Axially Chiral Bidentate N-Heterocyclic Carbene Ligands Derived from BINAM: Rhodium and Iridium Complexes in Asymmetric Ketone Hydrosilylation

Anthony R. Chianese and Robert H. Crabtree*

Chemistry Department, Yale University, 225 Prospect Street, New Haven, Connecticut 06520-8107

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New bis(N-heterocyclic carbene) and N-heterocyclic carbene−naphthoxy ligands are synthesized in two steps from (*S*)-1,1′-diamino-2,2′-binaphthyl. Rhodium and iridium complexes of the carbene−naphthoxy ligands were applied to the catalytic asymmetric hydrosilylation of acetophenone with diphenylsilane. Low enantioselectivities (12−13% ee) were observed for the rhodium-catalyzed reaction, but moderate enantioselectivities (50−60% ee) were seen for iridium.

Introduction

N-heterocyclic carbene ligands (NHCs), first reported by Öfele[1] and Wanzlick[2] and later isolated in the free state by Arduengo,[3] have emerged as an extremely useful class of ligands for transition-metal catalysis.[4−6] In addition to forming extremely strong metal−carbon bonds,[7,8] these compounds are also indicated by infrared spectroscopy of their carbonyl derivatives to be very powerful *σ*-donors, even in comparison to trialkylphosphines.[9−11] NHCs have found use as supporting ligands for many metal-catalyzed processes, such as olefin metathesis,[12−14] C−C and C−N cross-coupling,[15−20] olefin hydrogenation,[21−23] transfer hydrogenation of ketones,[24−26] and methane oxidation.[27]

The planarity of the imidazole ring severely complicates development of chiral NHCs for asymmetric catalysis. Many homochiral NHC ligands have been prepared,[28] however, and a handful have been employed in highly enantioselective transformations. Grubbs[29] has employed a monodentate NHC with a chiral imidazoline backbone for highly enantioselective ruthenium-catalyzed asymmetric ring-closing metathesis, but the majority of successful ligands have been bidentate. Burgess[22,23] has developed a carbene−oxazoline ligand that allows highly enantioselective iridium-catalyzed hydrogenation of unfunctionalized olefins using only 1 atm of hydrogen. RajanBabu prepared the first chelated bis-NHC complexes containing the 1,1′-binaphthyl scaffold.[30] Hoveyda has developed a bidentate NHC−naphthoxy ligand that is successful for asymmetric ruthenium-catalyzed ring-opening metathesis[31,32] and copper-catalyzed asymmetric allylic substitution.[33] Gade and Bellemin-Laponnaz[34] have reported a class of NHC−oxazoline ligands that are effective for rhodium-

* To whom correspondence should be addressed. E-mail: robert.crabtree@yale.edu. Fax: (203) 432-6144.

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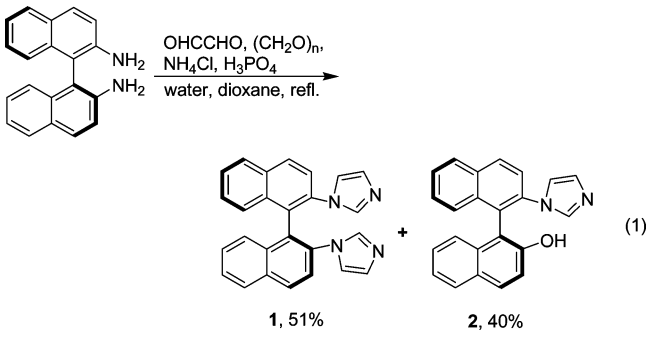
catalyzed asymmetric hydrosilylation of ketones. Douthwaite[35] has reported an NHC−imine ligand based on 1,2-diaminocyclohexane that is effective for palladium-catalyzed allylic alkylation. The only bis-NHC ligand that has given high enantioselectivities is a BINAM-derived bis-benzimidazole ligand synthesized by Shi,[36] which has been employed for rhodium-catalyzed asymmetric hydrosilylation of ketones.

In our studies on homogeneous catalysis using metal−NHC complexes,[19,24−26] we became interested in developing short syntheses of rigid, chiral NHC ligands for asymmetric catalysis. We report here the modular synthesis of bis-NHC and NHC−naphthoxy ligands in only two steps from commercially available resolved 2,2′-diamino-1,1′-binaphthyl (BINAM). Rhodium and iridium complexes of NHC−naphthoxy ligands have been synthesized and employed in the asymmetric hydrosilylation of acetophenone.

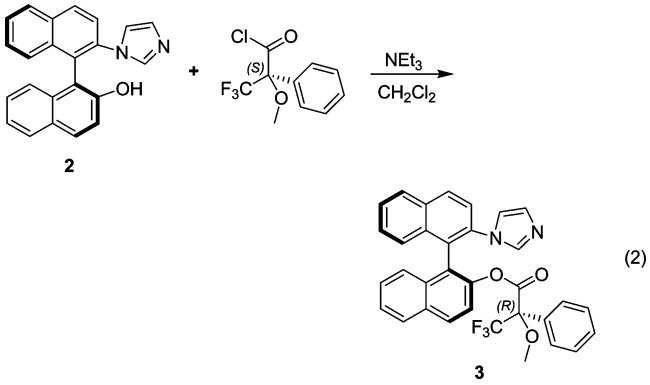
Results and Discussion

Synthesis of Ligands. The synthesis of 1-alkyl- or 1-arylimidazoles by reaction of equimolar amounts of glyoxal, ammonia, formaldehyde, and a monosubstituted amine under acidic conditions has been shown to proceed in poor to moderate yield (8−56%).[23,37] The low yields were proposed to arise from competitive side reactions of glyoxal and amines, such as the Cannizzaro rearrangement.[37] In order for this protocol to be useful for the synthesis of imidazoles with chiral N substituents from valuable chiral amines, it would be desirable to achieve the highest possible yield with respect to the chiral amine employed.

The reaction of (*S*)-BINAM with 1 equiv each of glyoxal, paraformaldehyde, and ammonium chloride under conditions reported by Burgess[23] gave a mixture of several unidentified products. By using an excess (5 equiv) of each reagent, two compounds were formed in approximately equal ratio, as indicated by ^{1}H NMR and TLC of the crude reaction mixture. Separation by flash chromatography gave the pure products, identified as **1**, the expected bis(imidazolyl)−binaphthyl compound, and **2**, apparently formed by competitive hydrolysis of the aromatic amine (eq 1).

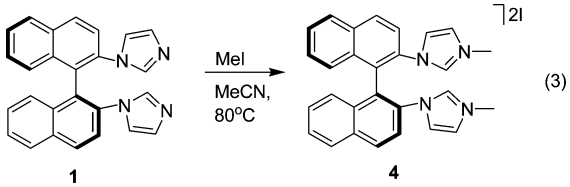


Both products have been fully characterized; the substitution of −OH for −NH_2 in **2** was verified by elemental analysis and electrospray ionization mass spectrometry (*m/z* 337.1; **2** + H^+). Characterization of derivatives (see below) also supports the assigned structure of **2**. It seemed conceivable, although unlikely, that racemization could occur under the conditions employed for the synthesis of **1** and **2**. To exclude this possibility, (*S*,*R*)-**3**, the Mosher ester of **2**, was synthesized (eq 2). Only one diastereomer was observed by ^{1}H

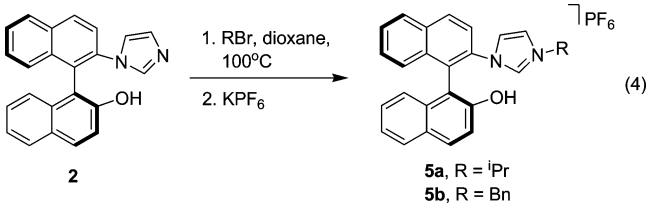


and ^{13}C NMR spectroscopy. Racemic **2** was prepared from *rac*-BINAM; derivatization to the Mosher ester clearly showed two diastereomers by ^{1}H NMR. We conclude that no appreciable racemization occurs during the synthesis of **1** and **2**.

Both **1** and **2** are easily alkylated at the free nitrogen atom(s) to give imidazolium salts. Reaction of **1** with an excess of iodomethane in acetonitrile gave **4** (eq 3).



Reaction of **2** with 2-bromopropane or benzyl bromide gave **5a**,**b**, respectively, after ion exchange and flash chromatography (eq 4). Very little (<2%) alkylation at the oxygen atom is observed.



Shi[36] has prepared a benzimidazolium-based NHC precursor similar to **4**, and Hoveyda[31−33] has prepared a series of imidazolinium-based NHC precursors similar to **5**. Our extremely short syntheses of **4** and **5a**,**b** from commercially available resolved BINAM make the present route attractive, however. Variation of the alkyl halide used for quaternization of the imidazole unit(s) allows for modulation of the ligands at the last synthetic step.

Synthesis of Rhodium and Iridium Complexes. Attempts to prepare a chelated bis-NHC complex from **4** failed, despite multiple attempts. However, stirring a THF solution of **5a** or **5b**, $[Rh(COD)Cl]_2$ or [Ir(COD)-

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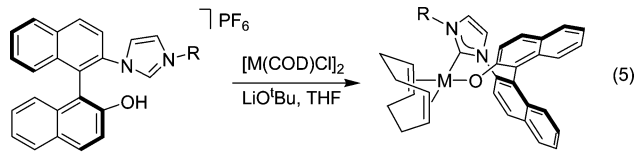
$Cl]_2$, and 2.2 equiv of LiO^tBu for 1 h gave moderate to good yields of the neutral chelated complexes **6a**,**b** and **7a**,**b**, which were purified by chromatography on basic alumina (eq 5; COD = 1,5-cyclooctadiene). It was



5a,**b**

6a, R = ^{i}Pr, M = Rh
6b, R = Bn, M - Rh
7a, R = ^{i}Pr, M = Ir
7b, R = Bn, M = Ir

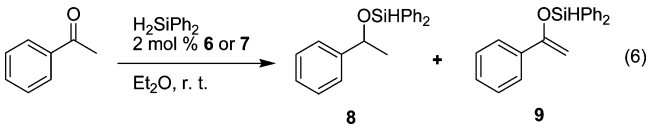
essential to prepare these complexes under dilute conditions (see Experimental Section), as more concentrated reaction conditions led to the formation of multiple (presumably oligomeric) species by ^{1}H NMR spectroscopy of the crude reaction mixture.

All four complexes are very soluble in ether and dichloromethane and moderately soluble in hexanes. Their identities are confirmed by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and ESI-MS (see below). As expected, four separate ^{1}H and ^{13}C COD vinyl resonances are observed, and the metal-bound carbene carbon resonates at 186.8−182.1 ppm. The complexes are air stable in the solid state and for several days in solution.

Complexes **6a**,**b** and **7a**,**b** have been characterized by cation-mode electrospray ionization mass spectrometry. In all four cases, mass peaks were observed for *m/z* $M^{\bullet+}$, $M + H^+$, and $M + Na^+$, with the expected isotope distribution patterns.

Asymmetric Ketone Hydrosilylation. Complexes **6a**,**b** and **7a**,**b** were tested for the hydrogenation of dimethyl itaconate but were inactive. All four complexes were active for the transfer hydrogenation of acetophenone in 2-propanol with catalytic KOH added at 80 °C, but the product *sec*-phenethyl alcohol was nearly racemic. The complexes were also active for the addition of phenylboronic acid to 2-naphthaldehyde at 100 °C, but the product carbinol was also found to be racemic.

Rhodium complexes **6a**,**b** were found to be very active precatalysts for the hydrosilylation of acetophenone with diphenylsilane, giving >98% conversion in less than 30 min at room temperature (eq 6) at 2% catalyst loading.



8 **9**

^{1}H NMR analysis of the crude reaction mixtures showed that a small amount of the silyl enol ether **9** was formed by dehydrogenative silylation of the enol of acetophenone, along with the reduced silyl ether **8** as major product. After methanolysis of the silyl ether, the product *sec*-phenethyl alcohol was produced in low enantiomeric excess (Table 1). Iridium complexes **7a**,**b** were slightly less active, requiring 2 h for full conversion, and a greater amount of **9** was formed. Moderate enantioselectivities were achieved for the reduced product **8**, although they do not compare well with the best results in the literature.[34,36,38−43] Diethyl ether was found to give the highest enantioselectivity of several solvents tested (dichloromethane, THF, toluene, hexanes). Increasing the catalyst loading and varying the temperature gave no benefit, nor did changing the order of addition of reactants.

Table 1. Asymmetric Hydrosilylation of Acetophenone

catalyst	time (min)	conversn (%)	**8**:**9**	ee for **8** (%) (abs confign)
6a	30	>98	97:3	12 (*S*)
6b	30	>98	97:3	13 (*S*)
7a	120	>98	85:15	50 (*R*)
7b	120	>98	83:17	60 (*R*)

Conclusions

New homochiral bis-NHC and NHC−naphthoxy ligands have been synthesized from (*S*)-BINAM in two steps. Neutral rhodium and iridium complexes of the monodentate NHC−naphthoxy ligands **5a**,**b** were synthesized. The complexes were catalytically active for the asymmetric hydrosilylation of acetophenone with diphenylsilane; low enantioselectivities were achieved with rhodium and moderate enantioselectivities with iridium. Our efficient synthesis of these ligands now makes them more readily available for future asymmetric catalytic work.

Experimental Section

General Methods. (*S*)-2,2-Diamino-1,1′-binaphthyl was obtained from Strem Chemicals or Aldrich Chemical Co. All other materials were obtained commercially and were used as received, except as noted. Ligand syntheses were performed in untreated solvents, without exclusion of air. Syntheses of metal complexes and catalytic reactions were performed under an atmosphere of argon, using solvents dried on an alumina-based solvent purification system. NMR spectra were recorded on Bruker spectrometers operating at 400 or 500 MHz (^{1}H NMR) and 100 or 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in parts per million). NMR spectra were obtained at room temperature. Assignments are based on COSY and HMQC experiments. Elemental analyses were performed by Atlantic Microlabs, Inc.

(*S*)-2,2′-Bis(imidazol-1-yl)-1,1′-binaphthyl (1) and (*S*)-2-(Imidazol-1-yl)-2′-hydroxy-1,1′-binaphthyl (2). (*S*)-2,2-Diamino-1,1′-binaphthyl (409 mg, 1.44 mmol) was added to 10 mL of deionized water, and 1 drop of concentrated H_3PO_4 was added. The mixture was stirred for 5 min, and 40% aqueous glyoxal (1.04 g, 7.2 mmol) and paraformaldehyde (216 mg, 7.2 mmol) were added along with 10 mL of dioxane. The mixture was heated with stirring to 80 °C, and ammonium chloride (385 mg, 7.2 mmol) was added. The solution was refluxed for 5 h and cooled to room temperature. A saturated aqueous solution of K_2CO_3 (10 mL) was added, and the mixture was extracted with dichloromethane (3 × 10 mL). The fractions were combined, dried over $MgSO_4$, and filtered. The solvent was evaporated, and the residue was purified by flash chro-

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matography on silica gel. Compound **2** was eluted with 3:1 ethyl acetate/hexanes, and compound **1** was eluted with 9:1 acetone/methanol. To obtain dry **1**, it was necessary to predry the silica gel in an oven overnight at 150 °C. Compound **1** yield: 284 mg, 51%. ^{1}H NMR ($CDCl_3$): δ 8.07 (d, 2H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 8.04 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, CH_{naph}); 7.62 (m, 2H, CH_{naph}); 7.47 (m, 2H, CH_{naph}); 7.39 (d, 2H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 7.35 (d, 2H, $^3J_{H-H}$ = 8.4 Hz, CH_{naph}); 6.87 (t, 2H, $^{3,4}J_{H-H}$ = 1.3 Hz, CH_{imid}); 6.85 (t, 2H, $^{3,4}J_{H-H}$ = 1.3 Hz, CH_{imid}); 6.36 (t, 2H, $^{3,4}J_{H-H}$ = 1.3 Hz, CH_{imid}). ^{13}C NMR ($CDCl_3$); δ 137.0, 133.9, 133.8, 132.5, 130.8, 128.9, 128.7, 128.2, 127.4, 127.0, 126.3, 123.7, 119.9 (C_{ar}). Anal. Calcd for $C_{26}H_{18}N_4$ (386.46): C, 80.81; H, 4.69; N, 14.50. Found: C, 80.61; H, 4.55; N, 14.39. ESI-MS (MeOH, 20 V): *m/z* 387.8 ($M + H^+$); 409.8 ($M + Na^+$). Compound **2** yield: 194 mg, 40%. ^{1}H NMR ($CDCl_3$): δ 10.5 (br s, 1H, OH); 8.05 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 7.99, (d, 1H, $^3J_{H-H}$ = 8.3 Hz, CH_{naph}); 7.86 (t, 1H, $^{3,4}J_{H-H}$ = 1.2 Hz, CH_{imid}); 7.85 (d, 1H, $^3J_{H-H}$ = 7.1 Hz, CH_{naph}); 7.58 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 7.55 (d, 1H, $^3J_{H-H}$ = 8.3 Hz, CH_{naph}); 7.54 (m, 1H, CH_{naph}); 7.44 (d, 1H, $^3J_{H-H}$ = 8.3 Hz, CH_{naph}); 7.37 (m, 1H, CH_{naph}); 7.29 (m, 1H, CH_{naph}); 7.19 (m, 1H, CH_{naph}); 6.91 (d, 1H, $^3J_{H-H}$ = 8.3 Hz, CH_{naph}); 6.86 (t, 1H, $^{3,4}J_{H-H}$ = 1.2 Hz, CH_{imid}); 6.83 (t, 1H, $^{3,4}J_{H-H}$ = 1.2 Hz, CH_{imid}); 6.75 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}). ^{13}C NMR ($CDCl_3$): δ 154.2, 137.7, 134.1, 134.0, 133.6, 133.5, 131.3, 130.2, 129.5, 128.3, 128.2, 128.1, 127.6, 127.2, 127.0, 126.8, 126.5, 124.0, 123.8, 122.8, 120.6, 118.4, 114.9 (C_{ar}). Anal. Calcd for $C_{23}H_{16}N_2O$ (336.39): C, 82.12; H, 4.79; N, 8.33. Found: C, 81.71; H, 4.89; N, 8.28. ESI-MS (MeOH, 20 V): *m/z* 337.8 ($M + H^+$); 359.7 ($M + Na^+$).

Preparation of 3, the *S,R* Mosher Ester of 2. Compound **2** (5 mg, 0.015 mmol) was dissolved in 5 mL of dichloromethane. (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride (Aldrich; 8 μL, 0.045 mmol) was added, followed by triethylamine (21 μL, 0.15 mmol). The mixture was stirred for 1 h at room temperature, and the solvent was removed. The residue was purified by flash chromatography on silica gel, with ethyl acetate as eluent. In the ^{13}C NMR spectrum, four resonances are broad at room temperature and are ascribed to slow rotation about the C−C_{Ph} bond. Yield: 7 mg, 85%. ^{1}H NMR ($CDCl_3$): δ 8.09 (d, 1H, $^3J_{H-H}$ = 8.6 Hz, CH_{naph}); 8.01 (d, 1H, $^3J_{H-H}$ = 8.3 Hz, CH_{naph}); 7.96 (d, 1H, $^3J_{H-H}$ = 8.9 Hz, CH_{naph}); 7.91 (d, 1H, $^3J_{H-H}$ = 8.3 Hz, CH_{naph}); 7.58 (m, 1H, CH_{naph}); 7.50 (d, 1H, $^3J_{H-H}$ = 8.6 Hz, CH_{naph}); 7.48 (m, 1H, CH_{naph}); 7.43−7.27 (m, 5H, CH_{ar}); 7.20−7.11 (m, 4H, CH_{ar}); 6.96 (m, 2H, CH_{naph}); 5.70 (br s, 1H, CH_{imid}); 5.65 (br s, 1H, CH_{imid}); 3.00 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 165.1 ($C_{carbonyl}$); 146.4 (C_{ar}); 137.3 (br, C_{Ph}); 134.9 (br, C_{Ph}); 133.6, 133.1, 131.9, 131.4, 130.8, 130.4, 129.7, 128.7 (C_{ar}); 128.6 (br, C_{Ph}); 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.4, 127.1, 127.0, 126.9, 126.5, 125.4, 124.4, 124.1 (C_{ar}); 123.0 (q, $^1J_{C-F}$ = 289 Hz, CF_3); 120.7, 120.6 (C_{ar}); 120.4 (br, C_{Ph}); 54.9 (OCH_3). ESI-MS (MeOH, 20 V): *m/z* 553.5 ($M + H^+$); 575.5 ($M + Na^+$).

(*S*)-2,2′-Bis(3-methylimidazolium-1-yl)-1,1′-binaphthyl Diiodide (4). Compound **1** (75 mg, 0.19 mmol) was dissolved in 5 mL of acetonitrile. Iodomethane (0.5 mL) was added, and the solution was heated at 80 °C for 5 h. The volatiles were removed, and the solid obtained was triturated with ether and dried in vacuo. The product was ca. 95% pure by NMR and was used in metalation attempts without further purification. Yield: 119 mg, 94%. ^{1}H NMR ($CDCl_3$): δ 10.3 (t, 2H, $^4J_{H-H}$ = 1.7 Hz, CH_{imid}); 8.33 (d, 2H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 8.16 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, CH_{naph}); 7.91 (d, 2H, $^3J_{H-H}$ = 8.9 Hz, CH_{naph}); 7.71 (m, 2H, CH_{naph}); 7.55 (m, 2H, CH_{naph}); 7.33 (t, 2H, $^{3,4}J_{H-H}$ = 1.7 Hz, CH_{imid}); 7.28 (d, 2H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 6.40 (t, 2H, $^{3,4}J_{H-H}$ = 1.7 Hz, CH_{imid}); 4.21 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$); 136.8, 133.6, 133.2, 132.9, 131.2, 129.9, 129.7, 128.9, 126.1, 126.0, 125.3, 123.8, 121.2 (C_{Ar}); 38.4 (CH_3). ESI-MS (MeOH, 20 V): *m/z* 208.1 (M^{2+}/2); 543.3 ($M^{2+} + I^-$).

(*S*)-2-(3-Isopropylimidazolium-1-yl)-2′-hydroxy-1,1′-binaphthyl Hexafluorophosphate (5a). Compound **2** (122 mg, 0.363 mmol) and 2-bromopropane (2 mL) were combined in 10 mL of dioxane. The solution was refluxed for 2 days, and additional 2-bromopropane (2 mL) was added after 1 day. The volatiles were removed, and dichloromethane (5 mL), deionized water (5 mL), and KPF_6 (200 mg, 1.089 mmol) were added. The mixture was stirred for 30 min, and the organic phase was collected. The aqueous phase was extracted twice with 10 mL of dichloromethane, and the organic fractions were combined and dried over $MgSO_4$. The solvent was removed, and the residue was purified by flash chromatography on silica gel, with 1:1 ethyl acetate/dichloromethane as eluent. The product was ca. 98% pure by NMR and was used in metalation attempts without further purification. Yield: 111 mg, 58%. ^{1}H NMR ($CDCl_3$): δ 8.25 (t, 1H, $^4J_{H-H}$ = 1.5 Hz, CH_{imid}); 8.04 (d, 1H, $^3J_{H-H}$ = 8.8, CH_{naph}); 7.94 (d, 1H, $^3J_{H-H}$ = 8.4, CH_{naph}); 7.78 (m, 2H, CH_{naph}); 7.86 (d, 1H, $^3J_{H-H}$ = 8.8, CH_{naph}); 7.58 (m, 1H, CH_{naph}); 7.38 (m, 2H, CH_{Ph}); 7.28 (m, 1H, CH_{Ph}); 7.23 (m, 2H, CH_{Ph}); 7.00 (t, 1H, $^{3,4}J_{H-H}$ = 1.5 Hz, CH_{imid}); 6.94 (t, 1H, $^{3,4}J_{H-H}$ = 1.5 Hz, CH_{imid}); 6.86 (d, 1H, $^3J_{H-H}$ = 8.4, CH_{naph}); 6.56 (br s, 1H, OH); 4.34 (sept, 1H, $^3J_{H-H}$ = 6.8 Hz, CH_{iPr}); 1.17 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, $CH_{3\ iPr}$); 1.15 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, $CH_{3\ iPr}$). ^{13}C NMR ($CDCl_3$): δ 152.0, 134.2, 133.9, 133.3, 132.8, 132.0, 131.3, 131.1, 130.8, 128.7, 128.6, 128.5, 128.2, 128.1, 127.9, 127.1, 124.0, 123.7, 123.4, 122.6, 119.2, 118.0, 113.0 (C_{ar}); 53.6 (CH_{iPr}); 22.22, 22.23 ($CH_{3\ iPr}$). ESI-MS (MeOH, 20 V): *m/z* 379.4 (M^+).

(*S*)-2-(3-Benzylimidazolium-1-yl)-2′-hydroxy-1,1′-binaphthyl Hexafluorophosphate (5b). Compound **5b** was prepared analogously to **5a**, from **2** (84 mg, 0.25 mmol) and benzyl bromide (45 μL, 0.375 mmol). Reaction was complete after 1 day. After chromatography, the product was ca. 95% pure and was used without further purification. Yield: 118 mg, 80%. ^{1}H NMR ($CDCl_3$): δ 8.29 (t, 1H, $^4J_{H-H}$ = 1.5 Hz, CH_{imid}); 7.91 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 7.85 (d, 1H, $^3J_{H-H}$ = 8.4 Hz, CH_{naph}); 7.75 (d, 1H, $^3J_{H-H}$ = 8.5 Hz, CH_{naph}); 7.74 (d, 1H, $^3J_{H-H}$ = 8.9 Hz, CH_{naph}); 7.56 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 7.51 (m, 1H, CH_{naph}); 7.12−7.32 (m, 8H, CH_{ar}); 6.93 (t, 1H, $^{3,4}J_{H-H}$ = 1.5 Hz, CH_{imid}); 6.74−6.79 (m, 3H, CH_{naph}); 6.73 (t, 1H, $^{3,4}J_{H-H}$ = 1.5 Hz, CH_{imid}); 6.69 (br s, 1H, OH); 4.98 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 152.4, 135.2, 134.2, 133.1, 132.7, 132.2, 131.7, 131.3, 130.9, 130.7, 129.4, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.0, 123.9, 123.7, 123.3, 121.5, 118.0, 112.8 (C_{ar}); 53.2 (CH_2). ESI-MS (MeOH, 20 V): *m/z* 427.3 (M^+).

Rhodium Complex 6a. Compound **5a** (73 mg, 0.14 mmol) and $[Rh(COD)Cl]_2$ (34 mg, 0.070 mmol) were combined in 100 mL of dry, degassed THF under argon. LiO^tBu (306 μL of a 1.0 M THF solution) was added via syringe. The solution was stirred for 1 h, opened to the atmosphere, and filtered through a pad of basic alumina. The volatiles were removed, and the residue was purified on a basic alumina column, with 1:1 ethyl acetate/hexanes as eluent. Yield: 51 mg, 62%. ^{1}H NMR (CD_2Cl_2): δ 8.2 (d, 1H, $^3J_{H-H}$ = 8.6 Hz, CH_{naph}); 8.1 (d, 1H, $^3J_{H-H}$ = 8.2 Hz, CH_{naph}); 7.77 (d, 1H, $^3J_{H-H}$ = 8.6 Hz, CH_{naph}); 7.58 (m, 1H, CH_{naph}); 7.53 (m, 1H, CH_{naph}); 7.44 (d, 1H, $^3J_{H-H}$ = 8.9 Hz, CH_{naph}); 7.31 (m, 2H, CH_{naph}); 6.90 (m, 3H, CH_{naph}); 6.83 (d, 1H, $^3J_{H-H}$ = 2.0 Hz, CH_{imid}); 6.57 (d, 1H, $^3J_{H-H}$ = 2.0 Hz, CH_{imid}); 6.36 (m, 1H, CH_{naph}); 5.18 (sept, 1H, $^3J_{H-H}$ = 6.6 Hz, CH_{iPr}); 4.41 (m, 1H, CH_{cod}); 3.89 (m, 1H, CH_{cod}); 2.94 (m, 1H, CH_{cod}); 2.80 (m, 1H, CH_{cod}); 2.53 (m, 1H, $CH_{2\ cod}$); 2.14 (m, 1H, $CH_{2\ cod}$); 1.98 (m, 1H, $CH_{2\ cod}$); 1.78 (m, 1H, $CH_{2\ cod}$); 1.68 (m, 2H, $CH_{2\ cod}$); 1.49 (m, 2H, $CH_{2\ cod}$); 1.31 (d, 3H, $^3J_{H-H}$ = 6.6 Hz, $CH_{3\ iPr}$); 1.07 (d, 3H, $^3J_{H-H}$ = 6.6 Hz, $CH_{3\ iPr}$). ^{13}C NMR (CD_2Cl_2): δ 185.4 (d, $^1J_{Rh-C}$ = 56 Hz, $C_{carbene}$); 170.5, 138.8, 138.5, 136.0, 135.1, 134.4, 128.8, 128.5, 128.4, 128.1, 128.0, 127.3, 127.1, 126.3, 125.6, 125.5, 124.0, 123.4, 121.7, 119.9, 116.1, 115.0 (C_{ar}); 99.2 (d, $^1J_{Rh-C}$ = 7.8 Hz, CH_{cod}); 95.6 (d, $^1J_{Rh-C}$ = 8.4 Hz, CH_{cod}); 64.0 (d, $^1J_{Rh-C}$ = 14.7 Hz, CH_{cod}); 62.9 (d, $^1J_{Rh-C}$ = 14.4 Hz, CH_{cod}); 52.1 (CH_{iPr}); 35.1, 31.2, 31.7, 28.8

($CH_{2\ cod}$), 24.8, 22.9 (CH_3). Anal. Calcd for $C_{34}H_{33}N_2ORh$ (588.56): C, 69.39; H, 5.65; N, 4.76. Found: C, 69.30; H, 5.90; N, 4.60. ESI-MS (MeOH, 20 V): *m/z* 588.2 ($M^{\bullet+}$); 589.3 ($M + H^+$); 611.3 ($M + Na^+$).

Rhodium Complex 6b. This complex was prepared analogously to **6a**, from **5b** (118 mg, 0.200 mmol), $[Rh(COD)Cl]_2$ (49 mg, 0.100 mmol), and LiO^{t}Bu (449 μL of a 1.0M THF solution). Yield: 69 mg, 54%. ^{1}H NMR (CD_2Cl_2): δ 8.23 (d, 1H, $^3J_{H-H}$ = 8.6 Hz, CH_{naph}); 8.12 (d, 1H, $^3J_{H-H}$ = 8.2 Hz, CH_{naph}); 7.78 (d, 1H, $^3J_{H-H}$ = 8.6 Hz, CH_{naph}); 7.57−7.62 (m, 3H, CH_{Ar}); 7.25−7.36 (m, 5H, CH_{Ar}); 6.98 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, CH_{naph}); 6.88−6.95 (m, 3H, CH_{Ar}); 6.84 (m, 2H, CH_{Ar}); 6.41 (d, 1H, $^3J_{H-H}$ = 1.9 Hz, CH_{imid}); 6.40 (m, 1H, CH_{Ar}); 5.92 (d, 1H, $^2J_{H-H}$ = 14.8 Hz, CH_2); 5.02 (d, 1H, $^2J_{H-H}$ = 14.8 Hz, CH_2); 4.53 (m, 1H, CH_{cod}); 3.98 (m, 1H, CH_{cod}); 2.97 (m, 1H, CH_{cod}); 2.85 (m, 1H, CH_{cod}); 2.53 (m, 1H, $CH_{2\ cod}$); 2.19 (m, 1H, $CH_{2\ cod}$); 1.96 (m, 1H, $CH_{2\ cod}$); 1.82 (m, 1H, $CH_{2\ cod}$); 1.56 (m, 2H, $CH_{2\ cod}$); 1.23 (m, 1H, $CH_{2\ cod}$). ^{13}C NMR (CD_2Cl_2): δ 186.8 (d, $^1J_{Rh-C}$ = 56.2, $C_{carbene}$); 170.2, 138.6, 138.1, 137.2, 136.1, 135.1, 134.5, 129.3, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.4, 127.2, 126.5, 126.1, 125.7, 124.1, 123.4, 122.1, 120.5, 120.0, 115.0 (C_{Ar}); 99.7 (d, $^1J_{Rh-C}$ = 7.6 Hz, CH_{cod}); 96.9 (d, $^1J_{Rh-C}$ = 8.1 Hz, CH_{cod}); 64.5 (d, $^1J_{Rh-C}$ = 14.2 Hz, CH_{cod}); 63.2 (d, $^1J_{Rh-C}$ = 14.6 Hz, CH_{cod}); 54.0 (CH_2); 34.8, 32.1, 28.6, 28.0 ($CH_{2\ cod}$). Anal. Calcd for $C_{38}H_{33}N_2ORh$ (636.60): C, 71.70; H, 5.23; N, 4.40. Found: C, 71.38; H, 5.35; N, 4.21. ESI-MS (MeOH, 20 V): *m/z* 636.4 ($M^{\bullet+}$); 637.5 ($M + H^+$); 659.5 ($M + Na^+$).

Iridium Complex 7a. This complex was prepared analogously to **6a**, from **5a** (100 mg, 0.190 mmol), $[Ir(COD)Cl]_2$ (64 mg, 0.095 mmol), and LiO^{t}Bu (418 μL of a 1.0 M THF solution). Yield: 80 mg, 59%. ^{1}H NMR (CD_2Cl_2): δ 8.17 (d, 1H, $^3J_{H-H}$ = 8.7 Hz, CH_{naph}); 8.08 (d, 1H, $^3J_{H-H}$ = 8.4 Hz, CH_{naph}); 7.73 (d, 1H, $^3J_{H-H}$ = 8.4 Hz, CH_{naph}); 7.55−7.61 (m, 3H, CH_{naph}); 7.26−7.34 (m, 2H, CH_{naph}); 6.93−7.03 (m, 3H, CH_{naph}); 6.82 (d, 1H, $^3J_{H-H}$ = 1.8 Hz, CH_{imid}); 6.61 (d, 1H, $^3J_{H-H}$ = 1.8 Hz, CH_{imid}); 6.46 (d, 1H, $^3J_{H-H}$ = 8.1 Hz, CH_{naph}); 5.19 (sept, 1H, $^3J_{H-H}$ = 6.7 Hz, CH_{iPr}); 4.18 (m, 1H, CH_{cod}); 3.56 (m, 1H, CH_{cod}); 2.63 (m, 1H, CH_{cod}); 2.51 (m, 1H, CH_{cod}); 2.34 (m, 1H, $CH_{2\ cod}$); 2.08 (m, 1H, $CH_{2\ cod}$); 1.81 (m, 1H, $CH_{2\ cod}$); 1.67 (m, 1H, $CH_{2\ cod}$); 1.41 (d, 3H, $^3J_{H-H}$ = 6.7 Hz, $CH_{3\ iPr}$); 1.20−1.39 (m, 3H, $CH_{2\ cod}$); 1.10 (d, 3H, $^3J_{H-H}$ = 6.7 Hz, $CH_{3\ iPr}$); 1.08 (m, 1H, $CH_{2\ cod}$). ^{13}C NMR (CD_2Cl_2): δ 182.1 ($C_{carbene}$); 170.5, 139.1, 137.5, 135.6, 135.0, 134.2, 129.0, 128.6, 128.5, 128.0, 127.9, 127.3, 127.2, 127.1, 125.8, 125.2, 123.9, 123.5, 121.3, 120.9, 116.3, 115.9 (C_{ar}); 85.1, 81.9 (CH_{cod}); 51.8 (CH_{iPr}); 46.7, 45.3 (CH_{cod}); 35.8, 32.6, 29.4, 28.6 ($CH_{2\ cod}$) 24.6, 23.0 ($CH_{3\ iPr}$). Anal. Calcd for $C_{34}H_{33}N_2OIr$ (677.81): C, 60.24; H, 4.91; N, 4.13. Found: C, 59.86; H, 5.21; N, 3.95. ESI-MS (MeOH, 20 V): *m/z* 676.5, 678.5 ($M^{\bullet+}$); 677.5, 679.5 ($M + H^+$); 699.5, 701.5 ($M + Na^+$).

Iridium Complex 7b. This complex was prepared analogously to **6a**, from **5b** (147 mg, 0.249 mmol), $[Ir(COD)Cl]_2$ (84 mg, 0.124), and LiO^{t}Bu (560 μL of a 1.0 M THF solution). Yield: 125 mg, 69%. ^{1}H NMR (CD_2Cl_2): δ 8.18 (d, 1H, $^3J_{H-H}$ = 8.6 Hz, CH_{naph}); 8.09 (d, 1H, $^3J_{H-H}$ = 8.2 Hz, CH_{naph}); 7.73 (d, 1H, $^3J_{H-H}$ = 8.7 Hz, CH_{naph}); 7.68 (d, 1H, $^3J_{H-H}$ = 8.7 Hz, CH_{naph}); 7.66 (d, 1H, $^3J_{H-H}$ = 8.4 Hz, CH_{naph}); 7.57 (m, 1H, CH_{naph}); 7.33 (m, 1H, CH_{naph}); 7.22−7.27 (m, 4H, CH_{ar}); 7.03 (d, 1H, $^3J_{H-H}$ = 8.7 Hz, CH_{naph}); 7.00 (m, 1H, CH_{naph}); 6.94 (m, 1H, CH_{naph}); 6.86 (d, 1H, $^3J_{H-H}$ = 1.8 Hz, CH_{imid}); 6.78 (m, 2H, CH_{ar}); 6.46 (d, 1H, $^3J_{H-H}$ = 8.2 Hz, CH_{naph}); 6.44 (d, 1H, $^3J_{H-H}$ = 1.8 Hz, CH_{imid}); 5.91 (d, 1H, $^2J_{H-H}$ = 14.8 Hz, CH_2); 4.99 (d, 1H, $^2J_{H-H}$ = 14.8 Hz, CH_2); 4.30 (m, 1H, CH_{cod}); 3.61 (m, 1H, CH_{cod}); 2.62 (m, 1H, CH_{cod}); 2.54 (m, 1H, CH_{cod}); 2.31 (m, 1H, $CH_{2\ cod}$); 2.11 (m, 1H, $CH_{2\ cod}$); 1.75 (m, 1H, $CH_{2\ cod}$); 1.67 (m, 1H, $CH_{2\ cod}$); 1.42 (m, 1H, $CH_{2\ cod}$); 1.30 (m, 2H, $CH_{2\ cod}$); 1.12 (m, 1H, $CH_{2\ cod}$). ^{13}C NMR (CD_2Cl_2): δ 183.2 ($C_{carbene}$); 170.2, 138.8, 137.1, 137.0, 135.6, 135.0, 134.3, 129.2, 128.9, 128.8, 128.6, 128.4, 128.1, 128.0, 127.9, 127.4, 127.3, 127.2, 125.9, 125.7, 123.9, 123.5, 121.6, 121.0, 120.2, 116.2 (C_{ar}); 85.6, 83.7 (CH_{cod}); 53.6 (CH_2); 47.2, 45.4 (CH_{cod}); 35.3, 33.0, 29.0, 28.9 ($CH_{2\ cod}$). Anal. Calcd for $C_{38}H_{33}N_2OIr$ (725.92): C, 62.87; H, 4.58; N, 3.86. Found: C, 62.79; H, 4.99; N, 3.55. ESI-MS (MeOH, 20 V): *m/z* 724.5, 726.5 ($M^{\bullet+}$); 725.5, 727.5 ($M + H^+$); 747.5, 749.5 ($M + Na^+$).

Ketone Hydrosilylation. A flame-dried Schlenk tube was charged with 5.0 mg of catalyst and a stir bar and placed under argon. Diethyl ether (2 mL) was added via syringe. Acetophenone (50 equiv relative to catalyst) was added, followed by diphenylsilane (100 equiv relative to catalyst). After the mixture was stirred at room temperature for the indicated time, the flask was opened, and 1 mL of a 1:30 solution of 50% aqueous NaOH/methanol was added slowly. After 10 min, the solvent was removed, and the residue was purified by flash chromatography on silica gel, with 9:1 hexanes/ethyl acetate as eluent. The enantiomeric excess of the product *sec*-phenethyl alcohol was determined by ^{1}H NMR, using the chiral shift reagent europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (Aldrich) in C_6D_6 solvent. The α-proton was found to split at 6.0 ppm, and the more downfield resonance was attributable to (+)-(*R*)-*sec*-phenethyl alcohol (verified by optical rotation).

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