Chiral N-Heterocyclic Carbene Ligands Derived from 2,2′-Bipiperidine and Partially Reduced Biisoquinoline: Rhodium and Iridium Complexes in Asymmetric Catalysis†

Wolfgang A. Herrmann,*,⊥ Denys Baskakov,⊥ Eberhardt Herdtweck,⊥ Stephan D. Hoffmann,‡ Tanasri Bunlaksananusorn,§ Florian Rampf,§ and Lars Rodefeld§

Lehrstuhl für Anorganische Chemie, Technische Universität München, D-85747 Garching bei München, Germany, Lehrstuhl für Anorganische Chemie mit Schwerpunkt Neue Materialien, Technische Universität München, D-85747 Garching bei München, Germany, and Lanxess Deutschland GmbH, BU Fine Chemicals, Process Development, D-51369 Leverkusen, Germany

Received February 1, 2006

New and reliable procedures for the preparation of both enantiomers of 2,2′-bipiperidine have been developed. Chiral imidazolinium salts derived from 2,2′-bipiperidine and partially reduced biisoquinoline were prepared in high yields. Rhodium and iridium complexes of new chiral N-heterocyclic carbenes were obtained by transmetalation from corresponding silver(I) complexes. The structures of these complexes were verified by X-ray diffraction. The novel carbenes seem to range between the very electron-rich bis(amido)carbenes and the imidazole-derived carbenes with regard to the electronic ligand properties (IR evidence). Rhodium and iridium complexes were applied to a variety of catalytic asymmetric reactions. Modest enantioselectivities of up to 28% ee were observed.

Introduction

Back in 1995, N-heterocyclic carbenes (NHC) were introduced to catalysis by our group.[1,2] They have meanwhile emerged as an important family of ligands with strong σ-donor electronic properties.[3] Numerous catalyst systems with NHC ligands have been described ever since our first reports.[4] In general it appears that catalytic reactions that employ transition-metal complexes of tertiary phosphines may also be catalyzed using complexes of NHC. In contrast to phosphine complexes, most of the complexes formed with these ligands are stable toward heat, air, and moisture, and the need for excess NHC ligand is not required.[5] Indeed, N-heterocyclic carbenes are tightly bound to the metal, thereby avoiding a decomposition pathway or deposition of free (and inactive) metal under catalytic conditions.[6] These compounds are indicated by infrared spectroscopy of their carbonyl derivatives to be very powerful σ-donors, even in comparison to trialkylphosphines.[7]

A logical extension of this development is the application of NHC ligands in stereoselective catalysis.[8] In comparison to tertiary phosphine chemistry, reported examples where chiral

† N-Heterocyclic Carbenes, Part 46. For Part 45, see: Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.

* Corresponding author. Tel: +49-89-289-13080. Fax: +49-89-289-13473. E-mail: lit@arthur.anorg.chemie.tu-muenchen.de.

⊥ Lehrstuhl für Anorganische Chemie, Technische Universität München.

‡ Lehrstuhl für Anorganische Chemie mit Schwerpunkt Neue Materialien, Technische Universität München.

§ Lanxess Deutschland GmbH, BU Fine Chemicals.

(1) (a) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12. (b) Herrmann, W. A.; Weskamp, T.; Böhm, V. P. W. *Adv. Organomet. Chem.* **2001**, *48*, 1. (c) Herrmann, W. A.; Werner, H. *J. Organomet. Chem.* **2002**, *661* (1−2), 215. (d) Cornils, B.; Herrmann, W. A. *J. of Catalysis* **2003**, *216* (1−2), 23. (e) Herrmann, W. A. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002; pp 591−598, 775−793, and 822−828. (f) Cornils, B.; Herrmann, W. A. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002; pp 601−633. (g) Böhm, V. P. W. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002; pp 639−645. (h) Herrmann, W. A.; Denk, K.; Gstöttmayr, C. W. K. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002; pp 829−835. (i) Herrmann, W. A.; Prinz, M. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002; pp 1119−1130.

(2) (a) Herrmann, W. A.; Fischer, J.; Elison, M.; Köcher, C.; Öfele, K. (Hoechst AG), DE 4447066.5 A1, 1994; EP 0721953 A1 [*Chem. Abstr.* **1996**, *125*, 143019y]. (b) Herrmann, W. A.; Fischer, J.; Elison, M.; Köcher, C. (Hoechst AG), DE 4447068.1 A1, 1994; EP 0719758 A1; US 5.703.269, 1997 [*Chem. Abstr.* **1996**, *125*, 167571y]. (c) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C. (Celanese GmbH), DE 4447067.3 A1, 1994; EP 0719753 A1, 1995 [*Chem. Abstr.* **1996**, *125*, 167338c]. (d) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C. (Hoechst AG), DE 4447070.3 A1, 1994; EP 0721951 A1 [*Chem. Abstr.* **1996**, *125*, 143016v]. (e) Herrmann, W. A.; Köcher, C. (Hoechst AG), DE 1961090.8 A1, 1996; EP 0721950; WO 97/34875 [*Chem. Abstr.* **1997**, *127*, 318962v]. (f) Herrmann, W. A.; Militzer, H.-C.; Scholz, U.; Gstöttmayr, C. (Bayer AG), EP 1308157 A1, 2003.

(3) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181. (c) Bourrissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(4) (a) Hill, J. E.; Nile, T. A. *J. Organomet. Chem.* **1977**, *137*, 293. (b) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217. (c) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C. P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239. (d) Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 4246. (e) Lee, S.; Beare, N. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 8410. (f) Grasa, G. A.; Viciu, M. S.; Huang, J. K.; Zhang, C. M.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866. (g) Jackstell, R.; Frish, A.; Beller, M.; Röttger, D.; Malaun, M.; Bildstein, B. *J. Mol. Catal. A: Chem.* **2002**, *185*, 105. (h) Muehlhofer, M.; Strassner, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1745. (i) Sholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1991**, *1*, 953.

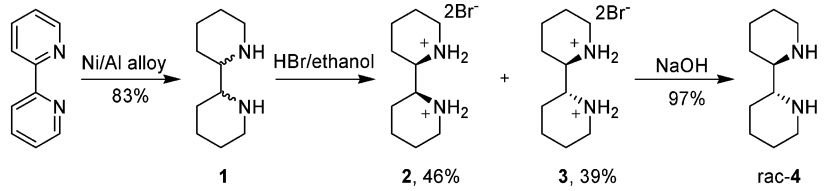
(5) (a) McGuinness, D. S.; Cavel, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1569. (b) Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773. (c) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201.

(6) (a) Huang, J. K.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370. (b) Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490.

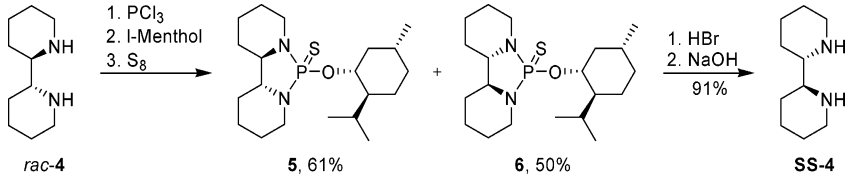
(7) Köcher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261−265. (b) Huang, J. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, *19*, 1194.

10.1021/om060098b CCC: $33.50
Publication on Web 04/08/2006

Scheme 1. Separation of Meso and *dl* Forms of bpip



Scheme 2. Optical Resolution of bpip



NHC complexes give good enantioselectivity are rare. However, the recent reports by Burgess et al. of >99% ee for the iridium-catalyzed asymmetric hydrogenation of aryl alkenes using the NHC-oxazoline ligand exemplify the potential of chiral NHC ligands.[9] Excellent levels of enantioselectivity have been observed for ruthenium-catalyzed asymmetric metathesis reactions using NHC ligands, also demonstrating that further investigation into chiral NHC ligands is justified.[10]

In our studies on homogeneous catalysis using metal−NHC complexes,[11] we became interested in the development of new rigid NHC ligands bearing a chiral backbone for asymmetric catalysis. We report here the synthesis of new NHC ligands derived from 2,2′-bipiperidine and partially reduced biisoquinoline. Rhodium and iridium complexes of these ligands have been synthesized and employed in asymmetric hydrogenation, hydrosilylation, and transfer hydrogenation.

Results and Discussion

Synthesis of Ligands. The heterocyclic diamine 2,2′-bipiperidine (bpip, **1**) was first synthesized by Blau in 1889.[12] Because of two asymmetric carbon atoms in 2,2′-bipiperidiene, this diamine exists as three isomers, meso (*RS*) and a pair of racemic forms, (*RR*) and (*SS*). Separation of meso and racemic forms via the corresponding hydrochloride salt was first reported in the literature in 1971.[13] Numerous attempts of separation, in our hands, however were completely unsuccessful. This difficulty prompted us to search for alternative methods. The use of bishydrobromide salt (**2**, **3**) instead of bishydrochloride salt was found highly advantageous, resulting in very quick and high-yielding separation of both isomers (Scheme 1). Because of the additional symmetry element, the mirror plane, the IR spectrum of the meso structure of bpip **2** is expected to be simpler than that of the racemic isomer **3**, so that the less soluble material could be assigned to the bishydrobromide of meso-bpip **2**, which was later confirmed by X-ray analysis.

Having successfully separated diastereomeric forms of bpip, we required access to the individual enantiomers of this compound in reasonable quantities. Yoshikawa et al. successfully resolved bpip utilizing its chiral cobalt complexes with a camphor sulfonic acid derivative.[14] However this is not the method of choice for the preparation of large quantities (>1 g) of enantiopure bpip, because of the many stages involved and extremely low yield (3%). Optical resolution of bpip utilizing its salt with L-tartaric acid was recently reported in the literature.[15] However all our numerous attempts to reproduce this result were unsuccessful. Even under changed conditions no tendency to resolve into optical isomers was observed. After much experimentation we found that both enantiomers of bpip are easily accessible via covalent diastereomers formed by one-pot reaction of 1 equiv of racemic bpip **4** 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 (Scheme 2). The resulting diastereomeric mixture was separated by two subsequent crystallizations from methanol in high yield.

This method produced crystals of **6** suitable for X-ray diffraction, so that the absolute stereochemistry of the liberated parent diamine has been established for the first time (Figure 1). The enantiomeric purity of **4** could be readily accessed by ^{31}P NMR spectroscopy of the corresponding diastereomeric compound (**5** or **6**). On the basis of these data we estimate the enantiomeric purity of resolved **4** to be better than 95%.

Enantiomericaly pure (1*S*,1′*S*)-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline (**7**) was synthesized according to Elliot et al.[21] Because of our own experimentation and a recent publication by Arai et al.[16] we strongly believe that the reported optical rotation of **SS-7** (+968°) is a mistake and should be written +268°.

Both enantimericaly pure bpip-bishydrobromide **3** and octahydrobiisoquinoline bishydrobromide **9** reacted easily with

(8) (a) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619. (b) Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402. (c) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951.

(9) (a) Powell, M. T.; Hou, D. R.; Perry, M. C.; Cui, X. H.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878. (b) Perry, M. C.; Cui, X. H.; Powell, M. T.; Hou, D. R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113.

(10) (a) Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225. (b) van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954. (c) van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502.

(11) (a) Frey, G. D.; Reisinger, C. P.; Herdtweck E. Herrmann, W. A. *J. Organomet. Chem.* **2005**, *690*, 3193. (b) Schütz, J.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2004**, *23*, 6084. (c) Herrmann, W. A.; Öfele K.; von Preysing, D.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235. (d) Denk, K.; Fridgen, J.; Herrmann, W. A. *Adv. Synth., Catal.* **2002**, *344*, 666. (e) Herrmann, W. A.; Härter, P. Gstöttmayr, C. W. K.; Bielert, F.; Seeboth, N.; Sirsch, P. *J. Organomet. Chem.* **2002**, *649*, 141.

(12) Blau, F. *Monatsh. Chem.* **1889**, *10*, 375.

(13) Forostyan, Y. N.; Efimova, E. I.; Soroka, I. I. *Zh. Org. Khim.* **1971**, *7*, 2198.

(14) Mitsunobu, S.; Yoichi, S.; Shigenobu, Y.; Yoshikawa, S. *J. Chem. Soc., Dalton Trans.* **1985**, 895.

(15) Hamada, T.; Izawa, K. (Ajinomoto Inc.), Eur. Pat. Appl. 2000, EP987271 A1 20000322.

(16) Arai, S.; Takita, S.; Nishida, A. *Eur. J. Org. Chem.* **2005**, 5262.

(17) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

(18) (a) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462. (b) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (c) Alaimo, P. J.; Bergman, R. G. *Organometallics* **1999**, *18*, 2707. (d) Prinz, M.; Veiros, L. F.; Calhorda, M. J.; Romão, C. C.; Herdtweck, E.; Kühn, F. E.; Herrmann, W. A. *J. Organomet. Chem.* **2006**, *691*, in press, doi: 10.1016/j.jorgchem.2006.02.031.

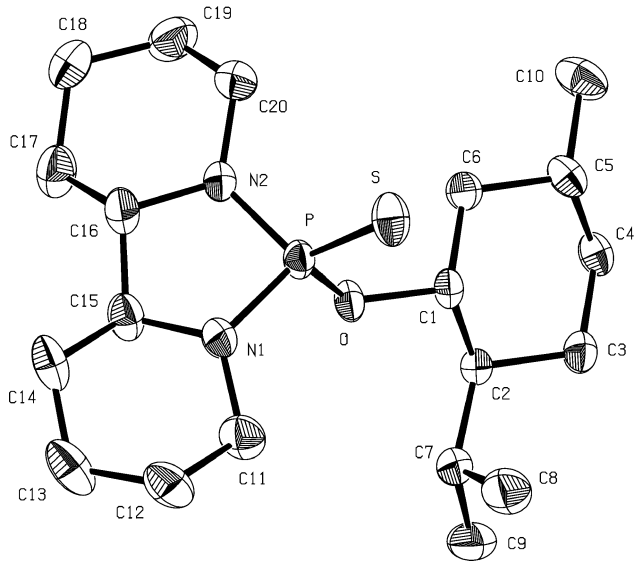
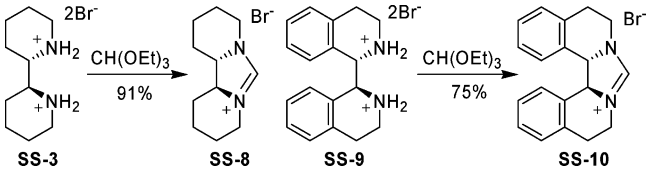


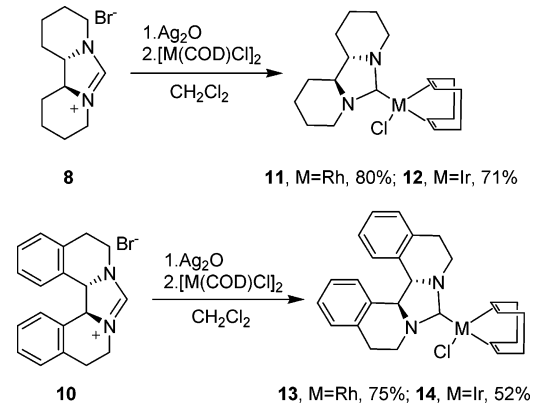
Figure 1. ORTEP style representation of the molecular structure of **6** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 3. Synthesis of Imidazolinium Salts

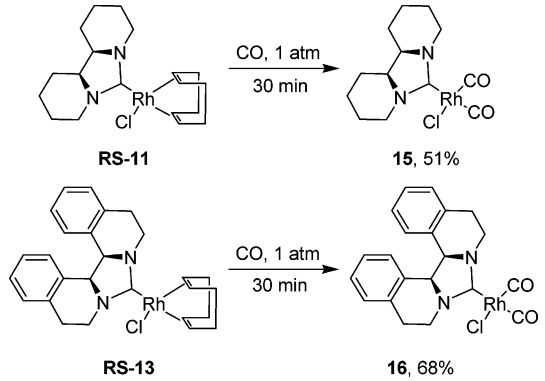


triethyl orthoformate, yielding corresponding imidazolinium salts **8** and **10**, Scheme 3. The ^{1}H and ^{13}C NMR spectra of **8** and **10** are indicative of C_2-symmetric compounds. For example, compound **10** exhibits a strong singlet at δ 5.41 ppm that is attributable to adjacent protons of two octahydroisoquinoline rings. In the ^{1}H NMR spectra of **8** and **10**, the imidazolinium protons appear at 10.20 and 10.28 ppm, respectively. The ^{13}C NMR shift of the N−C−N sp^2 carbons appears at 154.6 and 156.3 ppm for **8** and **10**, respectively. Compounds **8** and **10** are air-stable, hygroscopic white solids that are soluble in water, alcohols, chlorinated solvents, and THF, but are insoluble in diethyl ether and hydrocarbons.

Scheme 4. Synthesis of Rhodium and Iridium Complexes



Scheme 5. Synthesis of Dicarbonyl Rhodium Complexes



Synthesis of Rhodium and Iridium Complexes. We attempted to prepare rhodium(I) and iridium(I) complexes of **8** and **9** using a mild transmetalation method developed by Wang and Lin.[17] Reaction of imidazolinium precursors with silver(I) oxide in dichloromethane at room temperature in the darkness gave rather unstable silver complexes, observed by NMR spectroscopy, which decomposed too quickly to be isolated. Direct addition of [M(COD)Cl]$_2$ (M being rhodium or iridium) to a freshly prepared solution of silver complexes yielded upon workup the corresponding chiral complexes **11**−**14**, which were purified by chromatography on silica gel, Scheme 4. Rhodium complexes **RS-11** and **RS-13** were also synthesized utilizing achiral meso-compounds **RS-8** and **RS-10**.

All six complexes are very soluble in dichloromethane and THF and not soluble in saturated hydrocarbons. Their identities are confirmed by elemental analysis and ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. The complexes are air stable in the solid state and for several days in solution. Corresponding dicarbonyl compounds **15** and **16** were obtained by passing carbon monoxide through a solution of **RS-11** and **RS-13** in THF at room temperature. The products **15** and **16** were formed within minutes as air- and moisture-sensitive pale brown solids. Compared with IR data for the related NHC complexes, the novel carbenes seem to range between the acyclic bis(amido)-carbenes and the imidazole derivatives in terms of the electronic ligand properties (Table 1).

Structural Study. X-ray-quality crystals of **RS-11** and **SS-14** were easily grown by layering a dichloromethane solution of the corresponding complex with pentane. The X-ray single-crystal diffraction study of **RS-11** (Figure 2) and **SS-14** (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 Tables 2 (**RS-11**) and 3 (**SS-14**). The coordination around

(19) (a) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663. (b) Seo, H.; Park, H.-J.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618. (c) Seo, H.; Kim, B. Y.; Lee, J. H.; Park, H.-J.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 4783. (d) Chianese A. R.; Crubtree, R. H. *Organometallics* **2005**, *24*, 4432. (e) Duan, W. L.; Shi, M.; Rong, G. B. *Chem. Commun.* **2003**, 2916.

(20) Lunn, G.; Sansone, E. B. J. *Org. Chem.* **1986**, *51*, 513.

(21) Elliott, M. C.; Williams, E. *Org. Biomol. Chem.* **2003**, *1*, 3038.

(22) (a) Data Collection Software for Nonius κ-CCD devices; Delft, The Netherlands, 2001. (b) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307ff. (c) *CrysAlis* Data Collection Software and Data Processing Software for Oxford Xcalibur Diffractometer, Version 1.171; Oxford Diffraction Ltd.: Oxfordshire, U.K., 2005. (d) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *SIR92*. *J. Appl. Crystallogr*. **1994**, *27*, 435−436. (e) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2. (f) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001. (g) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1998.

(23) Denk, K.; Sirsch, P.; Herrmann W. A. *J. Organomet. Chem.* **2003**, *649*, 219.

(24) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher C.; Artus G. R. J. *Chem. Eur. J.* **1996**, *2*, 772.

Table 1. Carbonyl Stretching Frequencies for Compounds $Rh(CO)_2Cl(L)$

compound	ν(CO) I (cm^{-1})	ν(CO) II (cm^{-1})
$(i\text{-}Pr_2N)_2C$[23]	2057	1984
15	2069	1994
16	2074	2001
MesIm[a]	2076	2006

[a] 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.[24]

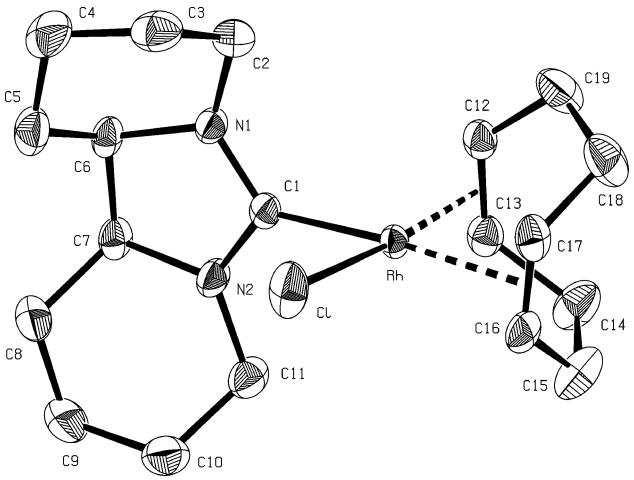


Figure 2. ORTEP style representation of the molecular structure of complex **RS-11** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity.

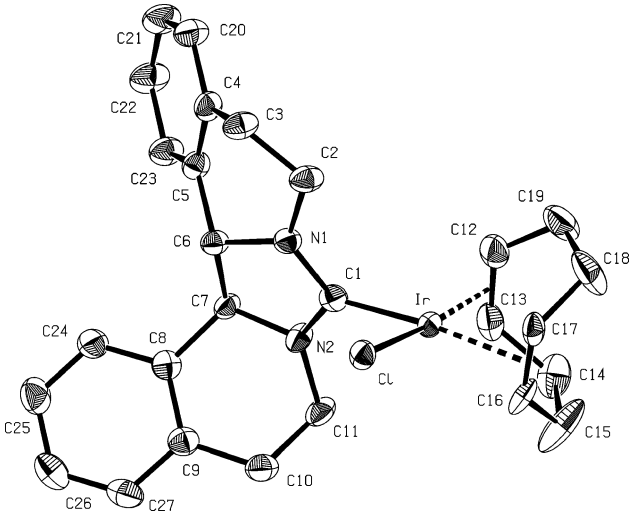


Figure 3. ORTEP style representation of the molecular structure of complex **SS-14** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity.

the metal center is square planar. The M−C1 bond distances (2.020(6) Å for iridium and 2.002(2) Å for rhodium) are typical for this type of carbene coordination.[18] 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 C16═C17 double bond trans to the NHC ligand is shorter (1.375(11) Å for iridium and 1.356(3) Å for rhodium) than the C12═C13 bond (1.424(12) Å for iridium and 1.403(3) Å for rhodium), owing to reduced back-donation from the metal to its π^* orbitals.

Catalytic Results. Rhodium and iridium complexes **11**−**14** were tried in the asymmetric hydrogenation of methyl-2-acetamidoacrylate. All of them showed significant activity,

Table 2. Selected Bond Lengths and Angles for RS-11

bond lengths (Å)[a]		bond angles (deg)[a]	
Rh−Cl	2.3692(7)	Cl−Rh−C1	85.91(6)
Rh−C1	2.002(2)	Cl−Rh−Cg1	174.48
Rh−C12	2.104(2)	Cl−Rh−Cg2	92.88
Rh−C13	2.126(2)	C1−Rh−Cg1	93.95
Rh−Cg1	1.995	C1−Rh−Cg2	176.08
Rh−C16	2.204(2)	Cg1−Rh−Cg2	87.61
Rh−C17	2.233(2)		
Rh−Cg2	2.113		

[a] Cg1 and Cg2 define the midpoints of C12−C13 and C16−C17.

Table 3. Selected Bond Lengths and Angles for SS-14

bond lengths (Å)[a]		bond angles (deg)[a]	
Ir−Cl	2.362(2)	Cl−Ir−C1	90.6(2)
Ir−C1	2.020(6)	Cl−Ir−Cg1	171.7
Ir−C12	2.099(8)	Cl−Ir−Cg2	90.5
Ir−C13	2.133(8)	C1−Ir−Cg1	92.6
Ir−Cg1	1.993	C1−Ir−Cg2	173.8
Ir−C16	2.170(7)	Cg1−Ir−Cg2	87.2
Ir−C17	2.204(6)		
Ir−Cg2	2.076		

[a] Cg1 and Cg2 define the midpoints of C12−C13 and C16−C17.

Table 4. Asymmetric Hydrosilylation and Transfer Hydrogenation of Acetophenone

	ee for *sec*-phenethyl alcohol (%)	
catalyst	hydrosilylation	transfer hydrogenation
11	7	7
12	15	14
13	28	7
14	2	24

resulting in complete conversions in 16 h at room temperature and 30 bar H_2, but only in the case of **14** was any optical induction (22% ee) observed.

Complexes **11**−**14** were also found to be active catalysts for the asymmetric hydrosilylation of acetophenone with diphenylsilane, giving >99% conversion at −20 °C in 16 h at 1% catalyst loading. After methanolysis of the silyl ether, the product *sec*-phenethyl alcohol was subjected to chiral GC analysis. However only low to modest enantiomeric excesses were obtained for all complexes studied here (Table 4). Changing the solvent, increasing the catalyst loading, and varying the temperature gave no benefit, nor did changing the order of addition of reactants.

Transfer hydrogenation of acetophenone with 2-propanol and potassium *tert*-butoxide was found to proceed smoothly with all complexes, but once again only low enantioselectivities were obtained in all cases (Table 4). All four complexes were also tested for the transfer hydrogenation of acetone with Et_3N/formic acid, but virtually no conversion was observed.

Despite good conversions in many reactions, the new catalytic systems appear to be inferior in enantioselectivity to the best results described in the literature.[19]

Experimental Section

General Methods. 2,2′-Bipiperidine[20] (**1**) and (1*S*,1′*S*)-1,-1′,2,2′,3,3′4,4′-octahydro-1,1′-biisoquinoline bishydrobromide[21] (**9**) were prepared according to literature procedures. 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, 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.

(*RS*)-2-((*RS*)-Piperidin-2-yl)piperidine Bishydrobromide (3) and *meso*-2-(S-piperidin-2-yl)piperidine Bishydrobromide (2). Concentrated hydrobromic acid was added to 2,2′-bipiperidine (11.13 g, 66.19 mmol) to reach a pH of about 2. After evaporation of water under reduced pressure, the resultant residue was dried under vacuum to obtain a mixture of the racemic (**3**) and meso (**2**) bishydrobromide salts as a white solid material. This solid was ground to powder in a mortar. The white powder was heated to boiling point in 200 mL of ethanol for 20 min and filtered hot. This washing was repeated three times to give meso bishydrobromide (**3**) (10.05 g, 46%) as a white powder, mp 254 °C. Combined ethanol washings were allowed to cool and filtered to give racemic bishydrobromide (**3**) (9.88 g, 39%) as an off-white solid, mp 245 °C. Compound **2**: ^{1}H NMR (D_2O): δ 3.42 (4H, apparent t, J = 11.9 Hz); 3.04 (2H, apparent t, J = 12.9 Hz); 1.88 (6 H, m); 1.55 (6H, m). ^{13}C NMR (D_2O): δ 59.5, 47.9, 24.8, 23.2, 23.1. Anal. Calcd for $C_{10}H_{22}Br_2N_2$ (328.01): C, 36.38; H, 6.72, N, 8.49. Found: C, 36.75; H, 7.01; N, 8.92. IR ν_{max} (KBr)/cm^{-1}: 2391, 1574, 1415, 1365, 1308, 902, 529, 448. Compound **3**: ^{1}H NMR (D_2O): δ 3.48 (4H, m); 3.08 (2H, apparent t, J = 12.8 Hz); 2.09 (2H, apparent d, J = 11.6 Hz); 1.93 (4H, m); 1.61 (6H, m). ^{13}C NMR (D_2O): δ 59.8, 47.8, 26.8, 23.3, 23.0. Anal. Calcd for $C_{10}H_{22}Br_2N_2$ (328.01): C, 36.38; H, 6.72, N, 8.49. Found: C, 36.63; H, 7.12; N, 8.81. IR ν_{max} (KBr)/cm^{-1}: 2912, 2720, 1575, 1454, 1415, 1308, 1013, 607.

(*RS*)-2-((*RS*)-Piperidin-2-yl)piperidine (4). (*RS*)-2-((*RS*)-Piperidin-2-yl)piperidine bishydrobromide (**3**) (9.88 g, 29.94 mmol) was stirred in CH_2Cl_2 (50 mL) and 5 M NaOH (50 mL) at room temperature for 1 h. The organic layer was separated and dried over NaOH. Removal of drying agent and solvent gave a colorless oil, which was distilled under reduced pressure (bp 87 °C, 0.1 mbar) to give racemic **4** (4.88 g, 97%) as large colorless crystals, mp 39−40 °C. ^{1}H NMR ($CDCl_3$): δ 3.03 (2H, d, J = 11.7 Hz); 2.57 (2H, t, J = 11.7 Hz); 2.33 (2H, d, J = 9.8 Hz); 1.77 (2H, d, J = 10.8 Hz); 1.55 (4H, t, J = 12.7 Hz); 1.43−1.17 (8H, m). ^{13}C NMR (D_2O): δ 61.8, 47.4, 28.2, 26.6, 24.9. Anal. Calcd for $C_{10}H_{20}N_2$ (168.16): C, 71.37; H, 11.98; N, 16.65. Found: C, 71.06; H, 12.11; N, 16.85. IR ν_{max} (KBr)/cm^{-1}: 2920, 2857, 2787, 1442, 1316, 1119, 772.

9-(2-Isopropyl-5-menthylcyclohexyloxy)decahydro-8a,9a-diaza-9-phosphafluorene-9-sulfide (bpip-P(*S*)-l-menthyl 5, 6). (*RS*)-2-((*RS*)-Piperidin-2-yl)piperidine (**4**) (4.88 g, 28.99 mmol) was dissolved in 100 mL of CH_2Cl_2 in a flame-dried flask. *N*,*N*-Dimethylaniline (20.19 mL, 159.50 mmol) was added with a syringe followed by slow dropwise addition of PCl_3 (2.53 mL, 28.99 mmol). The reaction mixture was stirred for 10 min, and the exothermic reaction took place. l-Menthol (4.53 g, 28.99 mmol) was added in one portion. The reaction mixture was stirred for another 10 min before sulfur (9.28 g, 289.90 mmol) was added in one portion. The mixture was stirred for additional 0.5 h. Solvent was removed under reduced pressure. The remaining residue was suspended in 200 mL of 5 M HCl and extracted three times with 200 mL of Et_2O. Organic phases were combined and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent to give a 1/1 mixture of *RR*- and *SS*-bpip-P(*S*)-l-menthyl (**5** and **6**) as colorless crystals (11.10 g, 99%). This mixture was dissolved in refluxing methanol (150 mL), and after approximately 3 h, large prismatic crystals (5.18 g) were filtered off. A further crystallization of these crystals from refluxing methanol (155 mL) gave *SS*-(+)-bpip-P(*S*)-l-menthyl (**6**) as large prismatic crystals (2.78 g, 50%), mp 103−104 °C. $[\alpha]^{25}_D$ = +88.1 (*c* 0.104, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 4.16 (1H, qd, J = 10.4 Hz; J = 4 Hz); 3.47−3.42 (1H, m); 3.32−3.22 (1H, m); 2.80 (1H, apparent t, J = 10.8 Hz); 2.64 (1H, apparent t, J = 8.8 Hz); 2.53 (2H, apparent q, J = 12 Hz); 2.14 (1H, pd, J = 6.8 Hz; J = 2 Hz); 1.97 (1H, apparent d, J = 11.6 Hz); 1.84−1.75 (4H, m); 1.65−1.61 (5H, m); 1.54−1.12 (7H, m); 1.06−0.94 (3H, m); 0.88 (6H, dd, J = 6 Hz; J = 5.2 Hz); 0.81 (3H, d, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 78.2 (d, J = 8.5 Hz), 77.0, 63.5 (d, J = 6.3 Hz), 60.6 (d, J = 4.6 Hz), 48.3 (d, J = 33.6 Hz), 43.3, 43.2 (d, J = 4.1 Hz), 41.3, 34.3, 31.5, 29.4 (d, J = 5.4 Hz), 29.3 (d, J = 2.3 Hz), 25.4 (d, J = 8.4 Hz), 25.1 (d, J = 10 Hz), 23.6, 23.2, 22.7, 22.2, 21.1, 15.8. ^{31}P NMR ($CDCl_3$): δ 76.51 (s). Anal. Calcd for $C_{20}H_{37}N_2OPS$ (384.56): C, 62.46; H, 9.70; N, 7.28. Found: C, 62.35; H, 9.81; N, 7.22. IR ν_{max} (KBr)/cm^{-1}: 2939, 2923, 2826, 1448, 1198, 1128, 990, 819, 716, 640. MS: *m*/*z* 384.2 (55%, M$^+$), 246.4 (100%), 228.4 (10%), 212.5 (20%).

Removal of the solvent from the mother liquor gave a solid, which was crystallized from refluxing methanol (37 mL). The white, long needles that separated overnight were filtered to obtain *RR*-(−)-bpip-P(S)-l-menthyl (**5**) (3.41 g, 61%), mp 99−100 °C. $[\alpha]^{25}_D$ = −87.3 (*c* 0.125, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 4.19 (1H, qd, J = 10.3 Hz; J = 4.1 Hz); 3.42−3.38 (1H, m); 3.29−3.19 (1H, m); 2.72 (1H, apparent t, J = 10.5 Hz); 2.69−2.52 (3H, m); 2.44 (1H, apparent t, J = 12 Hz); 2.06−1.99 (2H, m); 1.88−1.75 (4H, m); 1.64−1.59 (5H, m); 1.54−1.40 (3H, m); 1.37−1.16 (6H, m); 0.97 (3H, apparent t, J = 11.6 Hz); 0.88 (6H, dd, J = 7.2 Hz; J = 4 Hz); 0.80 (3H, d, J = 6.4 Hz). ^{13}C NMR ($CDCl_3$): δ 78.9 (d, J = 8.4 Hz), 77.0, 63.3 (d, J = 6.2 Hz), 61.0 (d, J = 3.8 Hz), 48.2 (d, J = 6.1 Hz), 43.5, 43.4, 41.3, 34.4, 31.6, 29.3 (d, J = 6.2 Hz), 29.1 (d, J = 8.4 Hz), 25.4 (d, J = 8.4 Hz), 24.9, 23.6, 23.3, 23.1, 22.2, 21.1, 16.2. ^{31}P NMR ($CDCl_3$): δ 76.86 (s). Anal. Calcd for $C_{20}H_{37}N_2OPS$ (384.56): C, 62.46; H, 9.70; N, 7.28. Found: C, 62.27; H, 9.95; N, 7.13. IR ν_{max} (KBr)/cm^{-1}: 2938, 2849, 1453, 1200, 1128, 1071, 1011, 991, 814, 764. MS: *m*/*z* 384.2 (50%, M$^+$), 246.4 (100%), 228.4 (15%), 212.5 (25%).

(+)-(*S*)-2-((*S*)-Piperidin-2-yl)piperidine (SS-4). *SS*-(+)-bpip-P(*S*)-l-Menthyl (**6**) (2.78 g, 7.23 mmol) was heated for 2 h under reflux with 50 mL of concentrated hydrobromic acid. The reaction mixture was cooled and extracted three times with 50 mL of CH_2Cl_2. The remaining aqueous phase was concentrated to give enantiopure bishydrobromide (**SS-3**) (2.21 g, 93%) as an off-white solid. To release free amine (**SS-4**), (+)-(*S*)-2-((*S*)-piperidin-2-yl)-piperidine bishydrobromide (**SS-3**) (0.25 g, 0.76 mmol) was stirred in CH_2Cl_2 (5 mL) and 5 M NaOH (5 mL) at room temperature for 1 h. The organic layer was separated and dried over NaOH. Removal of drying agent and solvent gave a colorless oil, which was distilled under reduced pressure (bp 87 °C, 0.1 mbar) to give enantiopure **SS-4** (0.12 g, 98%) as large colorless crystals, mp 39−40 °C. $[\alpha]^{25}_D$ = +12.3 (*c* 2.15, H_2O) [lit.[14] $[\alpha]^{25}_D$ = +12.2 (*c* 9.2, H_2O)].

1,2,3,4,8,9,10,11,(*S*)-11a,(*S*)-11b-Decahydrodipyrido[1,2-*c*;2′,1′-*e*]imidazol-5-ylium Bromide (8). A mixture of 2.50 g (7.57 mmol) of (+)-(*S*)-2-((*S*)-piperidin-2-yl)piperidine bishydrobromide (**SS-3**), 20 mL of triethyl orthoformate, and 1 drop of 96% formic acid was heated to 100 °C for 18 h. Upon cooling to room temperature, a colorless solid precipitated, which was collected by filtration, washed with 10 mL of dry Et_2O, and dried in vacuo to give the title compound (**(−)-SS-8**) (1.79 g, 91%) as colorless crystals, mp 157 °C. $[\alpha]^{25}_D$ = −64.1 (*c* 0.078, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 10.20 (1H, s); 4.39 (2H, dd, J = 13.2 Hz; J = 4.4 Hz); 3.59 (2H, d, J = 9.6 Hz); 3.21 (2H, td, J = 12.4 Hz, J = 2.8 Hz); 1.97 (3H, apparent q, J = 9.2 Hz); 1.81 (2H, d, J = 13.2 Hz); 1.65−1.42 (7H, m). ^{13}C NMR ($CDCl_3$): δ 154.6, 65.4, 45.9, 31.1, 25.6, 22.4. Anal. Calcd for $C_{11}H_{19}BrN_2$ (259.19): C, 50.97; H, 7.39; N, 10.81.

Found: C, 51.23; H, 7.62; N, 10.68. IR ν_{max} (KBr)/cm^{-1}: 2865, 1650, 1448, 1192, 1051, 979, 523. MS: *m*/*z* 179.3 (10%, M$^+$ − Br), 178.3 (100%, M$^+$ − Br − H), 146.7 (10%).

RS-8. Yield: 1.59 g, 81% as colorless crystals, mp 164 °C. ^{1}H NMR ($CDCl_3$): δ 9.69 (1H, s); 4.07−4.00 (4H, m); 3.08−3.01 (2H, m); 1.74 (2H, apparent s); 1.58 (4H, br), 1.31 (6H, apparent d, J = 4 Hz). ^{13}C NMR ($CDCl_3$): δ 153.7, 61.3, 45.3, 24.8, 24.6, 21.6. Anal. Calcd for $C_{11}H_{19}BrN_2$ (259.19): C, 50.97; H, 7.39; N, 10.81. Found: C, 50.69; H, 7.25; N, 10.47. IR ν_{max} (KBr)/cm^{-1}: 2945, 2866, 1642, 1448, 1292, 1189, 588, 494. MS: *m*/*z* 179.3 (12%, M$^+$ − Br), 178.3 (100%, M$^+$ − Br − H), 146.7 (15%).

5,6,8,9,(*S*)-13b,(*S*)-13c-Hexahydro-7a-aza-6a-azonia-dibenzo-[*c*,*g*]fluorene Bromide (10). A mixture of 1.00 g (2.35 mmol) of (−)-(1*S*,1′*S*)-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline bishydrobromide (**SS-9**), 20 mL of triethyl orthoformate, and 1 drop of 96% formic acid was heated to 100 °C for 60 h. Upon cooling to room temperature, a colorless solid precipitated, which was collected by filtration, washed with 10 mL of dry Et_2O, and dried in vacuo to give **(−)-SS-10** (0.62 g, 75%) as colorless crystals, mp 254 °C. $[\alpha]^{25}_D$ = −151.7 (*c* 0.168, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 10.28 (1H, s); 7.43−7.31 (6H, m); 7.26 (2H, d, J = 5.6 Hz); 5.41 (2H, s); 4.61−4.56 (2H, m); 3.79−3.71 (2H, m); 3.41−3.32 (2H, m); 3.04−2.97 (2H, m). ^{13}C NMR ($CDCl_3$): δ 156.3, 133.2, 133.1, 129.9, 129.1, 128.3, 124.4, 66.1, 43.1, 29.2. Anal. Calcd for $C_{19}H_{19}BrN_2$ (354.07): C, 64.23; H, 5.39; N, 7.89. Found: C, 63.94; H, 5.57; 7.76. IR ν_{max} (KBr)/cm^{-1}: 2884, 1645, 1452, 1431, 1195, 771, 636. MS: *m*/*z* 275.2 (M$^+$, 100%).

RS-10. Yield: 0.74 g, 89% as a colorless solid, mp 267 °C. ^{1}H NMR ($CDCl_3$): δ 10.32 (1H, s); 7.45−7.29 (6H, m); 7.24 (2H, d, J = 5.5 Hz); 5.40 (2H, s); 4.62−4.57 (2H, m); 3.79−3.72 (2H, m); 3.41−3.33 (2H, m); 3.02−2.98 (2H, m). ^{13}C NMR ($CDCl_3$): δ 155.9, 133.2, 129.9, 129.0, 128.2, 124.4, 66.0, 43.2, 29.2. Anal. Calcd for $C_{19}H_{19}BrN_2$ (354.07): C, 64.23; H, 5.39; N, 7.89. Found: C, 64.12; H, 5.23; 7.98. IR ν_{max} (KBr)/cm^{-1}: 2880, 1646, 1492, 1315, 1306, 773, 475. MS: *m*/*z* 275.2 (M$^+$, 100%).

General Procedure for Preparation of NHC Complexes. To a solution of 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 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 bromide 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.

(−)-[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) (SS-11). Yield: 340 mg, 80% as a yellow solid, mp 206 °C (dec). $[\alpha]^{25}_D$ = −20.3 (*c* 0.070, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.12−4.99 (2H, m); 4.98−4.88 (2H, m); 3.28−3.24 (2H, br); 3.23−3.08 (2H, m); 2.33−2.31 (4H, m); 1.91−1.67 (14H, m); 1.45−1.34 (4H, m). ^{13}C NMR ($CDCl_3$): δ 207.1 (d, J = 46.1 Hz), 99.0 (d, J = 6.8 Hz), 98.9 (d, J = 6.8 Hz), 68.1 (d, J = 14.6 Hz), 67.3 (d, J = 14.6 Hz), 66.5, 65.5, 62.3, 48.0, 47.8, 33.1, 32.8, 31.5 (d, J = 6.9 Hz), 28.9, 28.7, 26.9, 26.3, 23.7, 23.5. Anal. Calcd for $C_{19}H_{30}ClN_2Rh$ (424.81): C, 53.72; H, 7.12; N, 6.59. Found: C, 53.57; H, 7.37; N, 6.99. IR ν_{max} (KBr)/cm^{-1}: 2936, 2852, 1483, 1442, 1429, 1303, 1262, 1249, 1173, 639. MS: *m*/*z* 424.8 (5%, M$^+$), 422.8 (15%, M$^+$ − 2H), 387.8 (20%, M$^+$ − Cl), 178.7 (100%, M^{2+} − Cl + 2H).

[1,2,3,4,8,9,10,11,(*R*)-11a,(*S*)-11b-Decahydrodipyrido[1,2-*c*;2′,1′-*e*]imidazol-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium(I) (RS-11). Yield: 355 mg, 84% as a yellow solid, mp 217 °C (dec). ^{1}H NMR (D_8-toluene): δ 5.29 (2H, br); 5.17 (2H, dd, J = 12.1 Hz, J = 4.3 Hz); 3.26 (2H, apparent d, J = 3.2 Hz); 2.89−2.76 (4H, m); 2.37−2.17 (4H, m); 1.88−1.69 (5H, m); 1.53 (2H, apparent d, J = 12.8 Hz); 1.34 (2H, apparent d, J = 11.6 Hz); 1.18−1.09 (2H, m); 0.99−0.85 (5H, m). ^{13}C NMR (D_8-toluene): δ 209.8 (d, J = 46.1 Hz), 98.3 (d, J = 6.2 Hz), 66.3 (d, J = 14.7 Hz), 61.8, 47.8, 33.1, 28.9, 25.5, 25.1, 23.2. Anal. Calcd for $C_{19}H_{30}ClN_2Rh$ (424.81): C, 53.72; H, 7.12; N, 6.59. Found: C, 53.79; H, 7.56; N, 6.23. IR ν_{max} (KBr)/cm^{-1}: 2829, 2861, 1490, 1262, 1094, 1025, 803. MS: *m*/*z* 424.8 (10%, M$^+$), 422.8 (10%, M$^+$ − 2H), 387.8 (25%, M$^+$ − Cl), 178.7 (100%, M^{2+} − Cl + 2H).

(−)-[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]chloroiridium(I) (12). Yield: 363 mg, 71% as a yellow solid, mp 139 °C. $[\alpha]^{25}_D$ = −28.9 (*c* 0.080, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 4.89−4.77 (2H, m); 4.52−4.43 (2H, m); 3.23−3.11 (2H, m); 3.08−2.95 (4H, m); 2.18−2.12 (4H, m); 1.89−1.57 (8H, m); 1.44−1.34 (4H, m); 0.88−0.82 (4H, m). ^{13}C NMR ($CDCl_3$): δ 202.5, 84.7, 84.4, 66.5, 65.6, 51.9, 51.2, 47.8, 47.7, 33.7, 33.3, 31.6, 31.5, 29.6, 29.2, 26.9, 26.2, 23.6, 23.5. Anal. Calcd for $C_{19}H_{30}ClIrN_2$ (514.17): C, 44.39; H, 5.88; N, 5.45. Found: C, 44.05; H, 6.02; N, 5.44. IR ν_{max} (KBr)/cm^{-1}: 2928, 2852, 1482, 1441, 1304, 1263, 1250, 815, 646. MS: *m*/*z* 514.2 (100%, M$^+$), 479.2 (M$^+$ − Cl), 371.3 (M$^+$ − Cl − COD).

(−)-5,6,8,9,(*S*)-13b,(*S*)-13c-Hexahydro-7a-aza-6a-azonia-dibenzo[*c*,*g*]fluoren-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium(I) (SS-13). Yield: 393 mg, 75% as lemon yellow crystals, mp 241 °C (dec). $[\alpha]^{25}_D$ = −106.2 (*c* 0.095, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.34−7.14 (8H, m); 5.24−4.98 (6H, m); 3.86−3.78 (1H, m); 3.58 (1H, td, J = 12 Hz; J = 3.2 Hz); 3.54−3.45 (1H, m); 3.36 (2H, br); 3.24−3.15 (1H, m); 3.05−2.98 (1H, m); 2.85 (1H, apparent d, J = 15.6 Hz); 2.48−2.32 (4H, m); 1.95 (4H, apparent d, J = 9.6 Hz). ^{13}C NMR ($CDCl_3$): δ 209.2 (d, J = 47.6 Hz), 137.1, 136.5, 135.2, 134.5, 129.6 (d, J = 11.6 Hz), 127.7, 127.5, 127.2, 124.8, 124.4, 100.0 (d, J = 6.1 Hz), 99.7 (d, J = 6.1 Hz), 69.7 (d, J = 14.5 Hz), 67.8, 67.2 (d, J = 14.5 Hz), 66.0, 45.0, 44.4, 33.0 (d, J = 13.1 Hz), 30.1, 29.6, 28.8. Anal. Calcd for $C_{27}H_{30}ClN_2Rh$ (520.12): C, 62.26; H, 5.81; N, 5.38. Found: C, 62.06; H, 5.85; N, 5.28. IR ν_{max} (KBr)/cm^{-1}: 2927, 1480, 1464, 1441, 1295, 1221, 1187, 764, 740. MS: *m*/*z* 518.3 (5%, M$^+$ − 2H), 483.5 (5%, M$^+$ − Cl), 274.3 (30%, M$^+$ − Cl − COD − Rh).

5,6,8,9,(*R*)-13b,(*S*)-13c-Hexahydro-7a-aza-6a-azonia-dibenzo-[*c*,*g*]fluoren-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium(I) (RS-13). Yield: 429 mg, 82% as lemon yellow crystals, mp 207−208 °C (dec). ^{1}H NMR ($CDCl_3$): δ 7.35−7.12 (8H, m); 5.21−4.97 (6H, m); 3.85−3.78 (1H, m); 3.57 (1H, td, J = 12 Hz; J = 3.2 Hz); 3.54−3.45 (1H, m); 3.35 (2H, br); 3.24−3.15 (1H, m); 3.05−2.98 (1H, m); 2.85 (1H, apparent d, J = 15.6 Hz); 2.48−2.31 (4H, m); 1.95 (4H, apparent d, J = 9.6 Hz). ^{13}C NMR ($CDCl_3$): δ 208.8 (d, J = 46.8 Hz), 136.9, 136.4, 135.1, 134.3, 129.5 (d, J = 11.6 Hz), 127.6, 127.4, 127.1, 124.7, 124.3, 99.9 (d, J = 6.1 Hz), 99.6 (d, J = 6.1 Hz), 69.6 (d, J = 14.6 Hz), 67.7, 67.0 (d, J = 13.9 Hz), 65.9, 44.8, 44.3, 32.8 (d, J = 13.1 Hz), 30.0, 29.5, 28.7. Anal. Calcd for $C_{27}H_{30}ClN_2Rh$ (520.12): C, 62.26; H, 5.81; N, 5.38. Found: C, 62.18; H, 6.05; N, 5.44. IR ν_{max} (KBr)/cm^{-1}: 2927, 1644, 1467, 1096, 982, 802. MS: *m*/*z* 518.3 (3%, M$^+$ − 2H), 483.5 (10%, M$^+$ − Cl), 274.3 (25%, M$^+$ − Cl − COD − Rh).

(−)-5,6,8,9,(*S*)-13b,(*S*)-13c-Hexahydro-7a-aza-6a-azonia-dibenzo[*c*,*g*]fluoren-5-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chloroiridium(I) (SS-14). Yield: 320 mg, 52% as an orange solid, mp n.a. (dec). $[\alpha]^{25}_D$ = −91.7 (*c* 0.110, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.36−7.15 (8H, m); 5.10 (2H, dd, J = 42 Hz, J = 6.4 Hz); 5.02−4.94 (2H, m); 4.64−4.55 (2H, m); 3.67−3.59 (1H, m); 3.52 (1H, td, J = 11 Hz, J = 3.4 Hz); 3.46−3.35 (1H, m); 3.22−3.15 (1H, m); 3.02 (2H, br); 2.82 (1H, apparent d, J = 15.6 Hz); 2.29−2.13 (4H, m); 1.82−1.58 (5H, m). ^{13}C NMR ($CDCl_3$): δ 204.4, 137.0, 136.6, 135.2, 134.4, 129.7, 129.6, 127.7, 127.5, 127.3, 127.2, 124.9, 124.5, 86.3, 85.7, 68.1, 66.3, 53.6, 51.1, 44.7, 44.4, 33.8, 33.3, 30.0, 29.7, 29.6, 29.1. Anal. Calcd for $C_{27}H_{30}ClIrN_2$ (610.20): C, 53.14;

Table 5. Crystallographic Data for Compounds 6, RS-11, and SS-14

	6	RS-11	SS-14
formula	$C_{20}H_{37}N_2OPS$	$C_{19}H_{30}ClN_2Rh$	$C_{27}H_{30}ClIrN_2$
fw	384.56	424.81	610.20
color/habit	colorless/plate	yellow/fragment	orange/fragment
cryst dimens (mm^3)	$0.13 \times 0.38 \times 0.38$	$0.41 \times 0.56 \times 0.63$	$0.08 \times 0.20 \times 0.46$
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a, Å	9.3294(1)	10.6567(1)	7.8469(1)
b, Å	10.0515(2)	11.3869(1)	14.3361(1)
c, Å	12.3944(2)	15.1128(1)	19.9183(1)
β, deg	110.1033(7)	90	90
V, $Å^3$	1091.47(3)	1833.89(3)	2240.69(3)
Z	2	4	4
T, K	123	173	173
D_{calcd}, g cm^{-3}	1.170	1.539	1.809
μ, mm^{-1}	0.232	1.078	6.096
$F(000)$	420	880	1200
θ range, deg	1.75−25.33	2.24−25.31	3.13−25.30
index ranges (h, k, l)	±11, ±12, ±14	±12, ±13, ±18	±9, ±17, ±23
no. of rflns collected	25 947	40 406	62 018
no. of indep rflns/R_{int}	3992/0.038	3348/0.037	4086/0.0417
no. of obsd rflns ($I > 2\sigma(I)$)	3835	3314	3997
no. of data/restraints/params	3992/1/229	3348/0/209	4086/0/280
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0375/0.0978	0.0157/0.0381	0.0319/0.0646
R1/wR2 (all data)[a]	0.0394/0.0991	0.0161/0.0383	0.0326/0.0652
GOF (on F^2)[a]	1.049	1.082	1.204
largest diff peak and hole (e $Å^{-3}$)	+0.43/−0.20	+0.30/−0.30	+2.41/−1.19

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

H, 4.96; N, 4.59. Found: C, 53.49; H, 4.97; N, 4.36. IR ν_{max} (KBr)/cm^{-1}: 2966, 2927, 1441, 1260, 1095, 1021, 802. MS: *m*/*z* 610.2 (54%, M^+), 574.8 (53%, M − Cl).

General Procedure for the Preparation of Dicarbonyl Complexes. Carbon monoxide was bubbled for 30 min through a solution of NHC complex (250 mg) in THF (20 mL). After the color had changed to pale brown, the solvent was removed in vacuo and the crude product was washed with *n*-pentane (2 × 5 mL).

Dicarbonylchloro[1,2,3,4,8,9,10,11,(*R*)-11a,(*S*)-11b-Decahydrodipyrido[1,2-*c*;2′,1′-*e*]imidazol-5-ylidene]rhodium(I) (15). Yield: 112 mg, 51% as a brown semisolid. ^{1}H NMR ($CDCl_3$): δ 4.56−4.49 (2H, m); 3.76−3.69 (2H, m); 3.21−3.15 (1H, m); 3.11−3.04 (1H, m); 1.93−1.90 (4H, m); 1.61−1.55 (4H, m); 1.44−1.41 (4H, m). ^{13}C NMR ($CDCl_3$): δ 185.9 (d, J = 71.8 Hz), 183.1 (d, J = 75.9 Hz), 62.8 (d, J = 35.9 Hz), 48.6 (d, J = 27.6 Hz), 25.8 (d, J = 11.1 Hz), 25.5 (d, J = 12.4 Hz), 23.1. Anal. Calcd for $C_{13}H_{18}ClN_2O_2Rh$ (372.01): C, 41.90; H, 4.87; N, 7.52. Found: C, 42.12; H, 4.68; N, 7.65. IR ν_{max} (KBr)/cm^{-1}: 2937, 2069, 1994, 1640, 1555, 1388, 795. *m*/*z* 372 (M^+, 12%), 344 (M^+ − CO, 30%), 316 (M^+ − 2CO, 100%).

Dicarbonylchloro[5,6,8,9,(*S*)-13b,(*S*)-13c-hexahydro-7a-aza-6a-azonia-dibenzo[*c*,*g*]fluoren-5-ylidene]rhodium(I) (16). Yield: 152 mg, 68% as a brown semisolid. ^{1}H NMR ($CDCl_3$): δ 7.41−7.17 (8H, m); 5.21−5.19 (2H, m); 4.75−4.67 (2H, m); 3.73−3.66 (1H, m); 3.63−3.56 (1H, m); 3.53−3.45 (1H, m); 3.20−3.12 (1H, m); 2.97−2.93 (1H, m); 2.85−2.81 (1H, m). ^{13}C NMR ($CDCl_3$): δ 199.3 (d, J = 40 Hz), 185.5 (d, J = 52.3 Hz), 182.9 (d, J = 74.6 Hz), 136.3, 135.6, 134.7, 134.2, 129.8, 129.7, 128.0, 127.9, 127.7, 127.4, 124.7, 124.7, 67.8, 67.3, 45.3, 45.0, 29.6, 29.4. Anal. Calcd for $C_{21}H_{18}ClN_2O_2Rh$ (468.01): C, 53.81; H, 3.87; N, 5.98. Found: C, 53.52; H, 4.05; N, 6.26. IR ν_{max} (KBr)/cm^{-1}: 2074, 2001, 1636, 1388, 1103, 737. MS: *m*/*z* 468 (M^+, 6%), 440 (M^+ − CO, 24%), 377 (M^+ − 2CO − Cl, 40%).

Ketone Hydrosilylation. A flame-dried Schlenk tube was charged with 0.008 mmol of catalyst and a stir bar and placed under argon. Tetrahydrofuran (5 mL) was added via syringe. Acetophenone (100 mg, 0.832 mmol, 100 equiv relative to catalyst) was added, followed by diphenylsilane (153 mg, 0.832 mmol, 100 equiv relative to catalyst). After the mixture was stirred at −20 °C for 16 h, the flask was opened, and 1 mL of a 1% solution of *p*-toluenesulfonic acid in methanol was added slowly. After 10 min the solvent was removed, and the residue was purified by flash chromatography on silica gel, with *tert*-butyl methyl ether as eluent.

Transfer Hydrogenation. A flame-dried Schlenk tube was charged with 0.008 mmol of catalyst and a stir bar and placed under argon. 2-Propanol (10 mL) was added via syringe, followed by potassium *tert*-butoxide (1.87 mg, 0.017 mmol, 2 equiv relative to catalyst). After the mixture was stirred at room temperature for 15 min, acetophenone (100 mg, 0.832 mmol, 100 equiv relative to catalyst) was added. The reaction mixture was stirred for 72 h at 60 °C. Solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel, with *tert*-butyl methyl ether as eluent.

Hydrogenation. 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 indicated pressure of hydrogen 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.

Single-Crystal X-ray Structure Determination of Compounds 6, RS-11, and SS-14. Crystal data and details of the structure determination are presented in Table 5. Suitable single crystals for the X-ray diffraction studies were grown from methanol (**6**) and methylene chloride/pentane (**RS-11** and **SS-14**). A clear colorless plate (yellow fragment, orange fragment) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (Nonius, MACH3, κ-CCD or Oxford Diffractions; Xcalibur3) at the window of a rotating anode (Nonius, FR591 or sealed tube) and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 2125 (1942, 34 443) reflections. Data collection was performed at 123 (173, 173) K (Oxford Cryosystems) within a θ-range of $1.75° < \theta < 25.33°$ ($2.24° < \theta < 25.31°$, $3.13° < \theta < 25.30°$) and measured with 10 (9, 12) data sets in rotation scan modus with $\Delta\varphi/\Delta\omega$ = 2.0° (2.0°; 1.0°). A total of 25 947 (40 406, 62 018) intensities were

integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, latent decay and absorption effects. After merging [$R_{int} = 0.038$ (0.037, 0.042)] a sum of 3992 (3348, 4086) (all data) and 3835 (3314, 3997) [$I > 2\sigma(I)$], 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. 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 $U_{iso(H)} = 1.2U_{eq(C)}$. Methyl C−H distances are 0.98, and $U_{iso(H)} = 1.5U_{eq(C)}$. Full-matrix least-squares refinements with 229 (209, 280) 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/err < 0.001 (0.001, 0.001). The correct enantiomers are proved by Flack's parameters $x = -0.03(8)$ [−0.03(2), −0.03-(1)]. 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 International Tables for Crystallography. All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97.[22] **RS-11**: Small extinction effects were corrected with the SHELXL-97 procedure with $\epsilon = 0.0060(2)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-601922 (**6**), CCDC-601921 (**RS-11**), and CCDC-601923 (**SS-14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. This work was generously supported by the Fonds der Chemischen Industrie (studentship for D.B.).

Supporting Information Available: Crystallographic data for **SS-6**, **RS-11**, and **SS-14** are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060098B