaporated to dryness. The remaining solid was washed with ether yielding **4** (55 mg, 41%) as a yellow solid. δ_H (400 MHz, $CDCl_3$) 6.84–6.78 (2 H, m, CH_{imid}), 5.41 (1 H, m, $CH_{2\,linker}$), 5.2 (1 H, m, CH $_{linker}$), 5.14 (m, 1H, $CH_{2\,linker}$), 5.01 (2 H, br s, CH_{cod}), 4.07 (3 H, s, N-CH_3), 3.32 (2 H, m, CH_{cod}), 2.55 (1 H, m, CH_{Cp^*}), 2.37 (4H, m, $CH_{2\,cod}$), 2.14 (1 H, q, $^3J_{H\text{-}H}$ = 7.0 Hz, CH_{Cp^*}), 2.14 (4 H, m, $CH_{2\,cod}$), 1.76 (3 H, s, $CH_{3\,Cp^*}$), 1.63 (3 H, s, $CH_{3\,Cp^*}$), 1.15 (3 H, two d, $^3J_{H\text{-}H}$ = 7 Hz, $CH_{3\,Cp^*}$), 1.04 (3 H, d, $^3J_{H\text{-}H}$ = 7.0 Hz, $CH_{3\,Cp^*}$). δ_C(100 MHz, $CDCl_3$,) 181.7 (two d, $C_{carbene}$-Rh, $^1J_{C\text{-}Rh}$ = 51 Hz), 157.5 + 157.0 (C_{Cp^*}), 147.1 + 147 (C_{Cp^*}), 130.53 + 130.46 (C_{Cp^*}), 122.0 (CH_{Imid}), 120.1 (CH_{Imid}), 110.3 + 110.2 (CH_{linker}), 98.6 (d, CH_{cod}, $^1J_{C\text{-}Rh}$ = 7.0 Hz), 68.7-67.9 (m, CH_{cod}), 51.6 (CH_{Cp^*}), 49.6 + 49.4 ($CH_{2\,linker}$), 42.4 + 42.3 (CH_{Cp^*}), 37.9 (NCH_3), 33.4-32.9 + 29.2-28.9 ($CH_{2\,cod}$), 22.1 + 21.9 ($CH_{3\,Cp^*}$), 19.5 + 19.4 ($CH_{3\,Cp^*}$), 13.4 ($CH_{3\,Cp^*}$), 10.4 ($CH_{3\,Cp^*}$). *m*/*z* (Electrospray) 441.2 [M – Cl]$^+$.

Synthesis of [Cp*-CH_2-CH_2-NHC^{Me}]$IrCl_2$, 5

To a solution of **1** (212 mg, 0.592 mmol) in 1,2-dichloroethane (10 mL), Ag_2O (163 mg, 0.70 mmol) was added at room temperature. After refluxing for 1 h, [Ir(μ-Cl)(cod)]$_2$ (200 mg, 0.298 mmol) was added. The reaction mixture was refluxed for half an hour and glacial acetic acid (2 mL) was added. Stirring was continued for 16 h. The volatiles components were removed under vacuum and the remaining solid was purified by flash chromatography (CH_2Cl_2/acetone) yielding **5** (70 mg, 24%) as an orange solid. δ_H (500 MHz, $CDCl_3$) 6.91 (1 H, br s, CH_{Imid}), 6.77 (1 H, br s, CH_{Imid}), 4.13 (2 H, m, $CH_{2\,linker}$), 4.08 (3 H, s, NCH_3), 2.51 (2 H, m, $CH_{2\,linker}$), 1.7 (6H, br s, $CH_{3\,Cp^*}$), 1.6 (6 H, br s, $CH_{3\,Cp^*}$). δ_C (125 MHz, $CDCl_3$) 150.3 ($C_{carbene}$-Ir), 124.1 (CH_{Imid}), 121.3 (CH_{Imid}), 105.1 (C_{Cp^*}), 83.8 (C_{Cp^*}), 77.5 (C_{Cp^*}), 77.2 (C_{Cp^*}), 50.6 ($CH_{2\,linker}$), 39.8 (NCH_3), 29.9 ($CH_{2\,linker}$), 21.2 ($CH_{3\,Cp^*}$), 9.88 ($CH_{3\,Cp^*}$), 8.7 ($CH_{3\,Cp^*}$); *m*/*z* (Electrospray): 457.2 [M – Cl]$^+$.

X-Ray crystal structure data. $C_{15}H_{21}Cl_2IrN_2$, M = 492.44 monoclinic, space group *Pn*, a = 7.9908(5), b = 13.1311(9), c = 8.6289(6) Å, β = 116.0640(10)°, V = 813.34(9) Å^3, Z = 2, crystal dimensions: 0.06 × 0.14 × 0.531 mm^3, Mo Kα radiation, 298(2) K, 4917 reflections, 2241 independent, (μ = 8.528 mm^{-1}), R_{int} = 0.0334, refinement (on F^2) with SHELXTL (version 6.1), 176 parameters, 3 restraints, R_1= 0.0308 ($I > 2\sigma(I)$) and wR_2 (all data) = 0.0790, GOF = 1.248, max/min residual electron density: 2.107/−1.129 e Å^{-3}. CCDC 717567.

Synthesis of [Cp*-CH_2-CH_2-NHC^{Me}]$RhCl_2$, 6

To a solution of **1** (171 mg, 0.48 mmol) in 1,2-dichloroethane (10 mL), Ag_2O (132 mg, 0.57 mmol) was added at room temperature. After refluxing for 1 h, [Rh(μ-Cl)(cod)]$_2$ (100 mg, 0.2 mmol) was added. The reaction mixture was refluxed for half an hour and glacial acetic acid (2 mL) was added. Stirring was continued for 16 h. The volatiles components were removed under vacuum and the remaining solid was purified by flash chromatography (CH_2Cl_2/acetone) yielding **6** (30 mg, 37%) as an orange solid. δ_H (500 MHz, $CDCl_3$) 7.00 (1 H, d, $^3J_{H\text{-}H}$ = 2 Hz, CH_{Imid}), 6.85 (1 H, d, $^3J_{H\text{-}H}$ = 2 Hz, CH_{Imid}), 4.30 (2 H, m, $CH_{2\,linker}$), 4.00 (3 H, s, NCH_3), 2.55 (2 H, m, $CH_{2\,linker}$), 1.77 (6 H, br s, $CH_{3\,Cp^*}$), 1.48 (6 H, br s, $CH_{3\,Cp^*}$). δ_C(100 MHz, $CDCl_3$) 166.2 (d, $C_{carbene}$-Rh, $^1J_{C\text{-}Rh}$ = 55.7 Hz), 124.7 (CH_{Imid}), 121.6 (CH_{Imid}), 110.0 (d, C_{Cp^*}, $^1J_{C\text{-}Rh}$ = 4.0 Hz), 91.0 (d, C_{Cp^*}, $^1J_{C\text{-}Rh}$ = 8.0 Hz), 86.7 (d, C_{Cp^*}, $^1J_{C\text{-}Rh}$ = 9.6 Hz), 50.6 ($CH_{2\,linker}$), 40.4 (N-CH_3), 29.9 ($CH_{2\,linker}$), 21.4 ($CH_{3\,Cp^*}$), 9.8 ($CH_{3\,Cp^*}$), 9.4 ($CH_{3\,Cp^*}$); *m*/*z* (Electrospray): 366.8 [M – Cl]$^+$.

X-Ray crystal structure data. $C_{15}H_{21}Cl_2RhN_2{\cdot}2H_2O$, M = 439.15, orthorombic, space group $P2_12_12_1$, a = 9.1280(10), b = 10.8995(12), c = 18.2374(19) Å, V = 1814.5(3) Å^3, Z = 4, crystal dimensions: 0.20 × 0.23 × 0.25 mm^3, Mo Kα radiation, 273 (8)K, 9499 reflections, 3706 independent, (μ = 1.242 mm^{-1}), R_{int} = 0.0573, refinement (on *F2*) with SHELXTL (version 6.1), 204 parameters, 0 restraints, R_1= 0.0377 (I>2$\sigma(I)$) and wR_2 (all data) = 0.0859, GOF = 1.018, max/min residual electron density: 0.414/−0.513 e Å^{-3}. CCDC 717568.

The hydrogen atoms of the water molecules could not be located in the Fourier difference map.

Synthesis of [Cp*-CH_2-CPhMe-NHC^{Me}]IrI_2, 7

A mixture of Ag_2O (124 mg, 0.54 mmol) and **3** (200 mg, 0.45 mmol) was refluxed in 1,2-dichloroethane (15 mL) for 1 h. Then, [Ir(μ-Cl)(cod)]$_2$ (150 mg, 0.22 mmol) was added and the mixture was refluxed for 30 min, followed by addition of glacial acetic acid (1 mL). To complete the reaction, the mixture was refluxed overnight. The suspension was filtered through Celite, the filtrate was evaporated to dryness and KI (365 mg, 2.2 mmol) and methanol (10 mL) were added to the remaining residue. The

mixture was then refluxed for a further 16 h. After cooling, the solvent was removed in vacuum and the crude solid was purified by flash chromatography (CH_2Cl_2/acetone) yielding complex **7** (60 mg, 24%) as an orange solid. δ_H (400 MHz, $CDCl_3$) 7.27–7.20 (5 H, m, CH_{Ph}), 6.89 (1 H, d, $^3J_{H\text{-}H} = 2.16$ Hz, CH_{imid}), 6.84 (1 H, d, $^3J_{H\text{-}H} = 2.16$ Hz, CH_{imid}), 4.13 (3 H, s, N-CH_3), 2.98 (1 H, d, $^2J_{H\text{-}H} = 15.3$ Hz, $CH_{2\,linker}$), 2.66 (1 H, d, $^2J_{H\text{-}H} = 15.3$ Hz, $CH_{2\,linker}$), 2.02 (3 H, s, $CH_{3\,linker}$), 1.96 (3H, s, $CH_{3\,Cp^*}$), 1.92 (3 H, s, $CH_{3\,Cp^*}$), 1.73 (3 H, s, $CH_{3\,Cp^*}$), 0.82 (3 H, s, $CH_{3\,Cp^*}$). δ_C (100 MHz, $CDCl_3$) 148.3 ($C_{carbene}$–Ir), 145.4 (C_{Phenyl}), 129.2 (CH_{Phenyl}), 128.1 (CH_{Phenyl}), 126.3 (CH_{Phenyl}), 124.1 (CH_{imid}), 119.9 (CH_{imid}), 105.3 (C_{Cp^*}), 104.9 (C_{Cp^*}), 81,9 (C_{Cp^*}), 81.5 (C_{Cp^*}), 69.3 (C_{linker}), 47.1 (N–CH_3), 34.3 ($CH_{2\,linker}$), 33.8 ($CH_{3\,linker}$), 11.9 ($CH_{3\,Cp^*}$), 11.6 ($CH_{3\,Cp^*}$), 10.5 ($CH_{3\,Cp^*}$), 9.0 ($CH_{3\,Cp^*}$); *m/z* (Electrospray) 639.3 $[M - I]^+$.

Synthesis of [Cp*-CH_2-CPhMe-NHC^{Me}]RhI_2, 8

A mixture of Ag_2O (120 mg, 0.52 mmol) and **3** (200 mg, 0.45 mmol) was refluxed in 1,2-dichloroethane (15 mL) for 1 h. Then, $[Rh(\mu\text{-}Cl)(cod)]_2$ (116 mg, 0.235 mmol) was added and the mixture was refluxed for 30 min, followed by addition of glacial acetic acid (1 mL). The mixture was refluxed overnight and filtered through Celite, the filtrate was evaporated to dryness and KI (390 mg, 2.35 mmol) and methanol (10 mL) were added to the remaining residue.

The mixture was then refluxed overnight. After cooling, the solvent was removed in vacuum and the crude solid was purified by flash chromatography (CH_2Cl_2/acetone) yielding complex **8** (110 mg, 51%) as an orange solid. (Found: C, 39.44; H, 4.45; N, 4.05. Calc for $C_{22}H_{27}I_2N_2Rh$: C, 39.08; H, 4.14; N 4.02%); δ_H (400 MHz, $CDCl_3$) 7.35-7.22 (5 H, m, CH_{Ph}), 7.01 (1 H, d, $^3J_{H\text{-}H} = 2.0$ Hz, CH_{Imid}), 6.95 (1 H, d, $^3J_{H\text{-}H} = 2.0$ Hz, CH_{Imid}), 4.14 (3 H, s, N-CH_3), 3.05 (1 H, d, $^2J_{H\text{-}H} = 15.3$ Hz, $CH_{2\,linker}$), 2.77 (1 H, d, $^2J_{H\text{-}H} = 15.3$ Hz, $CH_{2\,linker}$), 2.09 (3 H, s, $CH_{3\,linker}$), 1.71 (3 H, s, $CH_{3\,Cp^*}$), 1.63 (3 H, s, $CH_{3\,Cp^*}$), 1.42 (3 H, s, $CH_{3\,Cp^*}$), 0.51 (3 H, s, $CH_{3\,Cp^*}$). δ_C (100 MHz, $CDCl_3$) 166.8 (d, $C_{carbene}$–Rh, $^1J_{C-Rh-} = -59.0$ Hz), 145.6 (C_{Phenyl}), 129.4 (CH_{Phenyl}), 128.3 (CH_{Phenyl}), 126.4 (CH_{Phenyl}), 124.9 (CH_{imid}), 121.5 (CH_{imid}), 109.6 (m, C_{Cp^*}), 90.9 (m, C_{Cp^*}), 87.4 (d, $^1J_{C-Rh} = 8$ Hz, C_{Cp^*}),70.4 (C_{linker}), 48.1 (N–CH_3), 35.1 ($CH_{2\,linker}$), 33.9 ($CH_{3\,linker}$), 12.7 ($CH_{3\,Cp^*}$), 12.4 ($CH_{3\,Cp^*}$), 11.4 ($CH_{3\,Cp^*}$), 9.9 ($CH_{3\,Cp^*}$). *m/z* (Electrospray) 549.1 $[M - I]^+$.

X-ray crystal structure data. $C_{22}H_{27}I_2RhN_2{\cdot}CH_2Cl_2$, $M = 761.09$, triclinic, space group $P\text{-}1$, $a = 9.702(10)$, $b = 12.165(12)$, $c = 12.351(12)$ Å, $\alpha = 71.958(19)$, $\beta = 67.00(2)$, $\gamma = 73.90(2)°$, $V = 1255(2)$ Å^3, $Z = 2$, crystal dimensions: $0.20 \times 0.23 \times 0.27$ mm^3, Mo Kα radiation, 293(2) K, 8108 reflections, 5801 independent, ($\mu = 3.366$ mm^{-1}), $R_{int} = 0.0245$, refinement (on F^2) with SHELXTL (version 6.1), 277 parameters, 0 restraints, $R_1 = 0.0449$ ($I > 2\sigma(I)$) and wR_2 (all data) = 0.1841, GOF = 1.097, max/min residual electron density: 1.563/–2.389 e Å^{-3}. CCDC 717569.

Synthesis of [Cp*-CH_2-CPhMe-NHC^{Me}]IrI, 9

In a J. Young NMR tube equipped with a Teflon screw cap, a solution of **7** (20 mg, 0.026 mmol) in deuterated methanol (0.5 mL) was treated with lithium acetate (20 mg, 0.3 mmol) and heated at 60 °C for 16 h. Compound **9** was obtained as an orange solid in quantitative yield. δ_H (400 MHz, $CDCl_3$) 7.85 (1 H, dd, $^3J_{H\text{-}H} = 7.5$ Hz, $^4J_{H\text{-}H} = 1.3$ Hz, CH_{Ph}), 7.11 (1H, m, CH_{Ph}), 7.10 (1 H, d, $^3J_{H\text{-}H} = 2.2$ Hz, CH_{Imid}), 7.03 (1 H, t, $^3J_{H\text{-}H} = 7.5$ Hz, CH_{Ph}), 6.86 (1 H, m, CH_{Ph}), 6.84 (1 H, d, $^3J_{H\text{-}H} = 2.$ Hz, CH_{Imid}), 3.97 (3 H, s, NCH_3), 2.18 (3 H, s, $CH_{3\,linker}$), 2.18 (3 H, s, $CH_{3\,Cp^*}$), 2.12 (3 H, s, $CH_{3\,Cp^*}$), 1.92 (1 H, d, $^2J_{H\text{-}H} = 14.9$ Hz, $CH_{2\,linker}$), 1.18 (3 H, s, $CH_{3\,Cp^*}$), 0.88 (3 H, s, $CH_{3\,Cp^*}$). δ_C (100 MHz, $CDCl_3$) 159.1 (C_{Phenyl}–Ir), 147.2 ($C_{carbene}$–Ir), 144.7 (C_{Phenyl}), 137.9 (CH_{Phenyl}), 128.1 (CH_{Phenyl}), 121.9 (CH_{Phenyl}), 121.8 (CH_{imid}), 120.7 (CH_{Phenyl}), 117.0 (CH_{imid}), 106.6 (C_{Cp^*}), 103.3 (C_{Cp^*}), 96.9 (C_{Cp^*}), 94.2 (C_{Cp^*}), 75.4 (C_{linker}), 59.4 (C_{Cp^*}), 36.6 (NCH_3), 34.5 ($CH_{2\,linker}$), 24.1 ($CCH_{3\,linker}$), 9.2 (C_{Cp^*}–CH_3), 9.1 (C_{Cp^*}–CH_3), 8.6 (C_{Cp^*}–CH_3), 8.4 (C_{Cp^*}–CH_3).

X-ray crystal structure data. $C_{22}H_{26}IIrN_2$, $M = 637.55$, monoclinic, space group $P2_1n$, $a = 15.0849(16)$, $b = 8.8037(10)$, $c = 16.2181(17)$ Å, $\beta = 98.598(2)°$, $V = 2129.6(4)$ Å^3, $Z = 4$, crystal dimensions: $0.05 \times 0.06 \times 0.13$ mm^3, Mo Kα radiation, 278(2) K, 9969 reflections, 3263 independent, ($\mu = 7.727$ mm^{-1}), $R_{int} = 0.1059$, refinement (on F^2) with SHELXTL (version 6.1), 241 parameters, 167 restraints, $R_1 = 0.0733$ ($I > 2\sigma(I)$) and wR_2 (all data) = 0.1916, GOF = 0.971, max/min residual electron density: 2.914/–1.414 e Å^{-3}. CCDC 717566.

β-Alkylation of 1-phenylethanol with benzylic alcohol

A mixture of 1-phenylethanol and benzylic alcohol (1:1), KOH (1 eq) and **5** (1% mol) in toluene (0.3 mL) was heated to 110° C in a sealed tube. The reaction was monitored by ^{1}H NMR using ferrocene as internal standard.

Alkylation of aniline with benzylic acid

A mixture of aniline and benzylic alcohol (1:1), *t*BuOK (1 eq) and **5** (0.7% mol) in toluene (0.3 mL) was heated to 110° C in a sealed tube. The reaction was monitored by ^{1}H NMR using ferrocene as internal standard.

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