Stereodynamics and Asymmetric Hydrosilylation with Chiral Rhodium Complexes Containing a Monodentate N-Heterocyclic Carbene

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Imidazolinium salts derived from (1*S*,2*S*)-diphenylethylenediamine were used to prepare chiral N-heterocyclic carbene (NHC) complexes of rhodium of the form (cod)Rh(NHC)Cl via silver transmetalation. The neutral complexes were readily converted to cationic amine analogues [(cod)Rh-(NHC)(L)]SbF_6, where L = isoquinoline and 3,5-lutidine. The NHC ligands contain unsymmetrically substituted wingtips that give rise to chiral axes; the conformations of the substituents, as well as other ligands, are influenced by the fixed chirality in the backbone of the ligand. The stereodynamics of both the neutral and cationic complexes were studied, and it was observed that strong conformational preferences exist both in solution and in the solid state. The interplay of the various chiral elements provides the environment that eventually controls the enantioselectivity in the catalytically active species. These complexes are active catalysts for the hydrosilylation of acetophenone with diphenylsilane and furnished (*S*)-1-phenylethanol in up to 58% enantiomeric excess.

Introduction

N-Heterocyclic carbenes (NHCs) represent a growing class of ligands for transition metal catalysis. Owing to their strong σ-donating ability, NHCs generally form strong metal−carbon bonds, which usually results in stable and robust metal complexes. This, along with their steric differences, makes NHCs an attractive and versatile alternative to phosphine ligands. Indeed, their impact in catalysis has been great, although their utility in asymmetric catalysis has lagged in comparison.[1]

A few examples exist of asymmetric reactions catalyzed by NHC complexes that give high levels of enantioselectivity: iridium-catalyzed hydrogenations of alkenes,[2] ruthenium-catalyzed metathesis reactions,[3] copper-catalyzed allylic alkylations,[4] and rhodium-catalyzed conjugate additions and hydosilylations.[5−7] Of these examples, only one uses a chiral *monodentate* NHC; the others employ chelates of varying design. The chiral NHC ligands developed by Grubbs *et al.* provide the only example, to our knowledge, of an enantiomeric excess (ee) of 90% that has been reported for a complex of a monodentate NHC.[3] Given this success, and the achievements that have been made in the area of asymmetric reactions catalyzed by rhodium complexes of chiral monodentate phosphine ligands,[8−17] we sought to prepare and study a series of rhodium complexes of these chiral NHCs.

We chose the class of compounds (cod)Rh(NHC)Cl as a starting point owing to their applicability in catalysis. These neutral species were prepared and could be readily converted to their cationic analogues by treatment with $AgSbF_6$ in the presence of an amine; complexes of isoquinoline and 3,5-lutidine were prepared for this study. Both the neutral and cationic complexes were fluxional, and their stereodynamics were examined in order to determine the conformational preferences and rates of interconversion. The results suggest that, while there are fast rearrangements occurring in solution, conformational preferences do exist that create an unsymmetrical environment at the metal center. This being the case, these complexes were tested as asymmetric catalysts for the hydrosilylation of acetophenone with diphenylsilane.

Owing to the possibility of rotation about various C−N, Rh−N, and Rh−C bonds, the potential of the chirality in the backbone of the carbene to influence the chiral conformations that can be adopted by other substituents can be investigated. There has been considerable interest in the relaying of chiral information between ligands and the use of mixtures of chiral

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and achiral ligands to influence chiral conformations.[18−23] The interplay of the various chiral elements in the NHC complexes we have investigated provides an excellent opportunity to examine the way in which chiral information can be conveyed within a complex. Ultimately this chiral induction controls the environment that eventually determines the enantioselectivity in the active form of the catalyst.

Results and Discussion

Synthesis of Rh−NHC Complexes. A relatively new but already widely used method for the preparation of transition metal NHC complexes is the silver transmetalation procedure that was first developed by Wang and Lin[24,25] and was later applied to the synthesis of neutral rhodium and iridium compounds.[26] The important feature of this synthetic method is the formation of a Ag−NHC complex, which acts as an efficient transfer agent for the NHC ligand. These reactions often proceed under mild conditions and give high yields; however, examples of the preparation of NHC complexes with saturated backbones from this method are comparatively scarce.[5,27,28] This may be related to the lower acidity of the C2 proton in the imidazolinium salts relative to that in the unsaturated analogues.

Indeed, for the case of imidazolinium salts **1a**,**b**, it was observed that stirring at room temperature for 4 h in CH_2Cl_2 did not yield the desired Ag−NHC complexes. However, heating to 60 °C in MeCN resulted in the rapid formation of the Ag−NHC complex, as was determined by ^{1}H NMR, which showed the disappearance of the C2 proton resonance along with a general broadening of the remaining resonances. Unfortunately, though, some decomposition was observed under these conditions, as some of the ring-opened formamide (15−25%) was produced. It should be noted that this decomposition is halted by using the BF_4^- analogues of **1**, perhaps due to the increased stability of these Ag−NHC complexes with respect to their halide counterparts, which has been attributed to the ion-pairing tendency of the halide variants.[25] For the purposes of this synthesis in particular, however, this is not a viable option, as the reaction with the rhodium dimer generates $AgBF_4$, which can then react with the halide ligand of the neutral rhodium species. The BF_4^- analogues could perhaps be useful in the preparation of cationic complexes, however.

The neutral species **2a**,**b** were prepared in this manner (Figure 1), where the only variations in these complexes were the unsymmetrical N-substituents. The products were air-stable yellow solids and were extremely soluble in many common organic solvents, including nonpolar solvents such as hexanes and diethyl ether. They were also stable in solution for extended periods and could be purified by chromatography on silica gel. Cationic analogues with amine ligands were readily prepared via chloride abstraction with $AgSbF_6$ in the presence of the desired amine. Specifically, the two amines (Figure 2) that were used for this study were isoquinoline and 3,5-lutidine. The isoquinoline complexes were readily obtained in high yields in each case; however, the 3,5-lutidine complex was only obtained in the case of the *o*-tolyl wingtips (**4a**). We attribute this effect to the unsymmetrical nature of isoquinoline, which allows for an orientation of the ligand that places its bulk away from the proximal methyl group of the *o*-tolyl moiety. For 3,5-lutidine this is not possible, and so for the bulkier wingtips of **4b** the steric clash prevents the formation of the cationic complex. These complexes, like their neutral precursors, were air-stable yellow solids and were now insoluble in nonpolar solvents, making recrystallization a viable purification method.

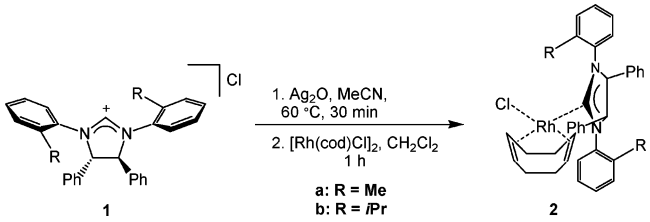

Figure 1. Synthesis of neutral rhodium complexes.

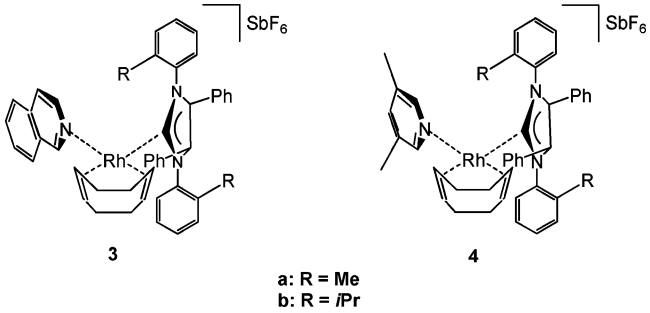

Figure 2. Cationic amine complexes.

Stereodynamics and Conformational Preferences. For each of the Rh complexes prepared in this study, a common feature in the ^{1}H NMR spectra is the inequivalency of the C4 and C5 protons in the backbone of the carbene ligand. These resonances appear as doublets with 3−6 Hz coupling; this is indicative of hindered rotation about the Rh−C bond. This is not surprising, given the similar behavior exhibited by other Rh−NHC complexes[26] and the relative bulk of the NHCs in this case. One would expect that an important feature of these complexes in terms of their potential use in asymmetric catalysis is the orientation of the unsymmetrical wingtips. That is, it is hoped that the fixed chirality in the backbone of the NHC, which is relatively distant from the metal center, will be transferred to the unsymmetrical wingtips. Because the wingtips are closer to the metal, it is likely that their orientation will have a significant influence on an asymmetric reaction. The conformations of the wingtips can be described as being axially chiral, where the axes of chirality reside along the N−Ar bonds. It might be predicted that the stable conformation of the wingtips would be that in which the R group was oriented in an *anti* conformation with respect to the phenyl group on the backbone of the NHC. The result of this would be that the fixed chirality of the *S*,*S* backbone would result in axial chirality, which would be described with the descriptors *aR*,*aR* (Figure 3).

Therefore, it would be useful to know there is a hindered rotation of the N−Ar bonds, since the rigidity of the ligand framework could affect the selectivity of a catalytic reaction. The results reported by Grubbs *et al.* suggest that a hindered rotation is possible. The reported NMR data show that, for the

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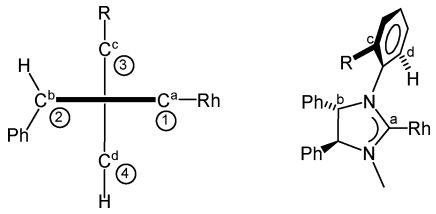


Figure 3. Axial chirality (*aR*) resulting from an *anti* conformation. Viewed along the N−C bond in the NHC toward the substituted phenyl (only the carbons proximal to the N−C are shown).

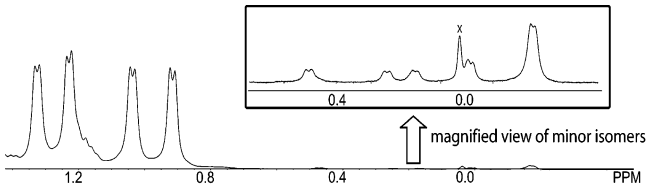


Figure 4. Region of the ^{1}H NMR spectrum of **2b** at −75 °C.

analogous imidazolinium tetrafluoroborate salt with symmetrical mesitylene wingtips, the two *o*-methyl groups are not equivalent in the room-temperature ^{1}H NMR spectrum, indicative of hindered N−Ar rotation.[3] The added steric bulk that would result from metal coordination, then, should serve to increase this rotation barrier. Indeed, those ruthenium complexes in their report with unsymmetrical aryl wingtips exist as mixtures of atropisomers. Evidence of isomeric mixtures has been observed in this study as well, as there is some broadness in the room-temperature ^{1}H NMR spectra for both of the neutral complexes **2a** and **2b**. As previously mentioned, one would perhaps expect that the favored orientation of the wingtips would be *anti*/*anti* with respect to the phenyl groups on the backbone on the NHC. However, three other isomers are possible, with *anti*/*syn*, *syn*/*anti*, and *syn*/*syn* conformations, respectively. The broadness in the NMR spectra is most likely due to the interconversion of these diastereomers, which indicates that the fluxional processes are approaching the fast exchange limit at room temperature since only a single isomer is observed in each case.

Indeed, upon cooling a solution of **2b**, very small amounts of two minor isomers become apparent. The four methyl groups on the *i*Pr moieties of **2b** are diastereotopic, and due to the hindered Rh−C rotation there is no possibility for averaging of their environments with one another. The room-temperature spectrum shows that there is significant broadness in only the most downfield methyl resonance. At lower temperatures (below −35 °C) this resonance has begun to sharpen, and the two minor isomers can now be seen. An interesting (and convenient) characteristic of **2b** is that the resonances for several of the methyl groups of the minor isomers are shifted a good deal upfield, such that they are not superimposed with any of the resonances of the major isomer. Most of these resonances from the minor isomers appear between δ 0.0 and 0.6, and one appears at −0.2 δ; while the cause of these upfield shifts is not clear, it may be that a *syn* arrangement of the aromatic wingtips gives rise to a ring current owing to the close proximity to the phenyl ring in the backbone. In any case, these upfield shifts in the resonances of the minor isomers of **2b** allow for the easy observation of the exchange processes.

Figure 4 shows an upfield region of the ^{1}H NMR spectrum of **2b** at −75 °C and includes a magnified view of the resonances corresponding to the minor isomers. At this temperature, which is nearing the low-temperature limit of the exchange processes, three isomers are present in a ratio of 96:3:1. The four resonances between δ 0.0 and 0.6 each integrate

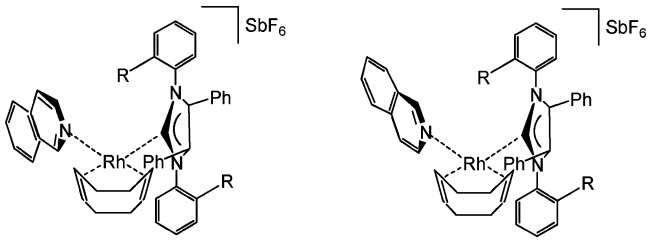


Figure 5. Two possible diastereomers for **3a**.

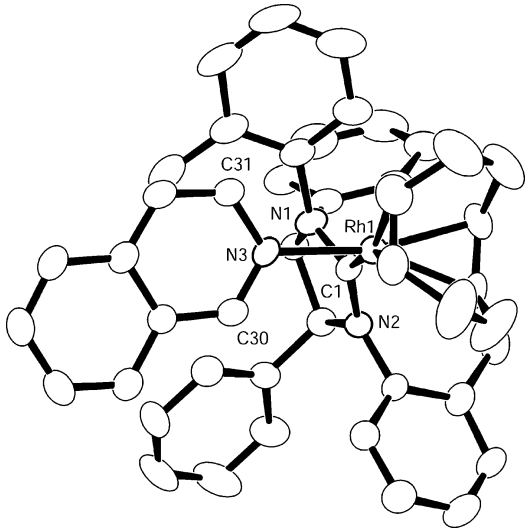


Figure 6. ORTEP diagram of *aR*,*aR*,*aR*-**3a**.

to ∼1% of the major isomer, while the most upfield resonance integrates to ∼3%. The broadness at room temperature for the most downfield methyl resonance might be explained by an exchange with the most upfield resonance of the minor isomers since the broadness depends on the chemical shift difference. As these isomers are likely mixtures of the *syn* and *anti* conformations of the wingtips, there is a strong control of the conformationally induced axial chirality since the major isomer is present in 96%.

Only two broad resonances are apparent in the room-temperature ^{1}H NMR spectrum of **2a**: one corresponding to one of the methyl groups along with the most downfield aromatic proton (at δ 8.66) that belongs to one of the wingtips. A low-temperature spectrum obtained at −55 °C showed a sharpening of these resonances; the aromatic proton is a doublet at this low temperature, perhaps an *ortho* proton from one of the wingtips. There was no sign of the minor isomer(s) in this spectrum; it is possible though that the resonances of the major isomer obscure those of the minor conformations. Nonetheless, it is clear that, as with **2b**, there is a strong preference for one of the possible conformations.

The coordination of isoquinoline in the cationic complexes creates another chiral axis along the Rh−N bond, so there are two possible diastereomers for a given conformation of the NHC ligand (Figure 5). The X-ray structure of **3a** shows that in the solid state there is a single conformation of both the NHC as well as the isoquinoline ligand, which orients the bulk of the ligand away from the nearby bulk of the NHC (Figure 6). This structure shows that the *S*,*S* backbone chirality has induced an *aR*,*aR* axial chirality in the wingtips, which in turn has induced an *aR* axial chirality stemming from the coordination of the amine ligand. This is promising in the sense that, at least in the solid state, the chirality from the backbone of the NHC is effectively transferred to produce the predicted *anti*/*anti* conformation in the wingtips, which has then influenced the

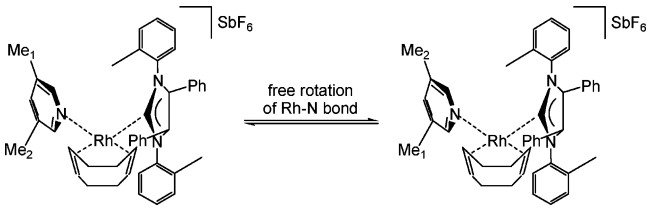


Figure 7. Interconversion of methyl groups in **4a**.

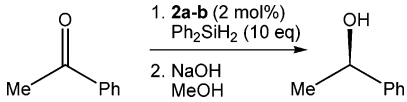
conformation of a proximal metal-bound species. One should also note that a significant tilting of the carbene relative to the square plane of the Rh(I) coordination is observed, and this provides another element of asymmetry (torsion angle N1−C1−Rh−N3 = 63.1°).

However, the observation of only a single isomer in the solid state does not preclude the existence of the other isomers in solution. The analogous complex with the symmetrical 3,5-lutidine (**4a**) ligand shows that there is a fast exchange process occurring at room temperature, which makes the two methyl groups of the amine equivalent by ^{1}H NMR. This could be occurring either by Rh−N bond rotation or by dissociation and reassociation of the amine. A spectrum that contained **3a** in the presence of excess isoquinoline showed discrete resonances for the free amine, indicating that the dissociation and reassociation process is slow on the NMR time scale. Therefore, the equivalency of the two methyl groups on 3,5-lutidine in **4a** is likely due to a fast Rh−N rotation (Figure 7). For both **3a** and **3b**, it was not possible to "freeze out" the Rh−N rotation, as the barriers must be quite low.

It is also interesting to note that once again upfield shifts were observed in the room-temperature ^{1}H NMR spectra for the methyl groups of both **3a** and **3b** upon the formation of the cations. For **3a** one methyl resonance appears at δ 1.23, while the spectrum of **3b** shows a similarly shifted resonance at δ 1.29 and another at δ −0.35. These resonances likely correspond to the wingtip substituents that are oriented toward the binding site of the amine ligand, since the other wingtip is directed away from the metal and should not undergo such a dramatic shift. The structure of **3a** shows the relatively close proximity of one of the methyl groups to the isoquinoline ligand, which in turn causes it to be turned closer to the phenyl ring in the NHC backbone, either of which could give rise to a ring current that could cause the upfield shift. Some clues to the solution structure were obtained with 1D NOE difference experiments on **3a**. Irradiation of the two methyl resonances both showed the largest effects on the protons of the NHC backbone (doublets at δ 5.32 and 5.06, respectively). This suggests that the solution structure resembles the crystal structure, which shows that the *anti*/*anti* conformation is retained (although the plane of one of the aromatic wingtips is no longer perpendicular to the plane of the NHC).

Catalytic Hydrosilylation of Acetophenone. Recent work has involved the application of chiral Rh−NHC complexes to the asymmetric hydrosilylation of methyl ketones. Generally, low to moderate levels of enantioselectivity (6−44% ee) were obtained;[29−32] only two catalysts were developed that furnished high selectivity (>90% ee).[6,7] Neutral and cationic variants have been successfully employed, although the catalysts showing high enantioselectivity both contained a chelating NHC framework. Given this precedent, we viewed this as a reasonable starting point for the testing of our complexes in asymmetric catalysis and began with the catalytic hydrosilylation of acetophenone with diphenylsilane. The results are shown in Tables 1 and 2.

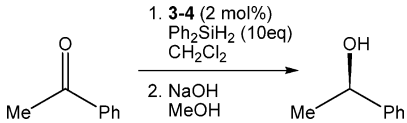
Table 1. Hydrosilylation of Acetophenone Catalyzed by Neutral Rh Complexes



entry	catalyst	solvent	temp (°C)	time (h)	% conv	ee[a]
1	**2a**	THF	rt	1	82	23
2	**2a**	Et_2O	rt	1	94	40
3	**2a**	CH_2Cl_2	rt	1	>98	44
4	**2a**	CH_2Cl_2	−20	24	77	41
5	**2a**	toluene	rt	1	>98	58
6[b]	**2a**	toluene	−20	24	>98	45
7	**2b**	toluene	rt	1	>98	49
8	**2b**	CH_2Cl_2	rt	1	>98	48

[a] Determined by NMR and a chiral shift reagent and is reproducible within 1%. [b] A higher catalyst loading of 5 mol % was necessary to obtain this conversion.

Table 2. Hydrosilylation of Acetophenone Catalyzed by Cationic Rh Complexes



entry	catalyst	temp (°C)	time (h)	% conv	ee[a]
1	**3a**	rt	2	>98	50
2	**3a**	−20	24	54	26
3	**4a**	rt	2	>98	43
4	**3b**	rt	2	51	15

[a] Determined by NMR and a chiral shift reagent and is reproducible within 1%.

Table 1 shows the results for catalysis by the neutral complexes; the enantiomeric excess ranged from 15 to 58%. Entries 1−4 show the effect of the solvent on the reaction catalyzed by **2a** at room temperature. The solvent was seen to play a role in both the activity and selectivity, and toluene gave the best result. When the temperature was lowered to −20 °C, the activity severely decreased. Interestingly, the larger wingtip groups resulted in lower selectivity for this reaction. There seems to be a trend that relates the loss of catalytic activity to lower selectivity; the catalyst with the larger wingtip groups, **2b**, performed worse in both categories.

The cationic analogues were also tested, and it was found that they generally gave comparable selectivity to and less activity than their neutral analogues (Table 2). The best among the cationic complexes was once again that with the smallest wingtip groups, **3a**, which was slightly more selective than **2a** in CH_2Cl_2 (50 % ee versus 45 % ee). Cooling to −20 °C once again resulted in a loss of activity and selectivity; these effects were somewhat worse for **3a** than for **2a**. A comparison of **3a** and **4a** shows that the unsymmetrical isoquinoline complex gave a slight improvement in selectivity, perhaps an effect of the additional element of chirality in **3a**. The differences in reactivity between the neutral and cationic complexes suggest that the nature of the active catalyst could be different for the two general cases.

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Conclusions

Neutral and cationic Rh complexes of chiral NHC ligands were prepared via silver transmetalation. Solution studies indicate that, while these complexes are not structurally rigid, there is a conformational preference that is induced by the chiral backbone of the NHC ligand. This results in the formation of chiral axes about the N−Ar bonds, which can in turn influence the orientation of the unsymmetrical isoquinoline ligand in the cationic complexes and create another chiral axis about the Rh−N bond. The X-ray structure of **3a** shows a single conformation of the isoquinoline ligand and is useful in illustrating this chirality transfer from the backbone of the NHC to the wingtip groups and then to the metal-bound amine ligand. It appears, though, that in solution there is a fast rotation about the Rh−N bond, which results in an averaged ^{1}H NMR spectrum. The barrier to this rotation was sufficiently low so as to prevent our evaluation of the degree of conformational preference in solution.

These complexes were applied to the catalytic hydrosilylation of acetophenone by diphenylsilane. Both the neutral and the cationic complexes were active catalysts for this reaction, though the neutral species were generally more active. Surprisingly, the larger wingtips of **2b/3b** did not improve the enantioselectivity. The low-temperature catalytic runs gave poor results, as the activity and the selectivity both suffered when the reactions were performed at −20 °C. The most selective catalyst was **2a**, the complex with the least steric bulk, which catalyzed the reaction with 58% ee in toluene at room temperature. While there are two previously known Rh−NHC catalysts that give better selectivity in this reaction, the results presented here represent a very good enantioselectivity for a monodentate NHC ligand. These preliminary findings are promising for the future implementation of these complexes in asymmetric reactions.

Experimental Section

General Methods. The manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene and THF were dried by distillation under a nitrogen atmosphere over Na/benzophenone; CH_2Cl_2 was dried by distillation under a nitrogen atmosphere over CaH_2. Acetonitrile was dried on an alumina-based solvent purification system. Acetone, Et_2O, pentane, MeOH, (*S*,*S*)-DPEN, $Pd(OAc)_2$, BINAP, NaO*t*Bu, 2-bromotoluene, 2-isopropylbromobenzene, NH_4Cl, triethylorthoformate, Ag_2O, acetophenone, diphenylsilane, and NaOH were purchased and used as received. $[Rh(cod)Cl]_2$ was prepared according to a reported protocol.[33] NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers.

Synthesis of Imidazolinium Salts. The imidazolinium salts were synthesized with the reported protocol.[3] A flame-dried flask was charged with $Pd(OAc)_2$, BINAP, NaO*t*Bu, and toluene under a nitrogen atmosphere. The mixture was stirred for 20 min, at which point (*S*,*S*)-DPEN and the aryl bromide were added, and the resulting solution was heated under reflux for 18 h. The solution was then cooled, diluted with pentane, and passed through a column of silica gel eluting with pentanes first to remove the unwanted material. The product diamine was then eluted with CH_2Cl_2, dried under vacuum, and used directly without further purification.

The diamine was then placed in a flask under a nitrogen atmosphere along with NH_4Cl and triethylorthoformate (2 mL) and was heated to 120 °C for 18 h. The mixture was then cooled, diluted with Et_2O, and filtered through Celite in order to remove the excess triethylorthoformate. The imidazolinium salts were then eluted with CH_2Cl_2, dried under vacuum, and used directly without further purification.

(33) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88−90.

(4*S*,5*S*)-1,3-Di(2-methylphenyl)-4,5-diphenylimidazolinium chloride (1a). Anal Calcd for $C_{29}H_{27}N_2Cl\cdot{}^1/_2CH_2Cl_2$: C, 73.59; H, 5.86; N, 5.82. Found: C, 73.52; H, 5.87; N, 6.15. $[\alpha]_D$ (*c* 0.00957, CH_2Cl_2): −347. ^{1}H NMR ($CDCl_3$, 500 MHz): 9.51 (1H, s, C*H*$_{imid}$); 7.68 (2H, d, J = 7.5 Hz), 7.53 (4H, d, J = 7.5 Hz), 7.44−7.34 (6H, m), 7.23−7.11 (6H, m), (C*H*$_{arom}$); 5.90 (2H, s, C_2H_{2imid}); 2.55 (6H, s, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 125.77 MHz): 157.6 (*C*H$_{imid}$); 133.0, 132.9, 132.4, 131.0, 129.5, 129.0, 128.9, 127.6, 126.9, 126.6, (*C*$_{arom}$); 75.3 (C_2H_{2imid}); 18.1 (*C*H$_3$).

(4*S*,5*S*)-1,3-Di(2-isopropylphenyl)-4,5-diphenylimidazolinium chloride (1b). Anal Calcd for $C_{33}H_{35}N_2Cl\cdot{}^1/_2CH_2Cl_2$: C, 74.85; H, 6.75; N, 5.21. Found: C, 74.88; H, 6.74; N, 5.22. $[\alpha]_D$ (*c* 0.00969, CH_2Cl_2): −241. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.76 (1H, s, C*H*$_{imid}$); 7.85 (2H, br), 7.53 (4H, br), 7.25−6.95 (12H, m), (C*H*$_{arom}$); 5.69 (2H, s, C_2H_{2imid}); 2.97 (2H, br sp, C*H*$_{isopropyl}$); 1.15 (6H, br d, J = 6.7 Hz, CH$_{3isopropyl}$); 1.02 (6H, br d, J = 6.7 Hz, C*H*$_{3isopropyl}$). ^{13}C NMR ($CDCl_3$, 125.77 MHz): 157.7 (*C*H$_{imid}$); 144.4, 132.5, 130.9, 130.1, 129.9, 129.2, 128.5, 128.4, 127.0, 126.3, (*C*$_{arom}$); 76.7 (C_2H_{2imid}); 28.2 (*C*H$_{isopropyl}$); 24.2, 23.7 (*C*H$_{3isopropyl}$).

Synthesis of Neutral Rhodium Complexes (2a,b). (4*S*,5*S*)-1,3-Di(2-methylphenyl)-4,5-diphenylimidazolin-2-ylidene(1,5-cyclooctadiene)chlororhodium (2a). A flask was charged with **1a** (299 mg, 0.681 mmol) and Ag_2O (790 mg, 3.41 mmol) and was evacuated and backfilled with nitrogen. MeCN (10 mL) was added, and the mixture was heated to 60 °C for 0.5 h, at which point it was filtered through Celite and the solvent was removed under vacuum. To the residue was added $[Rh(cod)Cl]_2$ (114 mg, 0.231 mmol), and the flask was once again evacuated and then backfilled with nitrogen. Some CH_2Cl_2 (6 mL) was added, and the resulting solution was stirred for 1 h at room temperature. Filtration through Celite removed the AgCl precipitate, and the solvent was removed under vacuum. The product was purified by column chromatography on silica gel. The impurities were eluted first with CH_2Cl_2, and then the product was eluted with $(CH_3)_2CO$ (275 mg, 92% based on Rh). Crystals were not forthcoming due to the extremely high solubility of **2a**, and the product retained ∼0.5 equiv of acetone even after drying under vacuum. Anal Calcd for $C_{37}H_{38}N_2ClRh\cdot{}^1/_2(CH_3)_2CO$: C, 68.19; H, 6.09; N, 4.13. Found: C, 67.75; H, 5.80; N, 4.49. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.66 (1H, br), 7.62−7.02 (17H, m), (C*H*$_{arom}$); 5.34 (1H, d, J = 4.8 Hz, C*H*$_{imid}$), 5.12 (1H, d, J = 4.8 Hz, C*H*$_{imid}$), 4.77 (1H, m, C*H*$_{cod}$), 4.60 (1H, m, C*H*$_{cod}$), 3.59 (1H, m, C*H*$_{cod}$), 2.96 (1H, m, C*H*$_{cod}$); 2.54 (3H, s, C*H*$_3$); 2.39 (3H, s, C*H*$_3$); 2.13 (1H, m, C*H*$_{2cod}$), 1.98 (1H, m, C*H*$_{2cod}$), 1.86−1.10 (4H, m, C*H*$_{2cod}$), 0.90 (2H, m, C*H*$_{2cod}$). ^{13}C NMR ($CDCl_3$, 125.7 MHz): 215.2 (d, $^2J_{Rh-C}$ = 47.9 Hz, *C*$_{carbene}$); 139.4, 138.9, 138.7, 138.1, 137.0, 133.4 (br), 132.7 (br), 131.6, 131.1, 130.3, 129.2, 129.1, 128.8, 128.7, 128.2, 127.5, 127.3, 127.0, 126.4, 125.4, (*C*$_{arom}$); 98.7 (d, $^2J_{Rh-C}$ = 7.9 Hz), 98.0 (d, $^2J_{Rh-C}$ = 7.0 Hz), (*C*H$_{cod}$); 76.7 (br), 75.4 (br), (*C*H$_{imid}$); 69.7 (d, $^2J_{Rh-C}$ = 14.2 Hz), 66.6 (d, $^2J_{Rh-C}$ = 14.6 Hz), (*C*H$_{cod}$); 32.8 31.6, 28.9, 27.3, (*C*H$_{2cod}$); 19.8, 19.4, (*C*H$_3$).

(4*S*,5*S*)-1,3-Di(2-isopropylphenyl)-4,5-diphenylimidazolin-2-ylidene(1,5-cyclooctadiene)chlororhodium (2b). A flask was charged with **1b** (127 mg, 0.245 mmol) and Ag_2O (284 mg, 1.22 mmol) and was evacuated and backfilled with nitrogen. MeCN (4 mL) was added, and the mixture was heated to 60 °C for 0.5 h, at which point it was filtered through Celite and the solvent was removed under vacuum. To the residue was added $[Rh(cod)Cl]_2$ (50 mg, 0.101 mmol), and the flask was once again evacuated and then backfilled with nitrogen. Some CH_2Cl_2 (3 mL) was added, and the resulting solution was stirred for 1 h at room temperature. Filtration through Celite was done to remove the AgCl precipitate, and the solvent was removed under vacuum. The product was purified by column chromatography on silica gel. The impurities were eluted first with CH_2Cl_2, and then the product was eluted with acetone (90 mg, 63% yield based on Rh). Crystals were not forthcoming due to the extremely high solubility of **2b**, and the

product retained ~0.5 equiv of acetone even after drying under vacuum. Anal Calcd for $C_{41}H_{46}N_2ClRh \cdot {}^1/_2(CH_3)_2CO$: C, 69.52; H, 6.72; N, 3.81. Found: C, 69.35; H, 6.72; N, 3.86. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.75 (1H, m), 7.65 (1H, d, J = 7.6 Hz), 7.60 (2H, d, J = 7.2 Hz), 7.41−7.19 (13H, m), 7.11 (1H, m), (CH_{arom}); 5.13 (1H, br d, J = 2.8 Hz, CH_{imid}), 5.04 (1H, br d, J = 2.8 Hz, CH_{imid}); 4.80 (1H, m, CH_{cod}), 4.62 (1H, m, CH_{cod}), 3.62 (1H, m, CH_{cod}); 3.33 (1H, sp, J = 6.8 Hz, C$H_{isopropyl}$), 3.12 (1H, sp, J = 6.8 Hz, C$H_{isopropyl}$), 3.04 (1H, m, CH_{cod}), 2.19 (1H, m, CH_{2cod}), 2.07 (1H, m, CH_{2cod}), 1.84−1.65 (3H, m, CH_{2cod}), 1.58−1.44 (2H, m, CH_{2cod}), 1.36 (1H, m CH_{2cod}), 1.33 (3H, br, C$H_{3isopropyl}$), 1.30 (3H, d, J = 6.8 Hz, C$H_{3isopropyl}$), 1.13 (3H, d, J = 6.8 Hz, C$H_{3isopropyl}$), 0.99 (3H, d, J = 6.8 Hz, C$H_{3isopropyl}$). ^{13}C NMR ($CDCl_3$, 125.7 MHz): 216.5 (d, $^2J_{Rh-C}$ = 48.2 Hz, $C_{carbene}$); 146.9, 144.1, 139.4, 138.5, 137.3, 137.0, 133.6, 131.0, 129.3, 129.1, 128.9, 128.7, 128.6, 128.2, 127.2, 127.0, 126.6, 126.0, 125.8, 125.1, (C_{arom}); 98.4 (d, $^2J_{Rh-C}$ = 6.4 Hz), 98.2 (d, $^2J_{Rh-C}$ = 6.9 Hz), (CH_{cod}); 78.1 (br), 77.6 (CH_{imid}); 70.3 (d, $^2J_{Rh-C}$ = 15.0 Hz), 66.5 (d, $^2J_{Rh-C}$ = 14.8 Hz), (CH_{cod}); 32.7, 31.7, 29.0, (CH_{2cod}); 27.9, 27.7 (C$H_{isopropyl}$); 27.4 (CH_{2cod}); 25.1, 24.4, 23.7, 23.5 (C$H_{3isopropyl}$).

Representative Procedure for Synthesis of Cationic Complexes 3−4. A flask was charged with the neutral Rh precursor compex (**2a**−**b**; 0.10 mmol) and was evacuated and backfilled with nitrogen. Some CH_2Cl_2 (5 mL) was then added, followed by $AgSbF_6$ (0.10 mmol) under a stream of nitrogen. To the resulting mixture was added the amine (0.12 mmol) by syringe. After stirring for 1 h, the mixture was filtered, and the solvent removed under vacuum. The residue was washed with pentane (3 × 5 mL) and dried under vacuum. Nearly quantitative yields were obtained in each case. Crystals were obtained by slow diffusion of Et_2O or pentane into a CH_2Cl_2 solution of the complex.

[(4*S*,5*S*)-1,3-Di(2-methylphenyl)-4,5-diphenylimidazolin-2-ylidene(1,5-cyclooctadiene)(isoquinoline)rhodium]-hexafluoroantimonate (3a). Anal Calcd for $C_{46}H_{45}F_6N_3RhSb$: C, 56.46; H, 4.64; N, 4.29. Found: C, 56.40; H, 4.67; N, 4.35. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.42 (1H, d, J = 5.6 Hz), 8.09−6.94 (24H, m), (CH_{arom}); 5.32 (1H, d, J = 5.2 Hz, CH_{imid}), 5.06 (1H, d, J = 5.2 Hz, CH_{imid}), 4.43 (1H, m, CH_{cod}), 4.24 (1H, m, CH_{cod}), 3.81 (1H, m, CH_{cod}), 2.69 (1H, m, CH_{cod}), 2.40 (3H, s, CH_3), 2.31 (1H, m, CH_{2cod}), 2.20 (2H, m, CH_{2cod}), 1.91 (1H, m, CH_{2cod}), 1.74 (2H, m, CH_{2cod}), 1.48 (1H, m, CH_{2cod}), 1.23 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 208.6 (d, $^2J_{Rh-C}$ = 46.5 Hz, $C_{carbene}$); 154.8, 143.1, 142.6, 138.4, 138.0, 137.9, 137.4, 135.9, 135.6, 134.8, 133.1, 132.2, 131.9, 130.7, 129.7, 129.61, 129.59, 129.54, 129.47, 129.45, 129.3, 128.6, 127.8, 127.53, 127.3, 127.2, 126.8, 126.6, 123.2 (C_{arom}); 98.1 (d, $^2J_{Rh-C}$ = 7.5 Hz), 97.3 (d, $^2J_{Rh-C}$ = 7.8 Hz), 78.8 (d, $^2J_{Rh-C}$ = 13.1 Hz), 78.3 (d, $^2J_{Rh-C}$ = 13.1 Hz), (CH_{cod}); 76.1, 75.7, (CH_{imid}); 33.3, 30.1, 30.0, 27.5 (CH_{2cod}); 19.4, 17.9 (CH_3).

[(4*S*,5*S*)-1,3-Di(2-isopropylphenyl)-4,5-diphenylimidazolin-2-ylidene(1,5-cyclooctadiene)(isoquinoline)rhodium]-hexafluoroantimonate (3b). Anal Calcd for $C_{50}H_{53}F_6N_3RhSb$: C, 58.04; H, 5.16; N, 4.06. Found: C, 57.99; H, 5.17; N, 4.11. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.39 (1H, d, J = 6.0 Hz), 8.03 (1H, d, J = 8.0 Hz), 7.96 (1H, d, J = 6.0 Hz), 7.91 (1H, d, J = 8.0 Hz), 7.78 (1H, m), 7.71 (1H, t, J = 7.5 Hz), 7.68−7.55 (6H, m), 7.48−7.38 (4H, m), 7.36 (dd, J = 6.0 Hz, 1.0 Hz), 7.30−7.24 (3H, m), 7.18 (2H, m), 7.14 (1H, d, J = 8.0 Hz), 7.02 (2H, m), (CH_{arom}); 5.16 (1H, d, J = 2.8 Hz, CH_{imid}), 5.04 (1H, br, CH_{imid}), 4.42 (1H, m, CH_{cod}), 4.12 (1H, m, CH_{cod}), 3.68 (1H, q, J = 7.0 Hz, CH_{cod}), 3.43 (1H, m, CH_{cod}), 2.96 (1H, sp, J = 6.8 Hz, C$H_{isopropyl}$), 2.74 (1H, br sp, C$H_{isopropyl}$), 2.42 (1H, m, CH_{2cod}), 2.34−2.21 (2H, m, CH_{2cod}), 2.15 (1H, m, CH_{2cod}), 1.89−1.73 (2H, m, CH_{2cod}), 1.61 (1H, m, CH_{2cod}), 1.43 (1H, m, CH_{2cod}), 1.29 (3H, d, J = 6.8 Hz, C$H_{3isopropyl}$), 1.09 (3H, d, J = 6.8 Hz, C$H_{3isopropyl}$), 0.76 (3H, br, C$H_{3isopropyl}$), −0.35 (3H, br d, C$H_{3isopropyl}$). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 211.3 (d, $^2J_{Rh-C}$ = 49.1 Hz, $C_{carbene}$); 154.7, 145.5, 144.4, 142.3, 138.0, 137.1, 137.0, 136.4, 135.5, 133.0, 130.8, 130.0, 129.8, 129.7, 129.6, 129.4, 129.3, 129.1, 128.2, 128.0, 127.7, 127.10, 127.08, 127.0, 126.9, 126.6, 126.2, 126.1, 123.5 (C_{arom}); 98.7 (d, $^2J_{Rh-C}$ = 7.4 Hz), 97.3 (d, $^2J_{Rh-C}$ = 8.2 Hz), 79.4 (d, $^2J_{Rh-C}$ = 12.5 Hz), 78.1 (d, $^2J_{Rh-C}$ = 14.8 Hz), (CH_{cod}); 78.0, 76.9, (CH_{imid}); 33.2, 30.1, 29.5, (CH_{2cod}); 28.1, 27.8, (C$H_{isopropyl}$); 27.1 (CH_{2cod}); 24.5, 24.4, 23.4, 21.2, (CH_3).

[(4*S*,5*S*)-1,3-Di(2-methylphenyl)-4,5-diphenylimidazolin-2-ylidene(1,5-cyclooctadiene)(3,5-lutidine)rhodium]hexafluoroantimonate (4a). Anal Calcd for $C_{44}H_{47}F_6N_3RhSb$: C, 55.25; H, 4.95; N, 4.39. Found: C, 55.54; H, 5.10; N, 4.20. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.88 (1H, d, J = 7.2 Hz), 7.66 (1H, d, J = 7.2 Hz), 7.52 (3H, m), 7.45 (1H, t, J = 7.2 Hz), 7.42−7.24 (10 H, m), 7.16 (1H, dd, J = 7.2, 1.6 Hz), 7.12 (2H, m), 6.99 (2H, m), (CH_{arom}); 5.27 (1H, d, J = 5.6 Hz, CH_{imid}), 5.13 (1H, d, J = 5.6 Hz, CH_{imid}), 4.34 (1H, m, CH_{cod}), 4.12 (1H, m, CH_{cod}), 3.76 (1H, m, CH_{cod}), 3.27 (1H, m, CH_{cod}), 2.60 (1H, m, CH_{2cod}), 2.37 (3H, s,C$H_{3wingtip}$), 2.33 (6H, s, (CH_3)$_{2lutidine}$), 2.27−2.05 (3H, m, CH_{2cod}), 1.86 (1H, m, CH_{2cod}), 1.72 (1H, m, CH_{2cod}), 1.64 (3H, s, C$H_{3wingtip}$), 1.59 (1H, m, CH_{2cod}), 1.43 (1H, m, CH_{2cod}). ^{13}C NMR ($CDCl_3$, 500 MHz): 209.3 (d, $^2J_{Rh-C}$ = 46.5 Hz, $C_{carbene}$); 148.3, 142.8, 140.0, 138.4, 137.8, 137.7, 137.6, 136.2, 135.3, 134.9, 133.6, 132.0, 131.6, 130.5, 129.7, 129.6, 129.5, 129.2, 129.1, 127.1, 127.0, 126.74, 127.65 (C_{arom}); 98.2 (d, $^2J_{Rh-C}$ = 6.9 Hz), 97.1 (d, $^2J_{Rh-C}$ = 7.0 Hz), 78.7 (d, $^2J_{Rh-C}$ = 11.4 Hz), 77.8 (d, $^2J_{Rh-C}$ = 10.3 Hz), (CH_{cod}); 76.0, 75.4, (CH_{imid}); 33.0, 30.2, 29.7, 27.6 (CH_{2cod}); 19.3 (C$H_{3wingtip}$); 18.4 (C$H_{3lutidine}$); 18.3 (C$H_{3wingtip}$).

Table 3. Crystallographic Data for 3a

color, shape	yellow block
empirical formula	$C_{46}H_{45}F_6N_3RhSb$
fw	978.53
radiation/Å	Mo Kα (monochr)
T/K	173
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
unit cell dimens	
a/Å	9.9459(3)
b/Å	18.3293(6)
c/Å	11.4953(3)
V/Å^3	2074.34(9)
Z	2
D_{calc}/g cm^{-3}	1.567
μ/cm^{-1} (Mo Kα)	22.10
cryst size/mm	0.07 × 0.12 × 0.12
no. of reflns tot, unique, used[a]	8835, 5031; 7670
R_{int}	0.033
no. of params, restraints	513, 0
R_1,[a] R_w,[b] GOF	0.037, 0.038, 1.91
resid density/e Å^{-3}	−0.73 < 0.60

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$. [b] $R_w = [\sum[w(|F_o| - |F_c|)^2]]^{1/2}$.

Crystal Structure Determination and Refinement. Data were collected on a Nonius KappaCCD (Mo Kα radiation) diffractometer and scaled using HKL2000.[34,35] The data were not specifically corrected for absorption other than the inherent corrections provided by Scalepack.[35] The structure was solved by direct methods (SIR92) and refined on F for all reflections.[36,37] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. The structure is shown in Figure 6. Relevant crystal and data parameters are presented in Table 3.

(34) Minor, W., Otwinowski, Z., Eds. *HKL2000 (Denzo-SMN) software package. Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology Macromolecular Crystallography*; Academic Press: New York, 1997.

(35) Otwinowski, Z.; Minor, W. In *International Tables for Crystallography*; Rossman, M. G., Arnold, E., Eds.; 2001; Vol. F.

(36) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(37) *TEXSAN for Windows version 1.06: Crystal Structure Analysis Package*; Molecular Structure Corporation, 1999.

The compound **3a** crystallized in the monoclinic space group $P2_1$, consistent with the observed absences. The absolute configuration was determined by inversion of coordinates ($R = 3.75$, $R_w = 3.76$ compared to $R = 4.27$, $R_w = 4.64$).

General Procedure for Catalytic Hydrosilylation of Acetophenone. A flask was charged with the desired Rh complex (0.0075 mmol) and was placed under a nitrogen atmosphere. The solvent (5 mL) was added by syringe, and the resulting solution was then brought to the desired temperature, at which point acetophenone (44 μL, 0.38 mmol) was added, followed by diphenylsilane (700 μL, 3.8 mmol). A large excess of silane was used in order to increase the rate of hydrosilylation relative to catalyst decomposition. A recent study has shown a linear rate dependence on silane concentration for a rhodium-catalyzed hydrosilylation of acetophenone, from which the authors proposed that the rate-limiting step might be oxidative addition of the silane.[38] We have observed that the use of only a 20% excess resulted in lower conversions, but the enantioselectivity was not affected. The mixture was stirred for the appropriate time period and was quenched by the slow addition of 2 mL of a 1:30 NaOH (50% aqueous)/MeOH solution. The solvent was removed under vacuum, and the crude residue was purified by column chromatography over silica gel eluting with 3:1 pentane/Et_2O. The ee of the product alcohol was determined with a chiral shift experiment with (+)-Eu(hfc)$_3$ in C_6D_6.

Supporting Information Available: Crystallographic data for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060650X

(38) Reyes, C.; Prock, A.; Giering, W. P. *Organometallics* **2002**, *21*, 546−554.