Chiral bidentate *N*-heterocyclic carbene complexes of Rh and Pd

Li Ren, Austin C. Chen, Andreas Decken, and Cathleen M. Crudden

Abstract: The synthesis of a new chiral, bidentate oxazoline/imidazolidene carbene precursor is described. This species is reacted with various metal salts in the presence of a base to generate rhodium and palladium complexes, which are characterized spectroscopically and crystallographically.

Key words: chiral *N*-heterocyclic carbene, rhodium, palladium, oxazolidine, asymmetric catalysis.

Résumé : On décrit la synthèse d'un nouveau précurseur chiral et bidentate du carbène oxazoline/imidazolidène. On a fait réagir cette espèce avec divers sels métalliques, en présence de base, pour générer des complexes du rhodium et du palladium qu'on a caractérisés par des méthodes spectroscopiques et cristallographiques.

Mots clés : carbène chiral *N*-hétérocyclique, rhodium, palladium, oxazolidine, catalyse.

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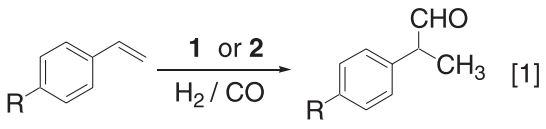
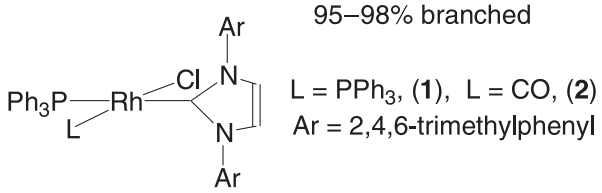
Introduction

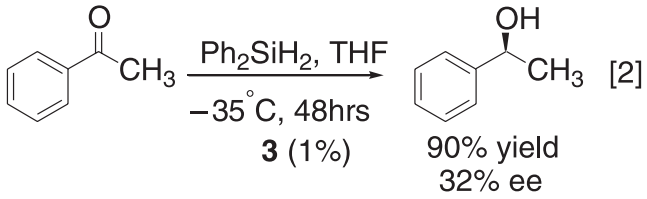
The use of *N*-heterocyclic carbenes as ligands for transition metals has experienced a renaissance of late (1). These ligands display intriguing properties relative to the more commonly employed phosphine ligands. Most importantly, the binding constants of carbene ligands with catalytically active transition metals such as Ru are approximately double that of the related phosphine ligands (2, 3). Carbene ligands have proven to be extremely useful in important reactions such as Ru–catalyzed metathesis reactions (4) and Pd–catalyzed coupling reactions (5).

We have reported that mixed rhodium complexes **1** and **2**, which contain both phosphine and *N*-heterocyclic carbene ligands, are effective catalysts for the hydroformylation of vinyl arenes, giving the branched isomer with up to 98:2 selectivity (eq. [1]) (6). The activity of the carbene/phosphine complex (**2**) was twice that of the related bis-phosphine ([$RhCl(CO)(PPh_3)_2$]) under identical conditions. Furthermore, the carbene complex was more selective for the branched isomer than the bis-phosphine complex (96:4 vs. 88:12). With the regioselectivity and reactivity of these complexes established for the important hydroformylation reaction, we began the more challenging task of preparing chiral versions of these carbene complexes.





Several examples of chiral *N*-heterocyclic carbenes and their corresponding metal complexes have been reported in the literature (7–13) and an increasing number are being tested in catalytic reactions (14–20). In 1997, Herrmann reported the hydrosilylation of acetophenone with chiral monodentate carbene complex **3**, which proceeded in 32% enantiomeric excess (ee) (eq. [2]) (14*b*). The hydrosilylation of cyclohexylmethyl ketone was also examined with chiral



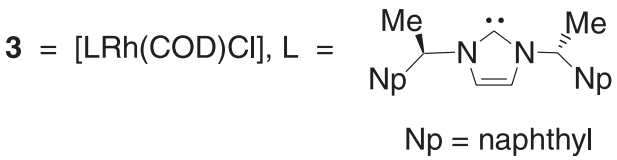


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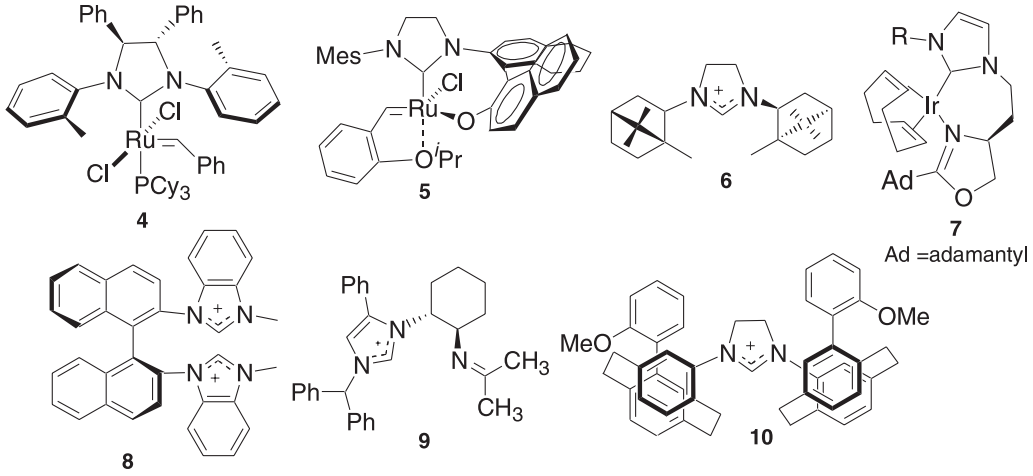
Chart 1. Successful chiral *N*-heterocyclic carbene complexes and carbene precursors.

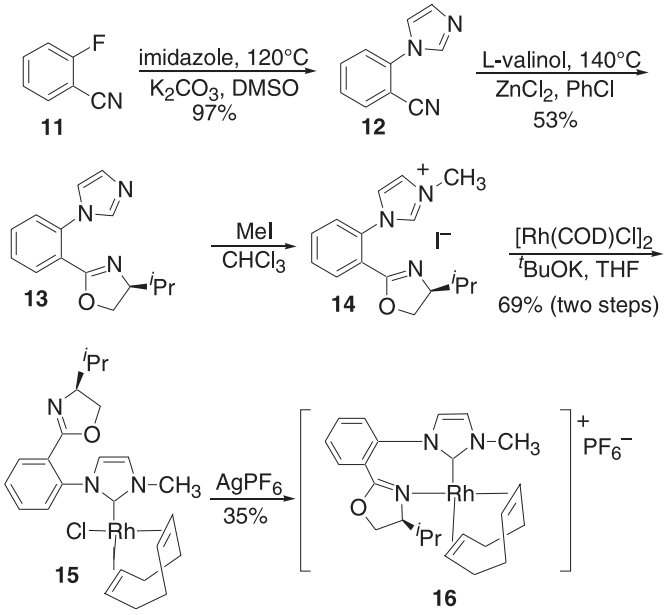


triazolium complexes and proceeded with up to 44% ee (14*c*, *d*).

Grubbs (15), Hoveyda (16), Hartwig (17), and Burgess (18) have reported carbene ligands that give high enantioselectivity for metathesis, arylation of ketones, and hydrogenation reactions, respectively (Chart 1). Recent reports from the groups of Shi (19), Douthwaite (14*h*), and Andrus (20) have described more complex carbenes that provide >90% ee in hydrosilylation, allylic alkylation, and enone arylation, respectively. Although high selectivities have been obtained using these catalysts for specific reactions, substrate generality still needs improvement.

Inspired by the successes of Pfaltz (21) and Brunner (22) with chiral phosphine/oxazoline ligands, we have prepared carbene ligands that have a chiral oxazoline as the second point of ligation. Related oxazoline/carbene complexes have been prepared by Herrmann (14), and complex **7** was introduced by Burgess during this study (18). With the aim of increasing the transfer of chiral information by increasing the rigidity between the carbene and the oxazoline, we embarked on the synthesis of carbene precursor, **14**.

Scheme 1. Synthesis of Rh complex **16**.



Results and Discussion

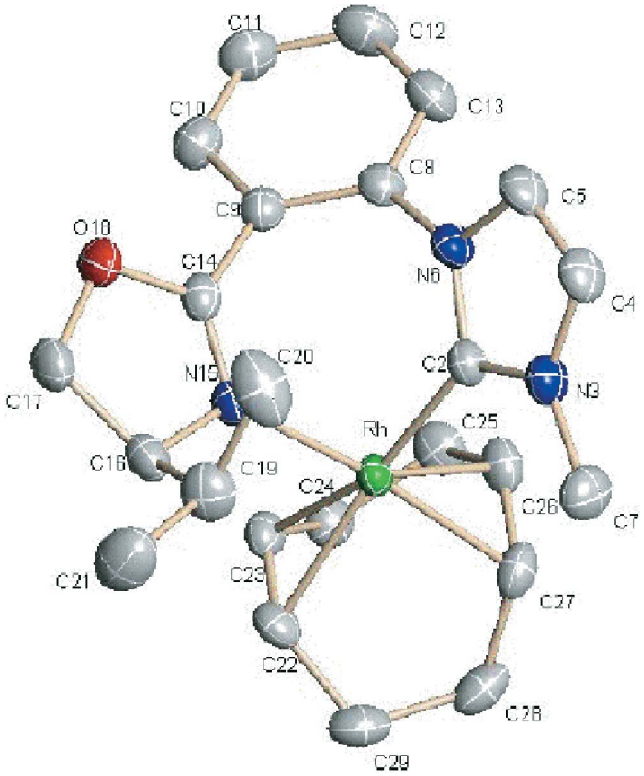
Beginning with commercially available 2-fluorobenzonitrile (**11**), nucleophilic aromatic displacement of the fluoride with imidazole proceeded quantitatively yielding **12** (Scheme 1). Subsequent condensation with optically pure valinol (23) followed by methylation with methyl iodide furnished carbene precursor **14**.

Although attempts to prepare and isolate the free carbene were unsuccessful, rhodium carbene complex **16** could be obtained in two steps from $[Rh(\eta^4\text{-}1,5\text{-}COD)(\mu\text{-}Cl)]_2$ and **14**. Thus, reaction of crude **14** and the rhodium complex in the presence of potassium *t*-butoxide followed by chlorine abstraction with silver hexafluorophosphate generated **16**. The ^{13}C NMR spectrum of this material contained a signal at 181 ppm, corresponding to the ligated carbene carbon, with a distinctive rhodium-carbon coupling constant of 50 Hz.

X-ray quality crystals[4] of **16** were obtained by recrystallizing the air-stable, yellow rhodium complex from dichloromethane/hexane. The crystal structure (see Fig. 1) revealed that the rhodium adopts a distorted square planar geometry with combined angles of 359.2°. The bite angle of the carbene-imidazoline ligand in complex **16** is 84.2°. As expected, the carbene–rhodium bond ((Rh—C(2) = 2.0150(16) Å) is much shorter than the oxazoline nitrogen–rhodium bond ((Rh—N(15) = 2.0954(14) Å). A stronger trans influence of the carbene ligand could be inferred from the longer distances separating the rhodium and the olefinic carbons trans to the carbene ((Rh—C(22) = 2.2085(16) Å, Rh—C(23) = 2.2097(17) Å) relative to those trans to the

[4] Crystal data for **16**: $C_{24}H_{31}F_6N_3OPRh$, crystal size 0.125 mm^3 × 0.150 mm^3 × 0.275 mm^3, orthorhombic, $P2_12_12_1$, a = 11.6588(4) Å, b = 13.3143(5) Å, c = 16.6038(6) Å, $\alpha = \beta = \gamma = 90°$, V = 2577.39(16) Å^3, Z = 4, 2θ (max) = 32.50°, ω and φ scans, 28 697 reflections scanned, 8910 unique reflections (R_{int} = 0.0179), T = 173(2) K, full-matrix least-squares on F^2, wR_2 = 0.0547, R_1 = 0.0231. Full details of the crystallographic analysis of **13** are described in the Supporting information.[6]

Fig. 1. View of the cation of **16**. Thermal ellipsoids are at the 30% probability level and hydrogen atoms have been removed for clarity.



oxazoline nitrogen ((Rh—C(26) = 2.1206(17) Å, Rh—C(27) = 2.1509(18) Å). However, the carbon–carbon double bond trans to the oxazoline ((C(26)—C(27) = 1.390(3) Å) is slightly longer than the C=C bond trans to the carbene ((C(22)—C(23) = 1.374(3)Å).

The corresponding palladium complex **17** could be prepared from either palladium acetate or [Pd(η^4-1,5-COD)Cl_2] (Scheme 2). Specifically, treatment of imidazolium salt **14** with [Pd(η^4–1,5–COD)Cl_2] in the presence of potassium *tert*-butoxide at room temperature, or simply heating **14** in DMSO with palladium acetate gave the same palladium-carbene iodide complex **17** (24). This structure was unambiguously demonstrated by X-ray crystallography[5] (see Fig. 2). The palladium, with the sum of the angles equal to 359.98°, is in a nearly perfect square-planar environment. Like its rhodium analogue, the palladium–iodide bond trans to the carbene (Pd—I(2) = 2.6571(3) Å) is longer than that trans to the oxazoline nitrogen (Pd—I(1) = 2.5657(3) Å). It is also noteworthy that within each asymmetric unit are two independent molecules with almost identical metric parameters. The main difference between them lies in the disposition of the two methyl residues of the isopropyl group (θ (C(21)—C(19)—C(20) = 112.0(4)° and C(41)—C(39)—C(40) = 115.3(4)°).

The catalytic activity of the new chiral rhodium-carbene

Scheme 2. Synthesis of Pd complex **17**.

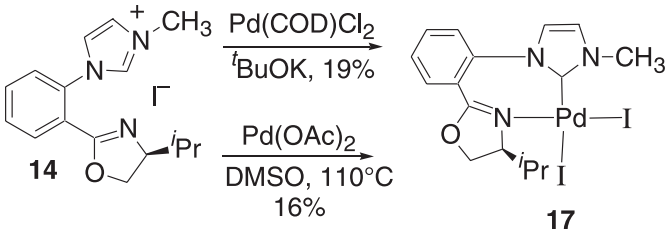
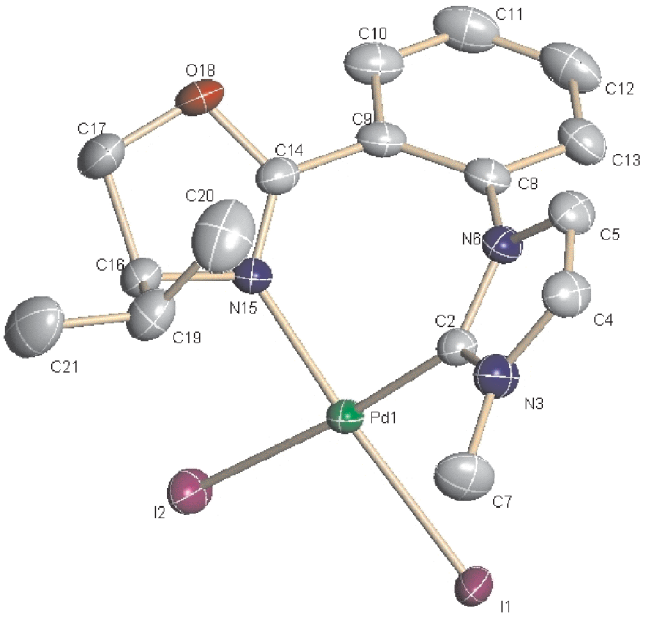


Fig. 2. View of the cation of **17**. Thermal ellipsoids are at the 30% probability level and hydrogen atoms have been removed for clarity.



complex **16** was evaluated in hydroboration and hydrosilylation reactions. Despite the chelating, monomeric form of the catalysts, the enantioselectivity of the described reactions never exceeded 10% ee. It is especially noteworthy that the bidentate ligand proved to be inferior to the monodentate ligand **3** in the hydrosilylation reaction under very similar conditions. One key difference between complex **16** and Herrmann's catalyst **3** is the C_2-symmetry of the latter species. This cannot be the sole reason for the poor performance of this species, as Pfaltz and co-workers (21) and Brunner (22) have shown that C_2-symmetry is not a necessary parameter for asymmetric induction. Regardless, it is clear that Herrmann's catalyst creates a chiral environment more effectively than the carbene derived from **14**.

Our synthetic method requires that the second group introduced onto the imidazole ring be a reactive electrophile. In this case methyl iodide was employed, with the consequence that the coordination site cis to the carbene is relatively unhindered. This may be the reason for the poor asymmetric induction observed in the reactions of complex **16**.

[5] Crystal data for **17**: $C_{32}H_{38}I_4N_3OPd$, crystal size 0.175 mm^3 × 0.250 mm^3 × 0.325 mm^3, monoclinic, *P*2(1), *a* = 8.8335(4) Å, *b* = 14.3771(7) Å, *c* = 15.7653(7) Å, α = γ = 90°, β = 99.630(1)°, *V* = 1973.98(16) Å^3, *Z* = 2, 2θ (max) = 30.00°, ω and φ scans, 19 249 reflections scanned, 10 005 unique reflections (R_{int} = 0.0168), *T* = 296(1) K, full-matrix least-squares on F^2, wR_2 = 0.0450, R_1 = 0.0206. Full details of the crystallographic analysis of **14** are described in the Supporting information.[6]

Conclusions

In conclusion, a chiral, bidentate oxazoline/carbene precursor can be prepared in three simple steps from commercially available starting materials. Herrmann's in situ deprotonation method obviates the need for the synthesis of the free carbene. The Rh catalyst **16** was examined in the hydrosilylation of acetophenone and the hydroboration of styrene. Although the catalyst was active, it gave less than 10% ee under all experimental conditions examined.

Experimental Section

General methods and materials

All solvents were dried according to standard procedures immediately prior to use and, where necessary, were purged using repeated freeze–pump–thaw cycles. Acetophenone was distilled under argon from phosphorous pentoxide. Styrene was fractionally distilled under a partial vacuum and percolated through a column of dry, neutral alumina immediately prior to use. Catecholborane was distilled from a partial pressure of argon to remove $B_2(catechol)_3$ and stored under argon in a Schlenk flask at –25 °C. All other reagents were used as received.

Instrumentation

Proton and ^{13}C NMR spectra were recorded on a Varian 400 MHz instrument using the solvent resonance as the internal standard. Gas chromatography (He carrier, 12.5 psi of head pressure (1 psi = 6.894 757 kPa), 1.14 mL/min flow) was performed with flame ionization (FI) detection using a split/splitless injector (split ratio 50) and hexane solutions. Retention times are given in min. All analyses were carried out using a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-β-cyclodextrin column (30 m, 0.25 mm diameter, 0.25 μm thickness).

Crystallography

Single crystals of **16** were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold nitrogen stream of the goniometer. Single crystals of **17** were coated with Paratone-N oil and mounted on a glass fibre with epoxy glue. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 30 s (for **16**) or 10 s (for **17**) exposure times. The detector distance was 4 cm. The data were reduced (SAINT) (25) and corrected for absorption (SADABS) (26). The structure was solved by direct methods and refined by full-matrix least squares on F^2(SHELXTL) (27). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model for **17**. For **16**, hydrogen atoms were found in Fourier difference maps and refined isotropically. Thermal ellipsoid plots are at the 30% probability level. In some plots, hydrogen atoms have been omitted for clarity.

(2-Cyanophenyl)imidazole (12)

A 100 mL flame-dried, round-bottomed flask was charged with 3.634 g of 2-fluorobenzonitrile (**11**, 30 mmol), 3.064 g of imidazole (45 mmol), and 8.293 g of potassium carbonate (60 mmol) in 30 mL of DMSO. The reaction mixture was stirred at 120 °C under argon for 36 h. The reaction mixture, after cooling to room temperature, was poured into 50 mL of water to precipitate **12** as a white powder. The resulting suspension was filtered, washed, and dried in vacuo to give 4.894 g (97% yield) of the desired product. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.88 (s, 1H), 7.85 (dd, 1H, J = 1.6, 7.6 Hz), 7.77 (dt, 1H, J = 1.6, 7.6 Hz), 7.56 (dt, 1H, J = 1.2, 7.6 Hz), 7.49 (dd, 1H, J = 1.2, 8.4 Hz), 7.38 (t, 1H, J = 1.2 Hz), and 7.30 (t, 1H, J = 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.4, 136.7, 134.5, 134.3, 130.8, 128.4, 125.6, 119.6, 115.8, and 108.1

2-[(4S)-4-Isopropyloxazolyl]phenyl imidazole (13)

Zinc chloride (0.331 g, 2.43 mmol) was fused in a 250 mL flame-dried, round-bottomed flask. Then 4.083 g of (2-cyano-phenyl)imidazole (**12**, 24.3 mmol), 3.756 g of L-valinol (36.4 mmol), and 80 mL of chlorobenzene were added sequentially. The reaction mixture was left stirring at 140 °C under argon for 60 h. Following removal of the volatiles in vacuo, the pinkish residue was taken up in 100 mL of dichloromethane and washed with water (30 mL × 3). The aqueous wash was back-extracted with another 100 mL of dichloromethane. The organic layers were combined and dried over magnesium sulfate. Filtration and concentration in vacuo afforded a viscous oil that was identified as a mixture of unreacted starting material and desired product. Due to its very low solubility in ether, the starting material was removed by trituration with diethyl ether. Filtration, followed by concentration of the filtrate in vacuo afforded 3.276 g of the desired product (53% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.87 (dd, 1H, J = 1.2, 7.6 Hz), 7.62 (d, 1H, J = 0.8 Hz), 7.56 (dt, 1H, J = 2.0, 7.6 Hz), 7.48 (dt, 1H, J = 1.2, 7.6 Hz), 7.34 (dd, 1H, J = 1.2, 8.0 Hz), 7.14 (d, 1H, J = 1.2 Hz), 7.10 (t, 1H, J = 1.2 Hz), 4.22 (dd, 1H, J = 7.6, 8.8 Hz), 4.01–3.89 (m, 2H), 1.80–1.70 (m, 1H), 0.94 (d, 3H, J = 6.8 Hz), and 0.88 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.8, 137.6, 131.5, 131.1, 129.2, 129.1, 128.5, 126.8, 120.6, 120.5, 72.7, 70.7, 32.7, 18.7, and 18.3.

1-(2-[(4S)-4-Isopropyloxazolyl]phenyl)-3-methyl imidazolium iodide (14)

255 mg of 2-[(4*S*)-4-isopropyloxazolyl]phenyl imidazole (**13**, 1.0 mmol) was dissolved in 20 mL of chloroform in a 50 mL round-bottomed flask. Excess methyl iodide (852 mg, 6.0 mmol) was then added dropwise to this mixture. After stirring for 16 h in the dark at room temperature, the volatiles were removed in vacuo to afford 395 mg of the desired product, which could not be purified by column chromatography or recrystallization. The crude material thus obtained was spectroscopically pure and was used in the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ: 9.69 (s, 1H), 8.09–8.06 (m, 1H), 7.86–7.83 (m, 1H), 7.73–7.66 (m, 2H), 7.52–7.48 (brs, 1H), 7.25 (s, 1H), 4.37 (dd, 1H, J = 8.0, 9.2 Hz), 4.27 (s, 3H), 4.02–3.89 (m, 2H), 1.68–1.60 (m, 1H), 0.86 (d, 3H, J = 2.8 Hz), and 0.84 (d, 3H, J = 2.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.9, 138.3, 133.0, 132.5, 131.4, 131.1, 128.3, 124.2, 123.6, 123.0, 73.4, 70.3, 37.6, 32.9, and 18.7 (2).

(η^4-1,5-Cyclooctadiene)(1-(2-[(4S)-4-isopropyloxazolyl]phenyl)-3-methylimidaz-olin-2-ylidene)rhodium-(I)-hexafluorophosphate (16)

In a 100 mL flame-dried, round-bottomed flask, 0.572 g of $[Rh(COD)Cl]_2$ (1.16 mmol) was dissolved in 15 mL of THF. Under vigorous stirring and an argon purge, 325 mg of potassium *tert*-butoxide (2.90 mmol, 1.25 equiv.) was then added. The resulting suspension was stirred at room temperature for 10 min and then transferred via cannula into another 100 mL flame-dried, round-bottomed flask containing 920 mg of 1-(2-[(4*S*)-4-isopropyloxazolyl]phenyl)-3-methyl imidazolium iodide (**14**, 2.32 mmol) dissolved in 5.0 mL of THF. After stirring under argon at room temperature for 40 h, the solvent was removed and the product was purified by column chromatography, eluting with solvent systems of increasing polarity (pure dichloromethane to 10% methanol in dichloromethane). The neutral rhodium(I) complex **12** was isolated as an orange foam in 69% yield (821.2 mg). This was then redissolved in 20 mL of THF and 402.7 mg of silver hexafluorophosphate (1.59 mmol) was added. A white precipitate formed immediately. After stirring for 1 h, the suspension was filtered through a sintered glass funnel and the filtrate concentrated in vacuo. The resulting residue was then purified by column chromatography, eluting with solvent systems of increasing polarity (pure dichloromethane to 2% methanol in dichloromethane). Crystallization from dichloromethane/hexane furnished the desired product as yellow crystals (500 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (dd, 1H, J = 1.6, 8.0 Hz), 7.79 (dt, 1H, J = 1.6, 7.6 Hz), 7.65 (dt, 1H, J = 1.2, 8.0 Hz), 7.48 (dd, 1H, J = 1.2, 8.0 Hz), 7.28–7.24 (m, 2H), 4.88–4.80 (m, 1H), 4.73 (dd, 1H J = 9.2, 10.4 Hz), 4.49–4.41 (m, 1H), 4.27 (dd, 1H, J = 7.2, 9.2Hz), 4.10–4.03 (m, 4H), 3.84–3.77 (m, 1H), 3.71–3.64 (m, 1H), 2.52–2.34 (m, 2H), 2.13–1.63 (m, 6H), 0.88 (d, 3H, J = 6.8 Hz), and 0.79 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 181.1 (d, $J_{Rh\text{-}C}$ = 50.2 Hz), 162.9, 137.7, 133.6, 130.6, 129.1, 126.3, 124.6, 123.73, 123.69, 98.8 (d, $J_{Rh\text{-}C}$ = 7.2 Hz), 95.7 (d, $J_{Rh\text{-}C}$ = 7.2 Hz), 79.3 (d, $J_{Rh\text{-}C}$ = 13.6 Hz), 72.1, 71.4, 71.2 (d, $J_{Rh–C}$ = 5.6 Hz), 37.7, 32.6, 31.9, 30.8, 29.6, 27.9, 17.2, and 17.1.

(1-(2-[(4S)-4-Isopropyloxazolyl]phenyl)-3-methylimidazolin-2-ylidene) palladium-(II)-diiodide (17)

In a 100 mL round-bottomed flask, 348.3 mg of $Pd(COD)Cl_2$ (1.22 mmol) was dissolved in 15 mL of THF. To this was added 161.6 mg of potassium *tert*-butoxide (1.44 mmol). An immediate colour change from yellow to black was observed. After stirring at room temperature for 10 min, the reaction mixture was transferred via cannula into another 100 mL flame-dried, round-bottomed flask containing 474 mg of 1-(2-[(4*S*)-4-isopropyloxazolyl]-phenyl)-3-methyl imidazolium iodide (**14**, 1.2 mmol) in 5.0 mL of THF. The resulting mixture was then stirred for another 24 h. The solvent was then removed and the residue purified by column chromatography, eluting with solvent systems of increasing polarity (6:1 hexane/dichlormethane to pure dichloromethane). The desired product was then crystallized from dichloromethane/hexane yielding dark orange crystals (100 mg, 19% yield).

Alternatively, the same complex can be prepared as follows: In a 100 mL flame-dried, round-bottomed flask, 0.444 g of 1-(2-[(4*S*)-4-isopropyloxazolyl]phenyl)-3-methyl imidazolium iodide (**11**, 1.12 mmol) and 0.251 g of palladium acetate (1.12 mmol) was dissolved in 10 mL of DMSO. The reaction mixture was stirred under argon at 50 °C for 2 h and then at 110 °C for another 48 h. The solvent was then removed and the residue purified by column chromatography, eluting with pure dichloromethane. The desired product was then crystallized from dichloromethane/hexane yielding dark orange crystals (102 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (dd, 1H, J = 1.6, 7.6 Hz), 7.80 (dt, 1H, J = 1.6, 8.0 Hz), 7.66 (dt, 1H, J = 1.2, 8.0 Hz), 7.55 (dd, 1H, J = 1.2, 8.0 Hz), 7.23 (d, 1H, J = 2.0 Hz), 7.19 (d, 1H, J = 2.0 Hz), 5.24 (ddd, 1H, J = 3.2, 3.6, 3.6 Hz, 1H), 4.64 (dd, 1H, J = 9.2, 10.4 Hz), 4.34 (dd, 1H, J = 6.8, 9.2 Hz), 4.16 (s, 3H), 2.40 (m, 1H), 0.88 (d, 3H, J = 6.8 Hz), and 0.60 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.4, 136.9, 134.1, 131.0, 129.5, 126.7, 124.3, 123.8, 122.2, 72.6, 70.4, 40.7, 30.4, 17.9, and 14.8.

Hydroboration of styrene

In a 10 mL flame-dried, round-bottomed flask, 12.5 mg of rhodium complex **9** (0.01 mmol) was suspended in 2 mL of dried, deoxygenated THF. Freshly purified styrene (0.11 mL, 0.96 mmol) was then added to the reaction vessel and the mixture was stirred at room temperature for 10 min. Upon cooling to the desired temperature (0 °C or –30 °C) catecholborane (0.16 mL, 1.5 mmol) was added dropwise as a solution in 1 mL of THF over 20 min. Care was taken to minimize the variation in internal reaction temperature during this addition. After 16 h, 2 mL of methanol was added. The temperature was brought to 0 °C and the boronate ester was treated, under an atmosphere of nitrogen, with 1 mL of a 2 mol/L aqueous sodium hydroxide solution and 0.2 mL of hydrogen peroxide (30% (*w*/*v*)). The resulting black reaction mixture was then diluted with ether and the organic layer was separated. The aqueous layer was extracted further with ether (5 mL × 3). The organic extracts were combined, washed with brine (5 mL), and dried over magnesium sulfate. Filtration through a sintered glass funnel, followed by concentration of the resulting mixture in vacuo yielded the crude alcohols. The linear-to-branched ratio was elucidated from ^{1}H NMR of the crude product mixture with a 30 s delay inserted between each acquisition. Spectroscopically pure 1-phenylethanol was obtained by flash chromatography with 4:1 hexane/ether as eluent and its enantiomeric purity was determined by chiral GC (temperature protocol, 80 °C, 3 min, then increase 1 °C per min to 130 °C; retention times (*R*) = 33.5 min, (*S*) = 35.4 min). The following results were obtained at 0 °C: 58% combined yield, branched:linear = 55:45, ee = 7%.

Hydrosilylation of acetophenone

In a 25 mL flame-dried, round-bottomed flask was dissolved 27 mg of rhodium complex **9** (0.04 mmol) in 2 mL of deoxygenated, dried THF. Then 0.5 mL of freshly purified acetophenone (4.3 mmol) was added to the reaction mixture and the resulting pale yellow solution was cooled to –25 °C. Next 0.8 mL of diphenylsilane (4.3 mmol) was added neat, dropwise, over a period of 15 min and the reaction mixture was stirred under argon at –25 °C for 41 h. Hydrolysis of the silyl ether was accomplished through the addition of 1 mL

of methanol and a few crystals of *p*-toluenesulfonic acid. Complete hydrolysis was achieved after 10 h at room temperature. Spectroscopically pure 1-phenylethanol was obtained by flash chromatography with 4:1 hexane/ether as eluent (141 mg, 27% yield, 34% conversion by NMR). Enantiomeric excess (2%) was determined by chiral GC (temperature protocol, 80 °C, 3 min, then increase 1 °C per min to 130 °C; R = 33.5 min, S = 35.4 min).

Supplementary material

Supporting information available lists details of the crystal structure determination for compounds **13** and **14**.[6]

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