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Enantiomerically Pure Cyclopentadienyl- and Indenyl-Functionalized N-Heterocyclic Carbene Complexes of Iridium and Rhodium

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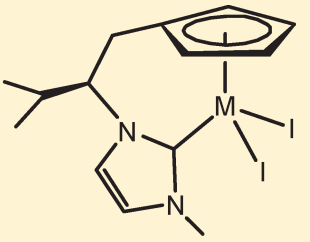
Supporting Information

ABSTRACT: Novel enantiomerically pure cyclopentadienyl- and indenyl-functionalized N-heterocyclic carbene ligands have been prepared by reaction of a chiral imidazole tosylate derivative with the corresponding cyclopentadienyl and indenyl lithium salts. Coordination of the Cp-functionalized NHC ligand to iridium and rhodium allowed the preparation of enantiomerically pure chelating cyclopentadienyl-functionalized Ir(III) and Rh(III) metal complexes. In contrast, the indenyl-functionalized NHC coordinates to iridium in a monodentate fashion, giving an Ir(I)-NHC complex containing a dangling indene group.

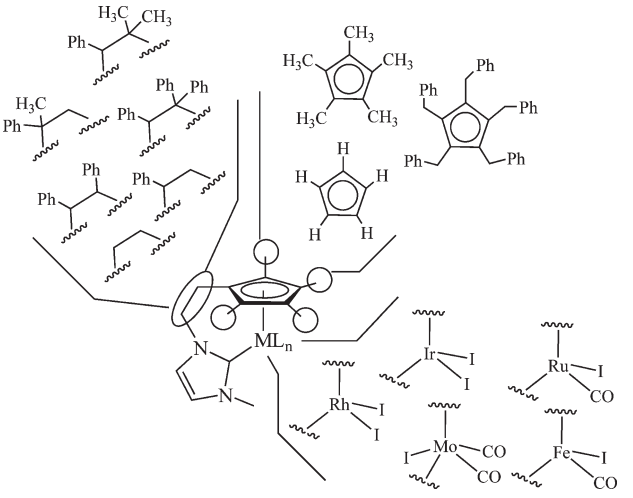


INTRODUCTION

Due to their special chemical properties and their ubiquitous implications in homogeneous catalysis, half-sandwich transition metal complexes have attracted the attention of the organometallic chemistry community for a very long time.[1−3] Chiral half-sandwich complexes were first studied in the late 1960s, and a renewed interest is evident from the most recent literature.[2] Among half-sandwich complexes, those containing d^6 transition metals have been extensively studied due to their applications in a wide variety of organic transformations. However, compared with the high number of ruthenium and rhodium chiral half-sandwich scaffolds, the iridium analogues have been investigated to a much lesser extent.[3] On the other hand, "Cp*Ir(III)" complexes have delivered a great performance in a large number of transformations, implying C*z*−H bond activations and all sorts of borrowing hydrogen processes.[3] In the same context, during the past few years, the introduction of N-heterocyclic carbenes (NHCs) has undoubtedly boosted the use of "Cp*Ir(NHC)" complexes due to their improved catalytic applications, although the preparation of such chiral and enantiopure complexes is limited to only a few examples.

We now have access to a very large variety of procedures for the preparation of new NHC ligands with different topologies,[4] and the incorporation of ancillary donor functionalities widens the scope for the preparation of new hemilabile chelating ligands.[5] We recently reported a series of synthetic pathways for the preparation of cyclopentadienyl-functionalized NHC ligands that we coordinated to a variety of metal centers, such as Ir,[6] Rh,[7] Ru,[8] Fe,[9] and Mo[10] (Scheme 1). The new complexes showed interesting catalytic properties, in reactions such as transfer hydrogenation,[6,9] amination of alcohols with primary amines,[6,7] *β*-alkylation of secondary alcohols,[6,7] epoxidation of olefins,[10] isomerization of allylic alcohols,[8] and hydrosilylation of carbonyl groups.[9] Most of these reactions are known to have their asymmetric version, for which the design of suitable chiral catalysts is a straightforward target. In the case of our mentioned Cp-NHC ligands, it may seem obvious that the introduction of a chiral center in the Cp-NHC tether should provide an easy access to chiral metal complexes, but all our efforts in this sense remained unsuccessful. However, we recently reported an example in which we were able to resolve enantiomerically pure chiral Cp-NHC-Ru complexes by separating the diastereomeric species resulting from the introduction of an auxiliary chiral amine. Although this protocol opened an access to chiral Cp-NHC-metal species, it lacked the simplicity required to be applied at a

Scheme 1



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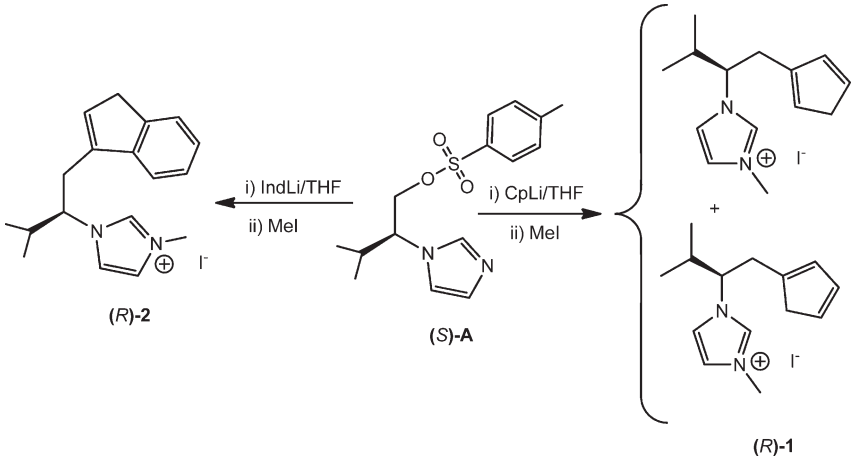
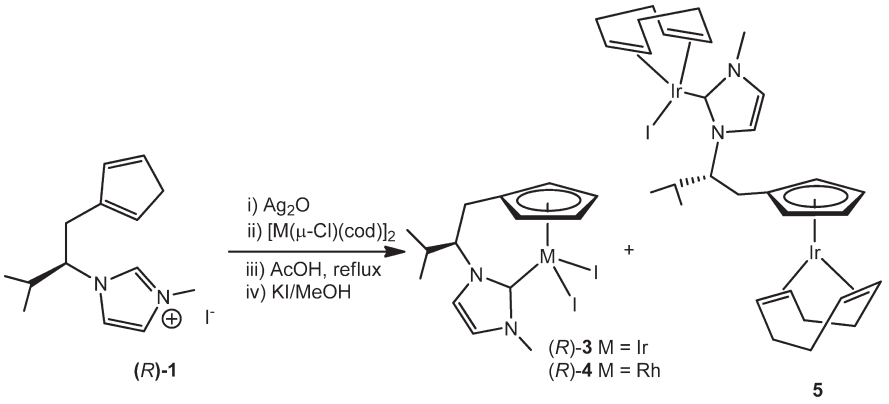
Scheme 2



Scheme 3



large scale and also provided very low yields.[8] The approach of controlling the metal configuration by using a chiral phosphine group tethered to a cyclopentadienyl ligand has been investigated for ruthenium half-sandwich complexes, although such complexes containing enantiopure chiral centers are limited to a few examples.[11] The use of chiral tethered Cp-NHC ligands could offer some advantages due to the robustness of the NHC−M bond. Because we believe that there is an interest in the design of feasible methods for the preparation of this type of ligands, we now disclose a new synthetic pathway for the synthesis of Cp-NHC synthons for the preparation of enantiomerically pure metal complexes. This method has been extended to the synthesis of pure chiral indenyl-functionalized ligands. NHCs bearing indenyl ligands were disclosed in a seminal work reported by Danopoulos in 2006,[12] and since then, its coordination chemistry has been explored for an array of transition metals, e.g., Ti, V, Cr, Rh, Ln, and Mo.[12−17] However, chiral Ind-NHC systems have not been reported yet.

RESULTS AND DISCUSSION

Starting from commercially available L-valinol, the imidazole tosylate (*S*)-**A** was synthesized following the procedure reported by Nagel and co-workers.[18] The reaction of (*S*)-**A** with CpLi (Cp = η^5-C_5H_5) followed by treatment with methyl iodide afforded the enantiomerically pure chiral cyclopentadienyl-functionalized imidazolium salt (*R*)-**1** (Scheme 2). A similar synthetic strategy can be used for the preparation of the corresponding chiral indenyl-functionalized imidazolium (*R*)-**2**. Both imidazolium salts have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy and by ESI-MS spectrometry ($[M - I]^+ = 217\ m/z$ for **1** and 267 for **2**). The ^{1}H and ^{13}C NMR spectra of (*R*)-**1** showed the presence of two isomers resulting from the different position of the double bond in the cyclopentadienyl ring.

The Cp-NHC ligand precursor (*R*)-**1** was coordinated to iridium and rhodium following the synthetic procedure depicted in Scheme 3. Treatment of (*R*)-**1** with silver(I) oxide generated the corresponding silver−NHC, which was subsequently transmetalated to $[M(\mu\text{-Cl})(cod)]_2$ (M = Ir, Rh). Further reflux in acetic acid was needed to promote C−H activation of the cyclopentadienyl ring, to afford the iridium(III) and rhodium(III) complexes (*R*)-**3** and (*R*)-**4**, respectively (Scheme 3). Further treatment with KI in methanol prevents the formation of mixtures of coordinate halides. Compounds (*R*)-**3** and (*R*)-**4** were purified by column chromatography, yielding crystalline red solids in moderate yields (35% for (*R*)-**3** and 30% for (*R*)-**4**). The relatively low yields obtained in these reactions are explained by the concomitant formation of bimetallic species, which in the case of iridium was isolated and characterized by ESI-MS spectrometry ($[M - I]^+ = 815\ m/z$) (complex **5**, Scheme 3). Crystals of

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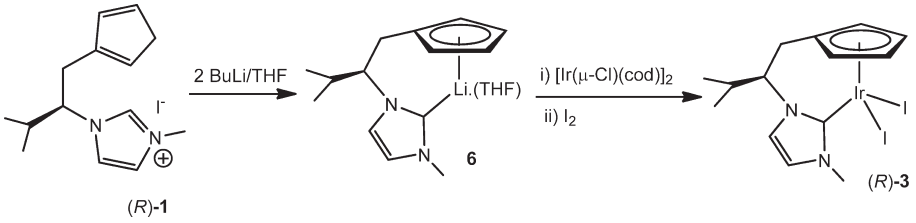
Scheme 4



5 were obtained from concentrated chloroform solutions. Although the X-ray resolution of the crystal structure of this complex was of not enough quality for the standards of publication, it allowed us to confirm the proposed structure. The crystallographic details can be found in the Supporting Information. The molecule contains two Ir(I) centers with different coordination spheres. One of the Ir atoms is coordinated to 1,5-cod, iodine, and an NHC, while the other Ir center is coordinated in a pentahapto fashion to the cyclopentadienyl ring, and one molecule of 1,5-cod completes its coordination sphere. A similar bimetallic rhodium species, in which two "Rh(cod)" fragments are linked through an indenyl-functionalized NHC ligand, was recently reported by Danopoulos, Cole-Hamilton, and co-workers.[16] The methodology described above was also successfully applied by us in the preparation of tetramethylcyclopentadienyl-functionalized NHC complexes of iridium(III) and rhodium(III), to afford the corresponding chelating complexes as the only products, (Cp*-NHC)MI_2 (Cp* = η^5-C_5Me_4, M = Rh, Ir), in good yields.[6,7] These results reveal that smooth changes in the electronic properties of the Cp^x-NHC ligands (Cp^x = Cp*, Cp) have important consequences in the accessibility of their metal complexes.

We also investigated an alternative synthetic pathway for the synthesis of (*R*)-**3**. The reaction of the lithium salt **6** with [Ir(μ-Cl)(cod)]$_2$ in THF, followed by oxidation with iodine, afforded (*R*)-**3** as the sole compound in good yield (48%) (Scheme 4).

The ^{1}H NMR spectrum of (*R*)-**3** shows the characteristic signals due to the protons of the imidazole ring at 6.87 and 6.79 ppm. The resonances assigned to the protons at the cyclopentadienyl ring appear at 5.65, 5.37, and 5.27 ppm and confirm the asymmetry of the molecule. The methylene protons of the linker are diastereotopic, exhibiting two double doublets at 2.70 and 2.47 ppm. The ^{13}C NMR spectrum of (*R*)-**3** confirms the coordination of both the Cp and the NHC fragments of the ligand, with a signal at 137.9 ppm attributed to the Ir−$C_{carbene}$ and five distinctive signals due to the Cp ring. The most significant signal in the ^{13}C NMR spectrum of complex (*R*)-**4** is the doublet at 156.1 ppm, assigned to the Rh−$C_{carbene}$. The ESI-MS spectra of **3** and **4** gave the peaks corresponding to [M − I]$^+$ at m/z = 535 and 445, respectively.

The crystal structure of (*R*)-**3** was determined by single-crystal X-ray diffraction analysis. Good-quality crystals were obtained by slow diffusion of Et_2O in a THF solution of (*R*)-**3**. The molecular structure and selected bond lengths and angles are depicted in Figure 1. The structure confirms that the complex exists as a pure enantiomer. The molecule can be described as a distorted three-legged piano stool with the cyclopentadienyl-NHC ligand chelating the iridium center. Two iodide ligands complete the coordination sphere about the metal. The distance between the iridium center and the centroid of the Cp ligand is 1.839 Å. The

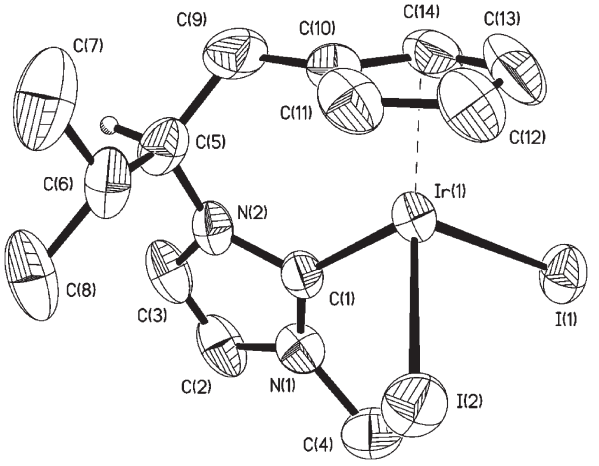


Figure 1. ORTEP of the iridium(III) complex (*R*)-**3**. Ellipsoids are at 50% probability level. Hydrogen atoms have been omitted for clarity except H(5). Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.041(7), Ir(1)−I(1) 2.7402(6), Ir(1)−I(2) 2.7050(7), Ir-(1)−$Cp_{centroid}$ 1.839, C(1)−Ir(1)−I(1) 95.8(2), C(1)−Ir−(1)−I(2) 90.6(2), I(1)−Ir(1)−I(2) 96.67(2).

Ir−$C_{carbene}$ bond distance is 2.041(7) Å, similar to the Ir−$C_{carbene}$ bond distances reported for related (Cp^x-NHC)IrI_2 complexes reported by us.[6]

The coordination of indenyl-functionalized N-heterocyclic carbenes to rhodium was recently reported by Danopoulos and co-workers.[16] They reported that reaction of the in situ generated Ag(Ind-NHC)Br with [Rh(μ-Cl)(cod)]$_2$ in THF afforded the Rh(I)-NHC complex with the monodentate Ind-NHC ligand containing a dangling indene group. In an effort to synthesize the corresponding chelate (Ind-NHC)IrI_2 complex, we attempted the synthetic pathways described above for the preparation of (Cp-NHC)IrI_2. Treatment of (*R*)-**2** with silver(I) oxide, subsequent addition of [Ir(μ-Cl)(cod)]$_2$, and further reflux in acetic acid afforded the Ir(I) complex **7** in high yield. Compound **7** is formed as a mixture of two diasterotopic rotamers (**7a** and **7b**, Scheme 5) in a 3:1 molar ratio, according to the integrals of the resonances due to the methyl groups in the ^{1}H NMR spectrum. These two rotamers arise from the restricted rotation of the N-heterocycle about the Ir−C(carbene) bond. Complexes **7a** and **7b** could not be separated by conventional chromatographic means, and variable-temperature NMR experiments revealed that they do not interconvert on the ^{1}HNMR time scale.

When the reaction is carried out between the imidazolium proligand (*R*)-**2**, previously treated with 2 equiv of *n*BuLi, and [Ir(μ-Cl)(cod)]$_2$, again, a mixture of **7a** and **7b** was obtained (Scheme 5). C−H activation of the indene group did not occur

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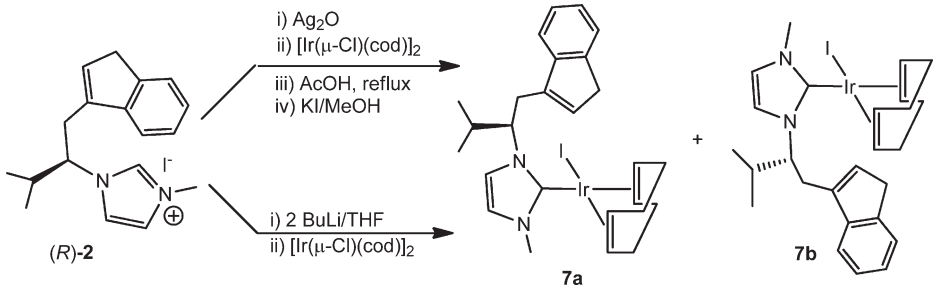
Scheme 5



under these conditions, in contrast to the results obtained for the cyclopentadienyl system (Scheme 4). Further addition of I_2 to **7** did not provide any transformation into any expected Ir(III) species. The ^{13}C NMR spectrum of **7** displays the characteristic Ir(I)-carbene signal at 178.4 ppm. Attempts to coordinate the dandling indene by refluxing complex **7** in different solvents such as toluene, methanol, or acetic acid/dichloromethane were unsuccessful.

In conclusion, we have presented here a new synthtetic pathway for the synthesis of enantiomerically pure cyclopentadienyl- and indenyl-functionalized ligands that have been coordinated to iridium and rhodium. We have demonstrated the preferred chelate coordination mode for cyclopentadienyl-NHC ligands compared to the indenyl systems. We are currently exploring the catalytic efficiency of our systems in enantioselective processes and investigating the coordination chemistry to other transition metal centers.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed using standard Schlenk techniques. The starting materials (*S*)-**A**,[18] $[Ir(\mu\text{-}Cl)(cod)]_2$,[19] and $[Rh(\mu\text{-}Cl)(cod)]_2$[20] were prepared following literature procedures. All other reagents were used as received from commercial suppliers and used without further purification. Elemental analyses were performed in our laboratories at ITQB.

^1H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 MHz. Infrared (IR) spectra were recorded on samples as KBr pellets using a Mattson 7000 FT-IR spectrometer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument, with nitrogen as drying and nebulizing gas.

Synthesis of Imidazolium Proligand Cp-NHC (*R*)-1. The imidazole tosylate (*S*)-**A** (560 mg, 1.8 mmol) was added to a solution of CpLi (0.626 mg, 8.7 mmol) in THF (10 mL) at −78 °C. The reaction mixture was stirred for 3 h, and the temperature was then warmed to −20 °C. After being stirred for 16 h, hexane (50 mL) was added, followed by addition of brine (100 mL). The reaction mixture was extracted several times with hexane (50 mL), and the organic phase was dried and evaporated to dryness. The remaining oil was dissolved in acetone, and iodomethane (0.5 mL, 9 mmol) was added at once. After being stirred overnight at room temperature, the reaction mixture was evaporated to dryness and the remaining solid/oil was washed several times with dry ether. The title compound **1** was isolated as a hygroscopic pale yellow solid (400 mg, 1.2 mmol, 64%). ^1H NMR (400 MHz, $CDCl_3$): δ 10.24 + 10.12 (2s, 1H, CH_{Imid}), 7.52 (m, 1H, CH_{Imid}), 7.39 + 7.27 (2 m, 1H, CH_{Imid}), 6.36−6.09 (4 m, 3H, CH_{Cp}), 4.63−4.65 (m, 1H, CH_{linker}), 4.08 + 4.06 (2s, 3H, NCH_3), 3.16−2.83 (2m, 4H, CH_{2Cp} + $CH_{2linker}$), 2.28−2.15 (m, 1H, CH_{iPr}), 1.11−1.08 (m, 3H, CH_{3iPr}), 0.90−0.89 (m, 3H, CH_{3iPr}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.97 (C_{Cp}), 140.6 (C_{Cp}), 136.7 (CH_{Imid}), 135.4 + 133.1 + 132.7 +132.1 + 130.6 + 130.5 (C*Cp*), 123.3 (CH_{Imid}), 121.2 (CH_{Imid}), 66.7 (CH_{linker}), 43.8 + 41.9 (CH_{2Cp}), 37.1 (NCH_3), 33.45 + 33.19 + 32.95 + 32.75 ($CH_{2linker}$) + CH_{iPr}), 19.7 + 19.14 + 18.9 (CH_{3iPr}). MS-ESI: *m*/*z* 217 $[M - I]^+$.

Synthesis of Imidazolium Proligand Ind-NHC (*R*)-2. The imidazole tosylate (*S*)-**A** (280 mg, 9.0 mmol) in THF (10 mL) was added to a solution of IndLi (550 mg, 45.0 mmol) in THF (20 mL) at −78 °C. The reaction mixture was stirred for 1 h at low temperature and then allowed to warm to 4 °C. After being stirred for 16 h the solution was evaporated to dryness and the product was extracted with diethyl ether, affording a yellow oil. This oil (140 mg, 5.4 mmol) was dissolved in 10 mL of acetone, and iodomethane (1.7 mL, 27.0 mmol) was added at once. After being stirred overnight at room temperature, the reaction mixture was evaporated to dryness and the remaining solid was washed several times with diethyl ether. Compound **2** was isolated as a hygroscopic light yellow solid (200 mg, 5.1 mmol, 57%). ^1H NMR (400 MHz, $CDCl_3$): δ 10.24 (s, 1H, CH_{Imid}), 7.42−7.20 (2m, 4H, CH_{Ind}), 7.05 (s, 1H, CH_{Imid}), 6.94 (s, 1H, CH_{Imid}), 6.34 (s, 1H, CH_{Ind}), 4.53−4.50 (m, 1H, CH_{linker}), 4.0 (1s, 3H, NCH_3), 3.40−3.25 (2m, 4H, CH_{2Ind} + $CH_{2linker}$), 2.34 (m, 1H, CH_{iPr}), 1.15 (d, 3H, CH_{3iPr}), 0.77 (d, 3H, CH_{3iPr}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.1 (C_{Ind}), 143.8 (C_{Ind}), 138.2 (C_{Ind}), 136.7 (CH_{Imid}), 132.2 (CH_{Ind}), 126.3 (CH_{Ind}), 125.2 (CH_{Ind}), 124.2 (CH_{Ind}), 123.0 (CH_{Ind}), 121.5 (CH_{Imid}), 118.4 (CH_{Imid}), 67.4 (CH_{linker}), 38.2 (CH_{2Ind}), 37.1 (NCH_3), 33.2 ($CH_{2linker}$), 30.8 (CH_{iPr}), 19.8 (CH_{3iPr}), 19.2 (CH_{3iPr}). MS-ESI: *m*/*z* 267 $[M - I]^+$.

Synthesis of (Cp-NHC)MI_2 (M = Ir, Rh) Complexes (*R*)-3 and (*R*)-4: General Procedure. The proligand (*R*)-**1** (1 equiv) was treated with Ag_2O (1.2 equiv), and the mixture was heated under reflux in 1,2-dichloroethane for 1 h. Then, $[M(\mu\text{-}Cl)(cod)]_2$ (0.5 equiv, M = Ir and Rh) was added, and the mixture was refluxed for 30 min, followed by addition of glacial acetic acid. After being refluxed overnight, the suspension was filtered through Celite, the filtrate was evaporated to dryness, and KI (5 equiv) and methanol were added to the remaining residue. The mixture was then refluxed for a further 1 h. After cooling, the solvent was removed in a vacuum and the crude solid was purified by flash chromatography with silica (CH_2Cl_2/acetone).

Compound (*R*)-3. Yield: 35%. Crystals of **3** suitable for X-ray crystallography were obtained by slow diffusion of Et_2O in a THF solution of **3**. ^1H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 1H, CH_{Imid}), 6.79 (s, 1H, CH_{Imid}), 5.65 + 5.37 + 5.27 (3s, 4H, CH_{Cp}), 4.05 (s, 3H, NCH_3), 3.80 (m, 1H, CH_{linker}), 2.70 (dd, 1H, J = 15.4 Hz, $^3J_{H-H}$ = 5.2 Hz, $CH_{2linker}$), 2.47 (dd, 1H, J = 15.4 Hz, $^3J_{H-H}$ = 3.3 Hz, $CH_{2linker}$), 2.20 (m, 1H, CH_{iPr}), 1.06 (d, 3H, J = 6.9 Hz, CH_{3iPr}), 0.82 (d, 3H, J = 6.6 Hz, CH_{3iPr}. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.9 (C_{NHC}), 121.5 (CH_{Imid}), 120.9 (CH_{Imid}), 92.2 (CH_{Cp}), 90.1 (CH_{Cp}), 87.5(C_{Cp}), 73.3 (CH_{Cp}), 72.8 (CH_{Cp}), 68.9 (CH_{linker}), 43.4 (NCH_3), 29.8 (CH_{iPr}) 23.2 ($CH_{2linker}$), 20.1 (CH_{3iPr}), 17.5 (CH_{3iPr}). Anal. Calcd for $C_{14}H_{19}I_2N_2Ir$: C, 25.42; H, 2.90; N, 4.24. Found: C, 25.30; H, 2.64; N, 4.46. MS-ESI: *m*/*z* 535 $[M - I]^+$.

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Compound (*R*)-4. Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (s, 1H, CH_{Imid}), 6.85 (s, 1H, CH_{Imid}), 5.82 + 5.74 + 5.3 + 5.21 (4s, 4H, CH_{Cp}), 3.99 (m, 4H, NCH_3 + CH_{linker}), 2.75 (dd, 1H, $^2J_{H-H}$ = 15.4 Hz, $^3J_{H-H}$ = 5.1 Hz, $CH_{2linker}$), 2.48 (dd, 1H, $^2J_{H-H}$ = 15.4 Hz, $^3J_{H-H}$ = 3.5 Hz, $CH_{2linker}$), 2.25 (m, 1H, CH_{iPr}), 1.07 (d, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_{3iPr}), 0.81 (d, 3H, $^3J_{H-H}$ = 6.0 Hz, CH_{3iPr}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.1 (d, $^1J_{Rh-C}$ = 54.1 Hz,C_{NHC}), 122.1 (CH_{Imid}), 121.8 (CH_{Imid}), 96.1 (CH_{Cp}), 95.6 (C_{Cp}), 94.0 (CH_{Cp}), 81.4 ($^1J_{Rh-C}$ = 6.6 Hz, CH_{Cp}), 80.8 ($^1J_{Rh-C}$ = 6.4 Hz, CH_{Cp}), 69.0 (CH_{linker}), 44.23 (NCH_3), 30.1 (CH_{iPr}), 23.8 ($CH_{2linker}$), 20.1 (CH_{3iPr}), 17.8 (CH_{3iPr}). Anal. Calcd for $C_{14}H_{19}I_2N_2Rh$: C, 29.39; H, 3.35; N, 4.90. Found: C, 29.42; H, 3.47; N, 4.68. MS-ESI: *m*/*z* 445 $[M - I]^+$.

Synthesis of (Cp-NHC)$^-$Li$^+$ (6). Two equivalents of BuLi (0.84 mL of 1.6 M solution in hexanes, 1.38 mmol) were dropwise added to a THF (10 mL) solution of (*R*)-**1** (0.24 mg, 0.66 mmol) at −30 °C. The mixture was then allowed to warm to room temperature and was stirred for 1 h. All volatiles were removed under vacuum, and the remaining white solid was washed several times with toluene. Compound **6** was isolated as a white powder in quantitative yield. ^{1}H NMR (400 MHz, THF-d_8): δ 6.77 (s, 1H, CH_{Imid}), 5.46, 5.21 (s, 4H, CH_{Cp}), 3.69 (m, 1H, CH_{linker}), 3.47 (m, 4H, OC_4H_8), 3.37 (s, 3H, NCH_3), 2.87, 2.34 (dd, $CH_{2linker}$), 2.34 (m, 1H, CH_{iPr}), 1.62 (m, 4H, OC_4H_8) 1.08 (d, 3H, $^3J_{H-H}$ = 6.9 Hz, CH_{3iPr}), 0.54 (d, 3H, $^3J_{H-H}$ = 6.6 Hz, CH_{3iPr}). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 198.9 ($LiC_{carbene}$), 120.4 (CH_{Imid}), 118.4 (CH_{Imid}), 112.3 (CH_{Cp}), 104.45 (CH_{Cp}), 101.85 (C_{Cp}), 70.19 (CH_{linker}), 67.25 (OC_4H_8), 36.36 (NCH_3), 33.74 ($CH_{2linker}$), 31.46 (CH_{iPr}), 25.39 (OC_4H_8) 20.19 (CH_{3iPr}), 19.35 (CH_{3iPr}).

Synthesis of (Ind-NHC)IrI(cod) (7). The proligand (*R*)-**2** (200 mg, 0.51 mmol) was treated with Ag_2O (141 mg, 0.61 mmol), and the mixture was heated under reflux in 1,2-dichloroethane for 1 h. Then, $[Ir(\mu\text{-}Cl)(cod)]_2$ (170 mg, 0.25 mmol) was added, and the mixture was refluxed for 30 min, followed by addition of glacial acetic acid. After being refluxed overnight, the suspension was filtered through Celite, the filtrate was evaporated to dryness, and the crude solid was purified by flash chromatography with silica (CH_2Cl_2/acetone), yielding 7 (150 mg, 0.21 mmol, 41%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, 1H, CH_{Ind} **7b**), 7.76 (d, 1H, CH_{Ind} **7a**), 7.42−7.07 (m, 4H **7a** + 4H **7b**, CH_{Ind} **7a** + **7b**), 7.02 (d, 1H, CH_{Imid} **7a**), 6.78 (d, 1H, CH_{Imid} **7a**), 6.60 (d, 1H, CH_{Imid} **7b**), 6.53 (d, 1H, CH_{Imid} **7b**), 6.16 (s, 1H, CH_{Ind} **7a**), 5.89 (s, 1H, CH_{Ind} **7b**), 5.27−5.25 (m, 1H, CH_{linker} **7b**), 5.14−5.09 (m, 1H, CH_{linker} **7a**), 4.85−4.83 (m, 2H, CH_{COD} **7b**), 4.68−4.63 (m, 2H, CH_{COD} **7a**), 4.42−4.36 (m, 2H, CH_{COD} **7a**), 4.20−4.28 (m, 2H, CH_{COD} **7b**), 3.81 (1s, 3H, NCH_3 **7b**), 3.79 (1s, 3H, NCH_3 **7a**), 3.23−2.59 (m, 12H **7a** + 12H **7b**, CH_{2Ind} + $CH_{2linker}$ + 4×CH_{2COD} **7a** + **7b**), 1.84−1.80 (m, 2H, CH_{iPr} **7a** + **7b**), 1.13 (d, 3H, CH_{3iPr} **7a**), 1.03 (d, 3H, CH_{3iPr} **7b**), 0.92 (d, 3H, CH_{3iPr} **7a**), 0.80 (d, 3H, CH_{3iPr} **7b**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 178.4 (Ir-$C_{carbene}$ **7a**), 176.9 (Ir-$C_{carbene}$ **7b**), 143.3 (C_{Ind} **7b**), 142.9 (C_{Ind} **7b**), 142.7 (C_{Ind} **7a**), 140.9 (C_{Ind} **7b**), 139.6 (C_{Ind} **7a**), 138.8 (C_{Ind} **7a**), 128.5 (CH_{Ind} **7b**), 128.1 (CH_{Ind} **7a**), 124.1 (CH_{Ind} **7b**), 124.0 (CH_{Ind} **7a**), 123.0 (CH_{Ind} **7b**), 122.6 (CH_{Ind} **7a**), 122.1 (CH_{Ind} **7b**), 121.8 (CH_{Ind} **7a**), 117.8 (CH_{Ind} **7b**), 117.4 (CH_{Ind} **7a**), 119.5 (CH_{Imid} **7b**), 118.9 (CH_{Imid} **7b**), 116.4 (CH_{Imid} **7a**), 115.8 (CH_{Imid} **7a**), 81.3 (CH_{COD} **7a**), 80.2 (CH_{COD} **7b**), 79.5 (CH_{COD} **7b**), 78.7 (CH_{COD} **7a**), 61.8 (CH_{linker} **7a**), 61.7 (CH_{linker} **7b**), 54.2 ($CH_{2linker}$ **7a**), 53.5 ($CH_{2linker}$ **7b**), 51.9 (CH_{iPr} **7b**), 51.7 ($CH_{i\text{-}Pr}$ **7a**), 36.0 (NCH_3 **7b**), 35.9 (NCH_3 **7a**), 33.2 (CH_{2Ind} **7a**), 32.2 (CH_{2Ind} **7b**), 30.9 (CH_{COD} **7a**), 27.5 (CH_{COD} **7a**), 26.2 (CH_{COD} **7a**), 24.8 (CH_{COD} **7a**), 29.6 (CH_{COD} **7b**), 27.2 (CH_{COD} **7b**), 24.9 (CH_{COD} **7b**), 24.6 (CH_{COD} **7b**), 19.3 (CH_{3iPr} **7a**), 18.4 (CH_{3iPr} **7b**), 18.2 (CH_{3iPr} **7b**), 14.3 (CH_{3iPr} **7a**). Anal. Calcd for $C_{26}H_{34}IN_2Ir$: C, 45.02; H, 4.94; N, 4.04. Found: C, 45.27; H, 5.13; N, 4.28. MS-ESI: *m*/*z* 567 $[M - I]^+$.

X-ray Diffraction Studies. A single crystal of **3** was 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.[21] 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 4 (Supporting Information). The diffraction frames were integrated using the SAINT package.[22]

■ ASSOCIATED CONTENT

Supporting Information. ESI-MS spectra of compounds **3**−**5** and **7**, molecular diagram of **5**, details concerning **3**, and CIF files giving the crystal structure of **3** are available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Cadierno, V.; Diez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *Coord. Chem. Rev.* **1999**, *193*, 5. (b) Coville, N. J.; Duplooy, K. E.; Pickl, W. *Coord. Chem. Rev.* **1992**, *116*, 1. (c) Paz-Sandoval, M. A.; Rangel-Salas, II. *Coord. Chem. Rev.* **2006**, *250*, 1071. (d) Poli, R. *Chem. Rev.* **1991**, *91*, 509.

(2) (a) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965. (b) Ganter, C. *Chem. Soc. Rev.* **2003**, *32*, 130.

(3) Liu, J. K.; Wu, X. F.; Iggo, J. A.; Xiao, J. L. *Coord. Chem. Rev.* **2008**, *252*, 782.

(4) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.

(5) (a) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, 2781. (b) Corberan, R; Mas-Marza, E.; Peris, E. *Eur. J. Inorg. Chem.* **2009**, 1700.

(6) da Costa, A. P.; Viciano, M.; Sanaú, M.; Merino, S.; Tejeda, J.; Peris, E.; Royo, B. *Organometallics* **2008**, *27*, 1305.

(7) da Costa, A. P.; Sanaú, M.; Peris, E.; Royo, B. *Dalton Trans.* **2009**, 6960.

(8) da Costa, A. P.; Mata, J.; Royo, B.; Peris, E. *Organometallics* **2010**, *29*, 1832.

(9) Kandepi, V. V. K. M.; Cardoso, J. M. S.; Peris, E.; Royo, B. *Organometallics* **2010**, *29*, 2777.

(10) Kandepi, V. V. K. M.; da Costa, A. P.; Peris, E.; Royo, B. *Organometallics* **2009**, *28*, 4544.

(11) (a) Trost, B. M.; Vidal, B.; Thommen, M. *Chem.—Eur. J.* **1999**, *5*, 1055. (b) van der Zeijden, A. A. H.; Jimenez, J.; Mattheis, C.; Wagner, C.; Merzweiler, K. *Eur. J. Inorg. Chem.* **1999**, 1919. (c) Ciruelos, S.;

Doppiu, A.; Englert, U.; Salzer, A. *J. Organomet. Chem.* **2002**, *663*, 183. (d) Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527.
(12) Downing, S. P.; Danopoulos, A. *Organometallics* **2006**, *25*, 1337.
(13) Downing, S. P.; Guadaño, S. C.; Pugh, D.; Danopoulos, A. A.; Bellarba, R. M.; Hanton, M.; Smith, D.; Tooze, R. P. *Organometallics* **2007**, *26*, 3762.
(14) Wang, B. L.; Wang, D.; Cui, D. M.; Gao, W.; Tang, T.; Chen, X. S.; Jing, X. B. *Organometallics* **2007**, *26*, 3167.
(15) Sun, H. M.; Hu, D. M.; Wang, Y. S.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2007**, *692*, 903.
(16) Downing, S. P.; Pogorzelec, P. J.; Danopoulos, A. A.; Cole-Hamilton, D. J. *Eur. J. Inorg. Chem.* **2009**, 1816.
(17) Takaki, D; Okayama, T.; Shuto, H.; Matsumoto, S.; Yamaguchi, Y.; Matsumoto, S. *Dalton Trans.* **2011**, *40*, 1445.
(18) Nagel, U.; Diez, C. *Eur. J. Inorg. Chem.* **2009**, 1248.
(19) Lin, Y.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6040.
(20) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.
(21) Sheldrick, G. M. *SHELXTL*, version 6.1; Bruker AXS, Inc: Madison, WI, 2000.
(22) *SAINT*, version 5.0; Bruker Analytical X-ray System: Madison, WI, 1998.