Chiral N-Heterocyclic Carbenes with Restricted Flexibility in Asymmetric Catalysis†

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A chiral C_2-symmetric diamine was prepared from (*S*)-3-phenyl-3,4-dihydroisoquinoline by the virtue of asymmetric transformation. Rhodium and iridium complexes of chiral N-heterocyclic carbenes with restricted flexibility derived from 3,3′-substituted partially reduced biisoquinoline were obtained by transmetalation from the corresponding silver(I) complexes. Unexpected double-bond formation in the carbene ligand has occurred during a transmetalation step. The structures of these complexes were verified by X-ray diffraction. Metal complexes of these N-heterocyclic carbenes were applied to the asymmetric hydrogenation of methyl 2-acetamidoacrylate. Good enantioselectivities of up to 67% ee were achieved.

Introduction

N-heterocyclic carbenes (NHC) have recently emerged as an important family of ligands with strong σ-donor electronic properties.[1] Since the concurrent reports of the first metal−NHC complexes in 1968 by Öfele[2] and by Wanzlick[3] and the isolation of the first stable free carbenes in 1991 by Arduengo et al.,[4] many catalyst systems with NHC spectator ligands have been described.[5]

A logical extension of this development is the application of NHC ligands in stereoselective catalysis.[6] In general, the chiral induction of NHC ligands remained low, which is probably due to the rapid internal rotation of the chiral substituents around the C−N axis. This leaves the active chiral space at the metal center relatively ill-defined. There are several papers reporting that complexes with restricted rotation around the C−N axis are superior to the classical chiral carbene ligands reported by our group in 1996.[7] In a recent paper, we have reported the development of new chiral carbene ligands derived from the partially reduced biisoquinoline **2** (Figure 1).[8] We reasoned that incorporation of the substituents into the 3,3′-positions of this carbene ligand should lead to the new useful C_2-symmetric rigid chiral architecture **3**. It is anticipated that the greater rigidity afforded by the structural motif of **3** will result in useful catalysts for asymmetric transformations (see Figure 1).

Results and Discussion

Synthesis of Ligands. We began our investigations with (*S*)-3-phenyl-3,4-dihydroisoquinoline (**7**), which was synthesized by a modification of the literature procedures.[9] The optical purity of **7** obtained in such a way was determined by a comparison of the optical rotation with the literature data.[10] In analogy to the procedures for the coupling of substituted imines into diamines, **7** was treated with zinc/TMSCl in acetonitrile (Scheme 1).[11]

Because of the 4 asymmetric carbon atoms in the resulting diamine **8**, it can have as many as 14 possible stereoisomers. Since optically pure **7** has been employed, only 3 isomers were

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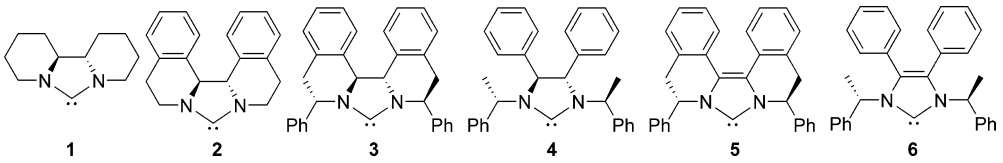
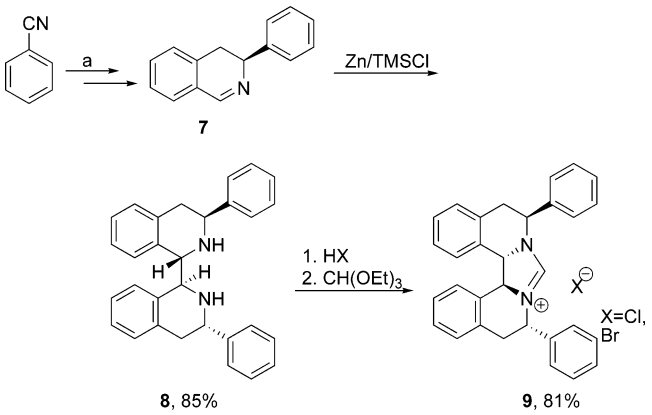


Figure 1. Carbene ligands in rhodium and iridium complexes.

Scheme 1 . Synthesis of Imidazolinium Salts[a]



[a] Legend: (a) (1) $PhCH_2MgBr$; (2) $LiAlH_4$; (3) (+)-tartaric acid; (4) EtOCHO; (5) $(COCl)_2$, $FeCl_3$; (6) H_2SO_4/MeOH.

expected to be obtained. However, according to ^1H and ^{13}C NMR spectra of the resulting product, only a single diastereomer was obtained. For example, just one singlet appears at 4.49 ppm, attributable to the protons in 1,1′-positions. Accordingly, only 13 signals were observed in the ^{13}C spectrum of this compound, as well as in its corresponding hydrobromide and hydrochloride salts.

For the determination of the absolute stereochemistry, crystals of **8** suitable for X-ray diffraction were grown out of ethyl acetate (Figure 2). Only one chiral diastereomer was detected.

The enantiomeric purity of **8** was readily accessible by the reaction of the diamine **8** with 1 equiv of PCl_3 in the presence of an excess of *N*,*N*-dimethylaniline followed by 1 equiv of l-menthol and oxidation with elementary sulfur in an NMR tube and subsequent measurement of the ^{31}P spectrum (Scheme 2). On the basis of these data, we estimate the enantiomeric purity of **8** to be better than 95%. We therefore assume that the phenyl group in the starting material acted as a chiral auxiliary, allowing only one possible enantiomer of **8** to be formed. The scope of this novel asymmetric transformation is under investigation in our laboratory.

Diamine **8** reacted easily with triethyl orthoformate in presence of hydrochloric or hydrobromic acid, yielding the corresponding imidazolinium salts **9-Cl** and **9-Br**. The ^1H and ^{13}C NMR spectra of **9-Cl** and **9-Br** are indicative of C_2-symmetric compounds. For example, **9-Br** exhibits a strong singlet at δ 5.14 ppm that is attributable to adjustment protons of two tetrahydroisoquinoline rings. In the ^1H NMR spectra of **9-Cl** and **9-Br**, the imidazolinium protons appear at 10.86 ppm. The ^{13}C NMR shift of the N−C−N sp^2 carbons appears at 154.98 ppm for **9-Cl** and **9-Br**. **9-Cl** and **9-Br** are air-stable, hygroscopic white solids that are soluble in water, alcohols, chlorinated solvents, and THF but are insoluble in diethyl ether and hydrocarbons.

To evaluate the advantages of the new rotationally hindered ligands, a known imidazolinium salt with unrestricted flexibility around the C−N axis (**4a**), as well as salts without substituents

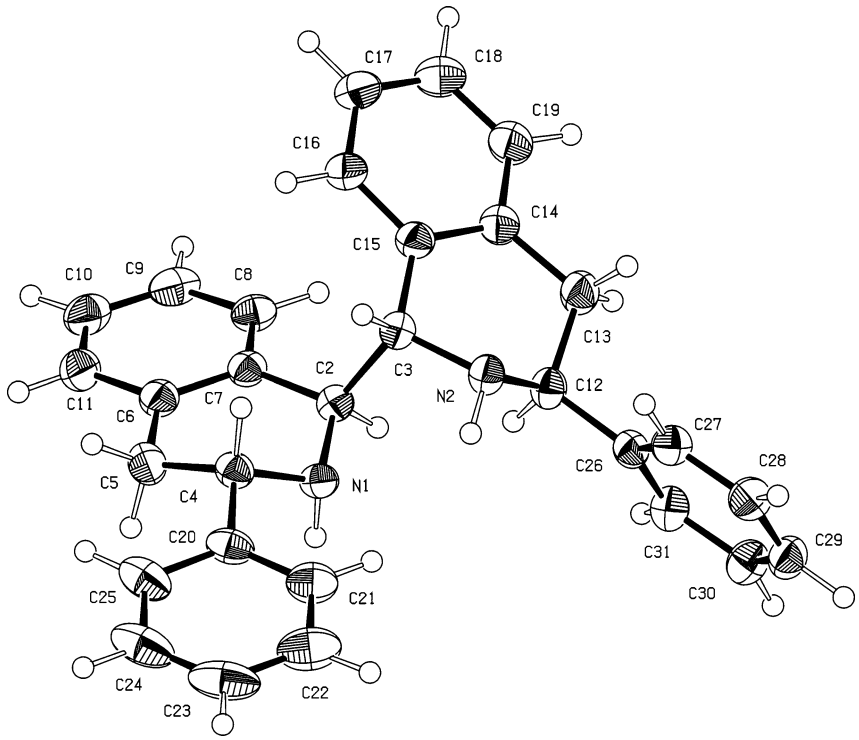
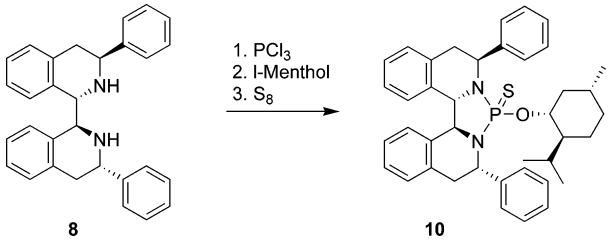
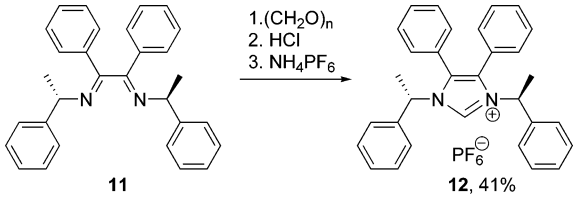


Figure 2. ORTEP style representation of the molecular structure of **8**, as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): N1−C2 = 1.473(1), N1−C4 = 1.468(2), N2−C3 = 1.473(1), N2−C12 = 1.469(1), C2−C3 = 1.577(1); C2−N1−C4 = 113.66(8), C3−N2−C12 = 112.63(9), N1−C2−C3 = 106.19(8), N2−C3−C2 = 109.20(8); N1−C2−C3−N2 = 60.9(1).

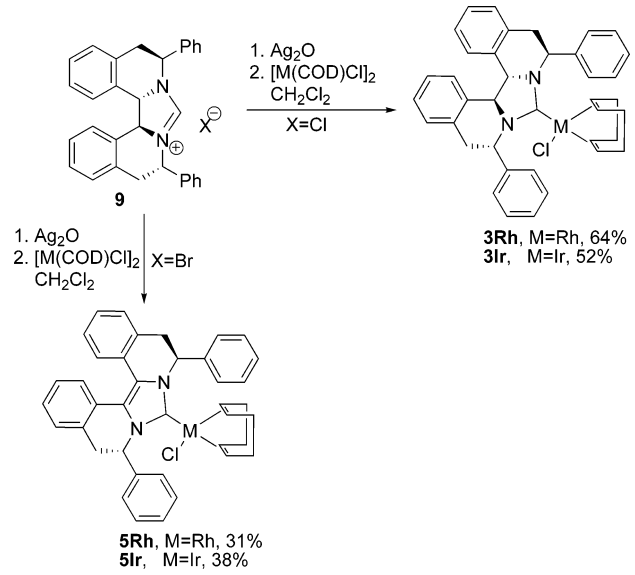
Scheme 2 . Determination of the Optical Purity of 8



Scheme 3 . Synthesis of 12



Scheme 4 . Synthesis of Rhodium and Iridium Complexes 3 and 5, Respectively



in the 3,3′-positions (**1a** and **2a**), were also synthesized. We have also synthesized the novel imidazolium salt **12**. In analogy to procedures for the transformation of glyoxal-derived diimines into imidazolium salts, **11** was treated with chloromethyl ethyl ether in THF at 40 °C. However, no reaction was observed. Fortunately, the reaction of bisimine **11** with paraformaldehyde led to clean conversion to the corresponding new chiral imidazolium salt **12** (Scheme 3).

Synthesis of Rhodium and Iridium Complexes. We attempted to prepare rhodium(I) and iridium(I) complexes of **9** using a mild transmetalation method developed by Wang and Lin.[12] Reaction of imidazolinium precursors with silver(I) oxide in dichloromethane at room temperature in the dark gave rather unstable silver complexes (NMR evidence) that decomposed too quickly to be isolated. Direct addition of $[M(COD)Cl]_2$ (M = Rh, Ir) to freshly prepared solutions of silver complexes yielded the corresponding chiral complexes of **3** and **5**; the products were purified by chromatography on silica gel (Scheme 4). The nature of the counterion in the imidazolinium salt **9** surprisingly plays an important role. With bromide as counterion, unexpected double-bond formation in the carbene ligand

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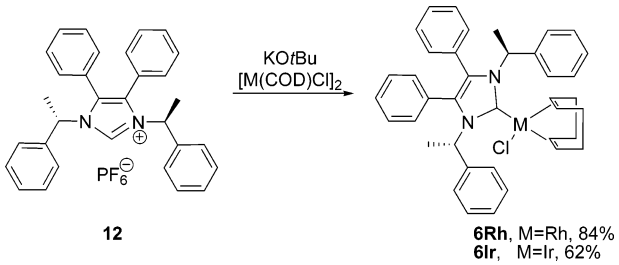
Scheme 5 . Synthesis of NHC Complexes 6



takes place during the transmetalation step. No such reaction occurs with the chloride. This was confirmed by ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction studies. For example, the chemical shift of the carbene carbon in the ^{13}C NMR of the rhodium complex **5Rh** (182.95 ppm) is diagnostic for an unsaturated imidazolin-2-ylidene ligand. On the other hand, the chemical shift of the carbene carbon in the ^{13}C NMR of rhodium complex **3Rh** (210.51 ppm) clearly indicates the saturated nature of the carbene.[13] The mechanism of this novel and unexpected transformation is not clear at the moment.

The synthesis of rhodium and iridium complexes bearing NHC ligands with unrestricted flexibility around the C−N axis, as well without substituents in 3,3′-positions, works either according to the transmetalation method of Wang and Lee (**1Rh** and **1Ir**, **2Rh** and **2Ir**, **4Rh** and **4Ir**) or following the established procedures for the preparation of monocarbene complexes by in situ deprotonation of imidazolium salts with KO*t*Bu (**18**) (Scheme 5).

All complexes are very soluble in dichloromethane and THF and insoluble in saturated hydrocarbons. Their identities have been confirmed by elemental analysis, ^{1}H and ^{13}C NMR, and mass spectroscopy. The complexes are air-stable in the solid state and in solution, at least for several days.

Structural Studies. Crystals were grown by layering a dichloromethane solution of **5Rh** with pentane. The X-ray single-crystal diffraction study of **5Rh** (Figure 3) reveals the expected square-planar arrangement of the ligands at the metal center, with the NHC plane orthogonal to the coordination plane. Selected bond lengths and angles are given in Table 1. The imidazolin-2-ylidene is almost completely planar, with a C2−C3 bond distance of 1.369(3) Å, which is clearly indicating the unsaturated nature and aromatic stabilization of the ligand.

The coordination around the metal center is square planar. The M−C1 bond distance (2.021(2) Å) is typical for this type of carbene coordination.[14] The different trans influences of the carbene and chloride ligands lead to different distances between the coordinated COD carbon atoms and the metal. As a result of the longer distance to the metal, the C36═C37 double bond trans to the NHC ligand is shorter (1.366(4) Å) than the C32═C33 bond (1.403(4) Å), owing to reduced back-donation from the metal into its π^* orbitals.

Catalytic Studies. Rhodium and iridium complexes of the novel NHC ligands **1**−**6** were applied to the asymmetric hydrogenation of methyl 2-acetamidoacrylate. All of the complexes showed significant activities, resulting in complete conversions after 16 h at room temperature and 30 bar of H_2. Rhodium complexes did not show any optical induction. Iridium

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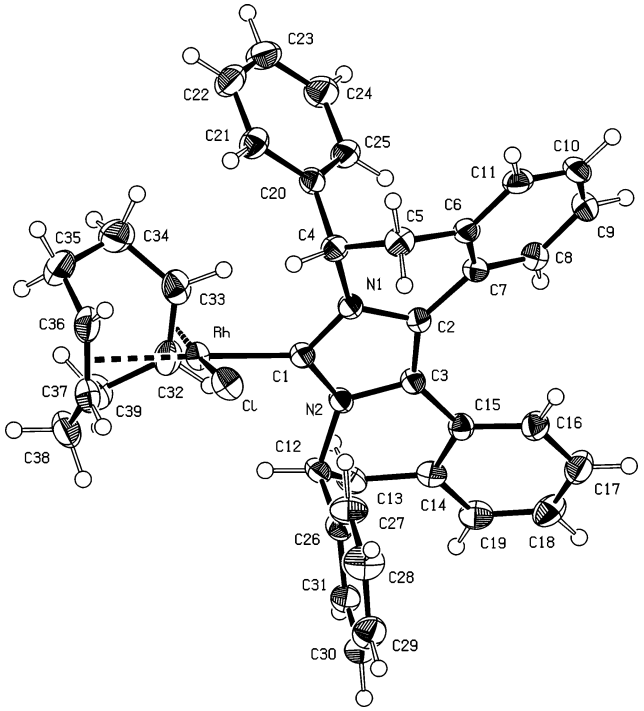

Figure 3. ORTEP style representation of the molecular structure of **5Rh**, as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at the 50% probability level. All hydrogen atoms are placed in ideal positions (riding model).

Table 1. Selected Bond Distances (Å) and Angles (deg) for 5Rh and *rac*-5Rh

	5Rh[a]	*rac*-**5Rh**[a,b]
Rh−Cl	2.3897(7)	2.3758(10)
Rh−C1	2.021(2)	2.005(3)
Rh−Cg1	1.998	1.994
Rh−Cg2	2.117	2.110
N1−C1	1.351(3)	1.361(5)
N2−C1	1.363(3)	1.362(4)
C2−C3	1.369(3)	1.368(4)
Cl−Rh−C1	89.57(8)	86.97(10)
Cl−Rh−Cg1	173.86	172.84
Cl−Rh−Cg2	92.07	91.71
C1−Rh−Cg1	91.17	94.21
C1−Rh−Cg2	177.47	176.57
Cg1−Rh−Cg2	87.40	87.50
Rh−C1−N1	126.2(2)	125.7(2)
Rh−C1−N2	130.3(2)	130.9(3)
N1−C1−N2	103.6(2)	103.2(3)

[a] Cg1 and Cg2 denote the midpoints of C32−C33 and C36−C37, respectively. [b] Racemic **5Rh** was synthesized by the analogous procedure utilizing racemic **7**.

Table 2. Asymmetric Hydrogenation of Methyl 2-Acetamidoacrylate with Complexes Ir(COD)Cl(ligand)

ligand	ee for *N*-acetylalanine methyl ester (%)
1	3
2	22
3	60
4	1
5	67
6	0

complexes bearing carbene ligands with restricted flexibility (**3** and **5**), however, yielded moderate to good enantioselectivity (Table 2). Enantiodiscrimination caused by iridium NHC complexes led to the *R* isomer of methyl 2-acetamidopropanoate. Changing the solvent, increasing the catalyst loading, and varying the temperature gave no benefit. As is evident from Table 2, complexes bearing the restricted NHC ligands **3** and **4** are superior to the analogous complexes bearing the 3,3′-unsubstituted NHC ligands **1** and **2** and unrestricted carbenes **4** and **6**. Better results obtained with the unsaturated NHC ligand **5** are likely due to the strict rigidity of this ligand as well as to the decrease in the quantity of chirality centers in the molecule as compared to **3**. The lower number of stereogenic centers in **5** (two vs four in **3**) probably results in a smaller number of mismatched interactions with a substrate in the course of catalytic reactions. To the best of our knowledge, these enantioselectivities presently represent the optimum results obtained with monodentate singly coordinating carbene ligands reported in the literature.

Conclusion

The new chiral 3,3′-substituted biisoquinoline-based NHC ligands **3** and **4** have been synthesized. Neutral rhodium and iridium complexes were obtained via in situ transmetalation from silver complexes. An unexpected double-bond formation in the NHC ligand during the transmetalation step was observed. The complexes were catalytically active in the asymmetric hydrogenation of methyl 2-acetamidoacrylate; good enantioselectivities were achieved with the respective iridium complexes. Our efficient synthesis of these ligands now makes them readily available for future work in stereoselective catalysis. The greater rigidity afforded by the structural motifs of **3** and **5** leads to promising catalysts for various kinds of asymmetric transformations. The synthesis of a larger library of 3,3′-subsituted biisoquinoline NHC ligands is currently underway in our laboratory.

Experimental Section

General Methods. Enantiomerically pure (−)-(*S*)-3-phenyl-3,4-dihydroisoquinoline (**7**), (1*R*,2*R*,1′*R*,1″*R*)-*N*,*N*′-bis(α-phenylethyl)-1,2-diphenyl-1,2-ethylenediamine (**19**), (*R*,*E*)-*N*-((*E*)-1,2-diphenyl-2-((*R*)-1-phenylethylimino)ethylidene)-1-phenylethanamine (**12**), (−)-[1,2,3,4,8,9,10,11,(*S*)-11a,(*S*)-11b-decahydrodipyrido[1,2-*c*;2′,1′-*e*]imidazol-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium(I) (**1Rh**) and -iridium(I) (**1Ir**), and 5,6,8,9,(*R*)-13b,(*S*)-13c-hexahydro-7a-aza-6a-azoniadibenzo[*c*,*g*]fluoren-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium(I) (**2Rh**) and -iridium(I) (**2Ir**) were prepared according to literature procedures.[8,15] All other materials were obtained commercially and were used as received, except as noted. All syntheses were performed under an atmosphere of nitrogen, using solvents dried on an alumina-based solvent purification system. NMR spectra were recorded on a JEOL JMX-GX 400 spectrometer operating at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), and 161 MHz (^{31}P NMR) at room temperature. Chemical shifts are given in ppm. The spectra are calibrated to the residual protons of the solvents or 85% H_3PO_4, as an external standard (^{31}P). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, sept = septet, m = multiplet, br = broad signal. MS spectra were measured at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 mass spectrometer using the CI or FAB technique. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. The ee values in catalysis were determined by chiral GC using a Macherey-Nagel Hydrodex β6 TBDM column.

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(+)-(3*S*,3′*S*)-Diphenyl-(1*S*,1′*S*)-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline (8). Zinc (12.62 g, 0.19 mol) and 1,2-dibromoethane (0.17 mL, 1.9 mmol) were heated to reflux in acetonitrile (30 mL) for 1 h. The mixture was cooled to room temperature, chlorotrimethylsilane (0.2 mL) was added, and this mixture was stirred for a further 45 min. (−)-(*S*)-3-Phenyl-3,4-dihydroisoquinoline (**7**; 20.00 g, 96.5 mmol) was added in one portion, and chlorotrimethylsilane (24.4 mL, 0.19 mol) was added dropwise to maintain a temperature between 25 and 30 °C. The reaction mixture was stirred for a further 12 h, after which NH_4OH (40% aqueous solution, 50 mL) and saturated aqueous NH_4Cl solution (50 mL) were added with external cooling (ice bath). The zinc was removed by filtration, and the organic phase was separated. The remaining aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL), and all the organic phases were combined and dried over sodium sulfate. A large quantity of Et_2O (0.75 L) was added, and the colorless precipitate was filtered off. The solution was concentrated under reduced pressure and recrystallized from ethyl acetate (15 mL) to give the title compound as large prismatic crystals (17.23 g, 85%). Mp: 139−140 °C. $[\alpha]_D^{25} = +61.7°$ ($c = 0.134$, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.45−7.26 (10H, m); 7.16 (4H, d, $J = 4$ Hz); 6.99 (2H, sept, $J = 4.0$ Hz); 6.57 (2H, d, $J = 7.6$ Hz, 2H); 4.55 (2H, X part of ABX system, $J = 4.8$, 8.8 Hz); 4.49 (2H, s); 3.20 (2H, B part of ABX system, $J = 4.8$, 16.4 Hz); 3.04 (2H, A part of ABX system, $J = 8.8$, 16.4 Hz); 2.35 (2H, br). ^{13}C NMR ($CDCl_3$): δ 144.4, 135.9, 135.1, 129.1, 128.7, 128.6, 127.2, 126.9, 126.7, 125.2, 59.0, 52.8, 36.8. Anal. Calcd for $C_{30}H_{28}N_2$ (416.54): C, 86.50; H, 6.78; N, 6.72. Found: C, 86.73; H, 6.95; N, 6.51. IR (KBr): ν_{max}/cm^{-1} 2925, 2853, 2483, 1453, 745, 698. MS: *m*/*z* 416.2 (5%, M^+), 208.1 (100%), 131.1 (10%).

The enantiomeric ratio of the material was obtained by conversion to **10**.

7(*R*)-((2(*S*)-Isopropyl-5(*R*)-methylcyclohexyl)oxy)-6,8-diphenyl-5,8,9,13c-hexahydro-6a,7a-diaza-7-phosphadibenzo[*c*,*g*]fluorene 7-Sulfide (10). In a dried NMR tube were placed diamine (0.05 g, 0.12 mmol) and $CDCl_3$ (0.5 mL). The tube was shaken until complete dissolution. *N*,*N*-Dimethylaniline (76 μL, 0.6 mmol) was added with a microsyringe, followed by addition of PCl_3 (10 μL, 0.12 mmol), also with a microsyringe. The NMR tube was shaken, and an exothermic reaction took place. L-Menthol (20 mg, 0.13 mmol) was added in one portion. The NMR tube was shaken, an excess of sulfur (40 mg, 1.2 mmol) was added, and the ^{31}P spectrum was recorded. ^{31}P NMR (3*S*,3′*S*,1*S*,1′*S* isomer): δ 79.49 (s). ^{31}P NMR (3*R*,3′*R*,1*R*,1′*R* isomer): δ 77.19 (s). The material was a 99:1 mixture of 3*S*,3′*S*,1*S*,1′*S* and 3*R*,3′*R*,1*R*,1′*R* isomers.

(+)-6(*S*),8(*S*)-Diphenyl-5,6,8,9,13b(*S*),13c(*S*)-hexahydro-7a-aza-6a-azoniadibenzo[*c*,*g*]fluorene Bromide (9-Br). To a solution of amine **8** (2.00 g, 4.80 mmol) in methanol was added concentrated hydrobromic acid (20 mL). The resulting solution was stirred overnight, and the solvent was removed in vacuo. The remaining colorless substance, 20 mL of triethyl orthoformate, and 1 drop of 96% formic acid were heated to 100 °C for 60 h. When the mixture was cooled to room temperature, a colorless solid precipitated, which was collected by filtration, washed with 10 mL of dry Et_2O, and recrystallized from acetone/Et_2O. Yield: 1.97 g, 81%. Mp: 270−271 °C. $[\alpha]_D^{25} = +172.9°$ ($c = 0.129$, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 10.86 (1H, s); 7.54−7.13 (18H, m); 5.89 (2H, X part of ABX system, $J = 6.4$, 2.4 Hz); 5.14 (2H, s); 3.68 (2H, B part of ABX system, $J = 17.2$, 6.4 Hz); 3.41 (2H, A part of ABX system, $J = 6.4$, 17.2 Hz). ^{13}C NMR ($CDCl_3$): δ 154.98, 135.49, 132.74, 132.69, 129.47, 129.19, 129.01, 128.09, 127.59, 124.14, 62.71, 55.73, 33.32. Anal. Calcd for $C_{31}H_{27}BrN_2$ (507.5): C, 73.37; H, 5.36; N, 5.52. Found: C, 73.26; H, 5.23; N, 5.12. IR (KBr): ν_{max}/cm^{-1} 1493, 1451, 1383, 1320, 1112, 762, 702. MS: *m*/*z* 427.2 (100%, $M^+ - Br$).

General Procedure for the Preparation of NHC Complexes. To a solution of the imidazolinium salt (1.00 mmol) in CH_2Cl_2 (25 mL) was added silver(I) oxide (115.9 mg, 0.50 mmol) in one portion. The suspension was stirred for 3 h in the darkness, during which time the black color gradually diminished. The reaction mixture was filtered through a small pad of Celite, and [M(COD)Cl]$_2$ (0.50 mmol) was added in one portion. A white precipitate of silver salt was formed almost immediately. The reaction mixture was stirred for an additional 16 h. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent.

(+)-[6(*S*),8(*S*)-Diphenyl-5,6,8,9,13b(*S*),13c(*S*)-hexahydro-6a,-7a-diazadibenzo[*c*,*g*]fluoren-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium(I) (3Rh). Yield: 460 mg, 64% as a yellow solid. Mp: 149−150 °C. $[\alpha]_D^{25} = +81.7°$ ($c = 0.046$, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.63 (2H, d, $J = 7.6$ Hz); 7.37−7.14 (12H, m); 7.09 (1H, t, $J = 7.4$ Hz); 6.93 (1H, d, $J = 8$ Hz); 6.83−6.80 (2H, m); 5.28 (1H, s); 5.18−5.07 (2H, m); 4.89 (1H, d, $J = 5.6$ Hz); 4.63 (1H, d, $J = 5.6$ Hz); 4.22−4.17 (1H, m); 3.70−3.64 (4H, m); 3.44 (1H, d, $J = 16.8$ Hz); 2.51−2.30 (5H, m); 2.04−1.91 (4H, m). ^{13}C NMR ($CDCl_3$): δ 210.51 (d, $J = 47.4$ Hz), 138.98, 137.76, 136.61, 135.63, 133.85, 133.42, 129.93, 129.46, 128.91, 128.71, 128.11, 127.88, 127.82, 127.56, 127.48, 127.34, 127.06, 127.05, 124.91, 124.75, 100.26 (d, $J = 6.2$ Hz), 100.11 (d, $J = 6.2$ Hz), 70.01 (d, $J = 14.5$ Hz), 66.76 (d, $J = 13.8$ Hz), 64.17, 63.43, 57.58, 56.80, 33.17, 32.95 (d, $J = 9.2$ Hz), 32.71, 28.85, 28.46. Anal. Calcd for $C_{39}H_{38}ClN_2Rh$ (673.1): C, 69.59; H, 5.69; N, 4.16. Found: C, 69.35; H, 5.46; N, 4.02. IR (KBr): ν_{max}/cm^{-1} 2923, 2856, 1494, 1458, 1385, 756, 698. MS: *m*/*z* 672.2 (10%, M^+), 426.2 (100%, $M^+ - Cl - COD - Rh$), 207.1 (85%).

(+)-[6(*S*),8(*S*)-Diphenyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[*c*,*g*]fluoren-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium(I) (5Rh). Yield: 310 mg, 31% as a yellow solid. Mp: 162−163 °C. $[\alpha]_D^{25} = +93.2°$ ($c = 0.042$, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.94 (2H, t, $J = 5.2$ Hz); 7.26−7.13 (10H, m); 7.06−6.99 (5H, m); 6.49 (1H, d, $J = 5.6$ Hz); 4.92−4.83 (4H, m); 3.78 (2H, ddd, $J = 6.4$, 8.8, 42 Hz); 3.86 (1H, d, $J = 15.2$ Hz); 3.22−3.05 (2H, m); 2.71−2.68 (1H, m); 2.46−2.29 (2H, m); 2.15−2.06 (2H, m); 1.88−1.80 (2H, m); 1.72−1.63 (2H, m). ^{13}C NMR ($CDCl_3$): δ 182.95 (d, $J = 50.24$ Hz), 141.37, 138.84, 132.13, 131.94, 129.82, 129.58, 128.73, 128.53, 128.29, 128.20, 127.55, 127.47, 127.11, 126.99, 126.89, 126.49, 125.79, 124.91, 123.68, 123.51, 99.09 (d, $J = 6.9$ Hz), 98.41 (d, $J = 6.9$ Hz), 70.24 (d, $J = 14.5$ Hz), 68.04, 66.44 (d, $J = 14.5$), 59.33, 58.24, 58.04, 38.38, 37.29, 33.05, 32.52, 29.37, 28.01. Anal. Calcd for $C_{39}H_{36}ClN_2Rh$ (671.04): C, 69.80; H, 5.41; N, 4.17. Found: C, 69.62; H, 5.37; N, 4.41. IR (KBr): ν_{max}/cm^{-1} 2957, 2924, 2847, 1261, 1095, 1030, 804, 758, 698. MS: *m*/*z* 670.2 (15%, M^+), 424.2 (100%, $M^+ - Cl - COD - Rh$).

(+)-[6(*S*),8(*S*)-Diphenyl-5,6,8,9,13b(*S*),13c(*S*)-hexahydro-6a,-7a-diazadibenzo[*c*,*g*]fluoren-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chloroiridium(I) (3Ir). Yield: 520 mg, 52% as a yellow solid. Mp: 181−182 °C. $[\alpha]_D^{25} = +98.3°$ ($c = 0.051$, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.57 (2H, d, $J = 7.2$ Hz); 7.37−7.09 (13H, m); 6.95 (1H, d, $J = 8$ Hz); 6.65 (1H, d, $J = 4.4$ Hz); 6.59 (1H, d, $J = 6$ Hz); 4.92 (1H, d, $J = 5.2$ Hz); 4.76−4.71 (1H, m); 4.68−4.64 (2H, m); 4.06 (1H, dd, $J = 6.4$, 16.4 Hz); 3.69−3.59 (2H, m); 3.44−3.36 (2H, m); 3.29−3.27 (1H, m); 2.37−2.12 (5H, m); 1.85−1.61 (5H, m). ^{13}C NMR ($CDCl_3$): δ 205.05, 138.77, 137.71, 136.52, 135.78, 133.78, 133.41, 129.88, 129.49, 128.86, 128.65, 127.93, 127.88, 127.78, 127.58, 127.45, 127.31, 127.13, 127.08, 124.91, 124.87, 86.81, 86.21, 64.33, 63.43, 57.35, 56.70, 53.58, 50.79, 33.86, 33.39, 32.82, 31.87, 29.53, 28.82. Anal. Calcd for $C_{39}H_{38}ClIrN_2$ (762.4): C, 61.44; H, 5.02; N, 3.67. Found: C, 61.09; H, 5.07; N, 3.61. IR (KBr): ν_{max}/cm^{-1} 2927, 2851, 1460, 1383, 1107, 741, 697. MS: *m*/*z* 760.2 (10%, M^+), 617.2 (7%, $M^+ - Cl - COD$), 424.2 (100%, $M^+ - Cl - COD - Ir$).

(+)-[6(*S*),8(*S*)-Diphenyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[*c*,*g*]fluoren-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chloroiri-

dium(I) (5Ir). Yield: 290 mg, 38% as a yellow solid. Mp: 174−175 °C. $[\alpha]_D^{25} = +104.2°$ ($c = 0.063$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.83 (2H, t, $J = 4.7$ Hz); 7.48−7.06 (12H, m); 7.01−6.68 (3H, m); 6.57 (1H, d, $J = 5.1$ Hz); 5.12−4.96 (4H, m); 4.12 (2H, dd, $J = 6.1, 7.9$ Hz); 3.99 (1H, m); 3.41−3.21 (2H, m); 2.83−2.74 (1H, m); 2.59−2.13 (4H, m); 1.95−1.72 (4H, m). ^{13}C NMR ($CDCl_3$): δ 179.23, 146.86, 141.15, 138.99, 137.53, 131.64, 131.33, 130.95, 130.28, 129.92, 129.47, 128.84, 128.16, 127.39, 127.01, 126.92, 126.37, 126.09, 125.12, 124.93, 124.84, 87.43, 86.12, 79.61, 65.75, 64.02, 62.64, 60.83, 59.73, 37.01, 36.52, 35.09, 34.71, 28.00, 26.79. Anal. Calcd for $C_{39}H_{36}ClN_2Ir$ (760.4): C, 61.60; H, 4.77; N, 3.68. Found: C, 61.95; H, 4.58; N, 3.51. IR (KBr): ν_{max}/cm^{-1} 3006, 2946, 2632, 1315, 1104, 1001, 812, 763, 687. MS: *m*/*z* 760.2 (21%, M^+), 424.2 (100%, $M^+ - Cl - COD - Ir$).

(−)-[(4*R*,5*R*)-4,5-Diphenyl-1,3-bis-(1(*S*)-phenylethyl)-4,5-dihydro-3*H*-imidazolin-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]-chloroiridium(I) (4Ir). Yield: 490 mg, 72% as a yellow solid. Mp: 221−222 °C. $[\alpha]_D^{25} = -17.4°$ ($c = 0.23$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.82 (2H, d, $J = 9.2$ Hz); 7.36−7.25 (2H, m); 7.11−7.09 (2H, m); 7.04−7.01 (6H, m); 6.89 (5H, d, $J = 11.2$ Hz), 6.60 (2H, d, $J = 9.2$ Hz); 6.49 (1H, q, $J = 7.2$ Hz); 4.97−4.93 (1H, m); 4.84−4.99 (1H, m); 4.39 (1H, d, $J = 3.6$ Hz); 4.26 (1H, d, $J = 3.2$ Hz); 3.77 (1H, t, $J = 8.2$ Hz); 3.53−3.48 (1H, m); 2.57−2.29 (6H, m); 1.90−1.86 (4H, m); 1.78 (3H, t, $J = 7.2$ Hz); 1.73 (3H, t, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 206.61, 141.92, 140.37, 138.67, 129.12, 128.91, 128.66, 128.46, 128.37, 127.79, 127.55, 127.51, 127.37, 127.28, 127.03, 126.08, 125.02, 86.09, 85.51, 71.16, 70.32, 58.58, 57.94, 53.77, 50.56, 34.02, 33.48, 30.48, 29.64, 29.09, 19.01. Anal. Calcd for $C_{39}H_{42}ClIrN_2$ (766.4): C, 61.12; H, 5.52; N, 3.66. Found: C, 61.31; H, 5.69; N, 3.74. IR (KBr): ν_{max}/cm^{-1} 2925, 2876, 1431, 1265, 1194, 1130, 754, 695, 529. MS: *m*/*z* 766.3 (55%, M^+), 729.3 (13%, $M^+ - Cl$), 622.2 (100%, $M^+ - Cl - COD$), 428.2 (29%, $M^+ - Cl - COD - Ir$).

(-)-[(4R,5R)-4,5-Diphenyl-1,3-bis-(1(S)-phenyl-ethyl)-4,5-dihydro-3*H*-imidazolin-2-yliden][(1,2,5,6-η)-1,5-cyclooctadiene]-chlororhodium (I) (4Rh)

Yield: 580 mg, 70% as a yellow solid. Mp: 217−218 °C. $[\alpha]_D^{25} = -12.3$ ($c = 0.34$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.48 (2H, d, $J = 10$ Hz); 7.36−7.23 (3H, m); 7.11−7.09 (2H, m); 7.03−6.93 (6H, m); 6.92−6.86 (6H, m); 6.74 (1H, q, $J = 13.4$ Hz); 5.37−5.32 (1H, m); 5.25−5.20 (1H, m); 4.30 (1H, d, $J = 3.6$ Hz); 4.23 (1H, d, $J = 3.2$ Hz); 4.07−4.04 (1H, m); 3.87−3.80 (1H, m); 2.71−2.35 (6H, m); 2.17−1.94 (4H, m); 1.84 (3H, d, $J = 5.6$ Hz); 1.82 (3H, d, $J = 5.6$ Hz). ^{13}C NMR ($CDCl_3$): δ 212.37 (d, $J = 46.7$ Hz), 141.95, 140.35, 139.01, 128.85, 128.59, 128.52, 128.44, 127.79, 127.64, 127.59, 127.47, 127.39, 127.35, 127.25, 126.21, 125.06, 99.57 (d, $J = 6.1$ Hz), 71.56, 70.30, 70.29, 70.25, 66.87 (d, $J = 14.6$ Hz), 58.97, 58.03, 53.53, 33.21, 32.96, 28.93, 28.74, 19.18 (d, $J = 5.4$ Hz). Anal. Calcd for $C_{39}H_{42}ClN_2Rh$ (677.1): C, 69.18; H, 6.25; N, 4.14. Found: C, 69.54; H, 6.54; N, 4.02. IR (KBr): ν_{max}/cm^{-1} 2930, 2873, 1433, 1264, 1194, 1130, 754, 695, 530. MS: *m*/*z* 676.2 (5%, M^+), 639.2 (8%, $M^+ - Cl$), 566.1 (22%, $M^+ - COD$), 531.2 (100%, $M^+ - Cl - COD$), 428.3 (8%, $M^+ - Cl - COD - Rh$).

(−)-(4,5)-Diphenyl-1,3-bis(1(*S*)-phenylethyl)-3*H*-imidazol-1-ium Hexafluorophosphate (12). To a solution of the bis-imine **11** (10 g, 24.0 mmol) in toluene (20 mL) was added paraformaldehyde (0.72 g, 24.0 mmol) in one portion. The reaction mixture was heated to 100 °C until most of the paraformaldehyde was dissolved. After the mixture was cooled to 40 °C, a solution of HCl in dioxane (14.1 mL, ∼1.7 M) was added in one portion. This mixture was then stirred at room temperature for 36 h. The solvent was removed in vacuo. The remaining residue was dissolved in water (30 mL) and the solution extracted with ether (2 × 50 mL). Ammonium hexafluorophosphate (3.91 g, 24.0 mmol) was added to the aqueous phase. The white precipitate was washed with dry Et_2O, filtered off, and dried in vacuo to give the title compound as a colorless solid. Yield: 5.65 g, 41%. Mp: 81 °C. $[\alpha]_D^{25} = -28.1°$ ($c = 0.249$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.81 (1H, s); 7.32−7.24 (7H, m); 7.18 (5H, t, $J = 6.8$ Hz); 7.02 (8H, d, $J = 6.8$ Hz); 5.51 (2H, q, $J = 7.2$ Hz); 1.97 (6H, d, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 138.14, 133.64, 131.41, 130.99, 130.24, 129.28, 128.88, 128.79, 126.58, 124.93, 59.46, 20.98. Anal. Calcd for $C_{31}H_{29}F_6N_2P$ (574.5): C, 64.81; H, 5.09; N, 4.88. Found: C, 65.06; H, 5.41; N, 4.62. IR (KBr): ν_{max}/cm^{-1} 1546, 1454, 1175, 839, 699, 557. MS: *m*/*z* 429.2 (100%, $M^+ - PF_6$), 324.2 (9%, $M^+ - CH_3CHPh - PF_6$), 219.1 (34%, $M^+ - 2CH_3CHPh - PF_6$).

General Procedure for the Preparation of Carbene Complexes by Deprotonation with KO*t*Bu. A solution of KO*t*Bu (0.03 g, 0.25 mmol) in THF (10 mL) was added dropwise to a stirred suspension of imidazolium salt (0.14 g, 0.25 mmol) in THF (15 mL) at room temperature. After the mixture was stirred for 30 min, $[M(COD)Cl]_2$ (0.089 mmol) was added in one portion. The reaction mixture was stirred for an additional 16 h. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent.

(+)-[(4,5)-Diphenyl-1,3-bis(1(*S*)-phenylethyl)-3*H*-imidazol-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chloroiridium(I) (6Ir). Yield: 42 mg, 62% as a yellow solid. Mp: 183−184 °C. $[\alpha]_D^{25} = +67.3°$ ($c = 0.055$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.41−7.39 (2H, m); 7.23−7.19 (5H, m); 7.09−7.06 (3H, m); 6.98 (1H, tt, $J = 17.6$, 0.6 Hz); 6.92 (1H, tt, $J = 16.4$, 0.7 Hz); 6.82 (2H, t, $J = 8$ Hz); 6.77 (2H, t, $J = 7.2$ Hz); 6.49 (2H, d, $J = 7.2$ Hz); 6.40 (2H, d, $J = 6.8$ Hz); 4.71−4.59 (2H, m); 3.62−3.57 (1H, m); 3.47−3.44 (1H, m); 3.18−3.09 (2H, m); 2.31−2.01 (4H, m); 1.84 (6H, t, $J = 6.4$ Hz); 1.76−1.66 (4H, m). ^{13}C NMR ($CDCl_3$): δ 179.18, 141.50, 140.55, 133.17, 132.96, 132.10, 132.02, 128.81, 128.24, 128.12, 128.06, 127.84, 127.63, 127.29, 127.09, 127.04, 126.97, 84.10, 84.08, 59.93, 58.68, 52.16, 51.39, 33.96, 33.25, 30.41, 29.77, 29.43, 29.28, 20.46, 19.67. Anal. Calcd for $C_{39}H_{40}ClIrN_2$ (764.4): C, 61.28; H, 5.27; N, 3.66. Found: C, 61.34; H, 5.32; N, 3.87. IR (KBr): ν_{max}/cm^{-1} 2926, 2868, 1496, 1444, 1361, 1277, 1065, 1028, 756, 696. MS: *m*/*z* 764.3 (39%, M^+), 727.2 (17%, $M^+ - Cl$), 619.2 (100%, $M^+ - Cl - COD$), 514.1 (35%, $M^+ - Cl - COD - CH_3$-CHPh), 426.2 (24%, $M^+ - Cl - COD - Ir$).

(+)-[(4,5)-Diphenyl-1,3-bis(1(*S*)-phenylethyl)-3*H*-imidazol-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium(I) (6Rh). Yield: 51 mg, 84% as a yellow solid. Mp: 179−180 °C. $[\alpha]_D^{25} = +52.5°$ ($c = 0.059$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.44 (2H, d, $J = 8$ Hz); 7.40−6.89 (11H, m); 6.83 (2H, t, $J = 7.2$ Hz); 6.77 (2H, t, $J = 7.2$ Hz); 6.70 (2H, d, $J = 7.2$ Hz); 6.42 (1H, d, $J = 6.8$ Hz); 5.12−4.99 (2H, m); 3.95−3.92 (1H, m); 3.73−3.69 (1H, m); 2.41−2.17 (4H, m); 1.97 (2H, d, $J = 7.2$ Hz); 1.93 (5H, d, $J = 6.8$ Hz); 1.87 (5H, d, $J = 6.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 181.70 (d, $J = 51.3$ Hz), 141.81, 140.90, 133.61, 131.96, 131.02, 130.14, 129.22, 128.73, 128.31, 128.16, 127.99, 127.67, 127.17, 127.96, 126.73, 126.61, 97.96 (d, $J = 5.1$ Hz), 97.79 (d, $J = 5.1$ Hz), 69.01 (d, $J = 15.3$ Hz), 67.63 (d, $J = 14.6$ Hz), 60.35, 58.72, 54.47, 32.98, 32.93, 28.92, 28.59, 20.99, 20.54, 19.75. Anal. Calcd for $C_{39}H_{40}$-ClN_2Rh (675.11): C, 69.38; H, 5.97; N, 4.15. Found: C, 69.55; H, 6.03; N, 4.32. IR (KBr): ν_{max}/cm^{-1} 2996, 2839, 1510, 1491, 1392, 1304, 1161, 1009, 793, 712. MS: *m*/*z* 674.2 (100%, M^+), 639.2 (51%, $M^+ - Cl$), 531.1 (42%, $M^+ - Cl - COD$), 428.2 (48%, $M^+ - Cl - COD - Rh$).

Hydrogenation. The catalyst (0.005 mmol) was dissolved in dichloromethane (5 mL) under argon. Methyl 2-acetamidoacrylate (0.5 mmol, 100 equiv relative to catalyst) was added in one portion. The resulting mixture was transferred to a Parr autoclave (4591) via syringe under argon. The pressure of hydrogen (30 bar) was set. After the mixture was stirred at room temperature for 16 h, the autoclave was opened and the solvent removed in vacuo. The residue was purified by flash chromatography on silica gel with *tert*-butyl methyl ether as eluent. The mixture of enantiomers was subjected to chiral GC. The retention time of the *R* isomer was

Table 3. Crystallographic Data for 8, 5Rh and *rac*-5Rh

	8	5Rh	*rac*-5Rh
formula	$C_{30}H_{28}N_2$	$C_{39}H_{36}ClN_2Rh$	$C_{39}H_{36}ClN_2Rh$
fw	416.54	671.06	671.06
color/habit	yellow/fragment	yellow/fragment	yellow/fragment
cryst dimens, mm^3	$0.41 \times 0.46 \times 0.48$	$0.30 \times 0.38 \times 0.51$	$0.08 \times 0.25 \times 0.30$
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)
a, Å	5.6811(3)	8.7505(4)	11.0849(1)
b, Å	19.6890(9)	17.5279(8)	14.3306(1)
c, Å	20.2676(8)	20.1836(10)	20.1878(1)
β, deg	90	90	100.5025(3)
V, $Å^3$	2267.0(2)	3095.7(3)	3153.17(4)
Z	4	4	4
T, K	173	173	173
D_{calcd}, g cm^{-3}	1.220	1.440	1.414
μ, mm^{-1}	0.071	0.669	0.657
F(000)	888	1384	1384
θ range, deg	4.11−25.25	3.24−26.76	1.75−25.37
index ranges (h, k, l)	±6, ±23, ±24	±11, ±22, ±25	±13, ±17, ±24
no. of rflns collected	27 084	39 503	78 141
no. of indep rflns/R_{int}	4087/0.040	6539/0.067	5779/0.057
no. of obsd rflns ($I>2\sigma(I)$)	3753	6300	4680
no. of data/restraints/params	4087/0/402	6539/0/388	5779/0/388
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0255/0.0615	0.0275/0.0607	0.0452/0.1159
R1/wR2 (all data)[a]	0.0288/0.0624	0.0299/0.0625	0.0589/0.1236
GOF (on F^2)[a]	1.014	1.099	1.032
largest diff peak/hole (e $Å^{-3}$)	+0.10/−0.10	+0.30/−0.53	+2.85/−0.88

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

7.52 min and that of the *S* enantiomer 8.32 min. The absolute configuration of enantiomers with these retention times was accessible by comparison with optically pure samples of methyl 2-acetamidopropanoate prepared from commercially available optically pure alanine via standard organic transformations.

Single-Crystal X-ray Structure Determination of 8, 5Rh, and *rac*-5Rh. Crystal data and details of the structure determination are presented in Table 3. Single crystals suitable for the X-ray diffraction study were grown from CH_2Cl_2/pentane (**5Rh** and ***rac*-5Rh**) and ethyl acetate (**8**). A clear yellow fragment (yellow fragment, yellow fragment) was stored under perfluorinated ether, transferred to a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on area detecting systems (Stoe IPDS 2T or Nonius Mach3, κ-CCD) at the window of a rotating anode (Nonius, FR591) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 26 818 (24 213, 6036) reflections. Data collections were performed at 173 K (Oxford Cryosystems) within a θ range of $4.11° < \theta < 25.25°$ ($3.24° < \theta < 26.76°$, $1.75° < \theta < 25.37°$). A total number of 27 084 (39 503, 78 141) intensities were integrated. Raw data were corrected for Lorentz and polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging ($R_{int} = 0.040$ (0.067, 0.057)) sums of 4087 (6539, 5779) (all data) and 3753 (6300, 4680) ($I > 2\sigma(I)$), respectively, remained, and all data were used. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. For **8**, all hydrogen atoms were found and refined with individual isotropic displacement parameters. The correct enantiomer could not be determined by Flack's parameter $\epsilon = -0.9(17)$ but was given by synthesis. For **5Rh** and *rac*-**5Rh**, all hydrogen atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C−H distances of 1.00, 0.99 and 0.95 Å, respectively, and $U_{iso}(H) = 1.2[U_{eq}(C)]$. For **5Rh**, the correct enantiomer is proved by Flack's parameter $\epsilon = -0.02(2)$. Full-matrix least-squares refinements with 402 (388, 388) parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the Shelxl-97 weighting scheme and stopped at shift/error < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography. All calculations were performed on an Intel Pentium 4 PC, with the WinGX system, including the programs Platon, Sir92, and Shelxl-97.[16] For *rac*-**5Rh**, the relatively high R values and the abnormal positive residual electron density are the result of very bad crystal quality and, as a consequence, an incomplete absorption correction. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-626528 (**8**), CCDC-626527 (**5Rh**), and CCDC-626526 (*rac*-**5Rh**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: CIF files giving crystallographic data for **8**, **5Rh**, and *rac*-**5Rh**. This material is available free of charge via the Internet at http://pubs.acs.org.

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