Stereoselective Synthesis of Rhodium(I) 4-(Dialkylamino)triazol-5-ylidene Complexes

Abel Ros,[†] Manuel Alcarazo,[‡] Javier Iglesias-Sigüenza,[†] Elena Díez,[†] Eleuterio Álvarez,[‡] Rosario Fernández,*[,†] and José M. Lassaletta*[,‡]

Departamento de Química Orgánica, Facultad de Química, Universidad de Sevilla, Apartado de Correos 1203, 41071 Seville, Spain, and Instituto de Investigaciones Químicas (CSIC-US), C/ Americo Vespucio 49, 41092 Seville, Spain

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The synthesis of 1-alkyl-1,2,4-triazolium salts containing chiral 4-dialkylamino substituents was accomplished by selective alkylation at N-1 of the corresponding 4-(dialkylamino)-1,2,4-triazoles. The latter were synthesized by reaction of *N*,*N*-dimethylformamidazine dihydrochloride with *N*,*N*-dialkylhydrazines in pyridine. Alternatively, the synthesis of 4-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-1-phenyl-1,2,4-triazolium perchlorate was performed by reaction of 3-phenyl-1,3,4-oxadiazolium perchlorate with (2*S*,5*S*)-1-amino-2,5-diphenylpyrrolidine. These triazolium salts were transformed into neutral [RhCl(NHC)(COD)] complexes (NHC = 4-(dialkylamino)-1-alkyl(phenyl)triazol-5-ylidene) by reaction with $[RhCl(COD)]_2$ in the presence of triethylamine. The products, featuring restricted C(carbene)−Rh bond rotation, were formed with high levels of selectivity in all cases, the de's being >98% for complexes bearing the (2*S*,5*S*)-2,5-diphenylpyrrolidino group. A cationic heterobidentate NHC/S complex was also synthesized in a highly stereoselective way by alkylation of 4-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-1,2,4-triazole with (*R*)-1-bromo-2-(cyclohexylthio)-3-methylbutane, followed by treatment of the resulting triazolium salt with $[RhCl(COD)]_2/Et_3N$ and ensuing bromide abstraction by $AgSbF_6$. A preliminary evaluation of the neutral and cationic Rh complexes in the asymmetric hydrosilylation of acetophenone indicated good catalytic activity and moderate enantioselectivities for most complexes, reaching a promising 62% ee in the case of the cationic complex.

Introduction

N-heterocyclic carbenes (NHCs) have emerged over the past decade as an important group of ligands for transition-metal-based homogeneous catalysts.[1] In some aspects, these compounds can be viewed as phosphane surrogates, the σ-donor ability of NHC ligands matching or improving upon that of the most basic phosphines. Additionally, NHC-based catalysts are usually stable and kinetically robust compounds with a low tendency to dissociation, valuable characteristics of particular interest in the field of asymmetric catalysis.[2] Selected examples of asymmetric reactions catalyzed by NHCs are the Rh-[3] or Ir-catalyzed[4] olefin hydrogenations and conjugate additions of arylboronic acids,[5] palladium-catalyzed allylic alkylations,[6] copper- or silver-catalyzed conjugate addition of organometallics to enones,[7] ring-opening olefin metathesis,[8] and rhodium-catalyzed hydrosilylations.[9]

In the frame of our interest in the development of new types of NHC ligands and the application in catalysis of their transition-metal complexes, we have recently reported the synthesis and structure of chiral *N*-(dialkylamino)imidazolin-2-ylidenes[10] and imidazopyridine-3-ylidenes,[11] and the catalytic performance in the palladium-catalyzed allylic substitutions of NHC/thioether mixed ligands **A** and **B** (Figure 1).[6b,c] However,

* To whom correspondence should be addressed. E-mail: ffernan@us.es (R.F.); jmlassa@iiq.csic.es (J.M.L.).
[†] Universidad de Sevilla.
[‡] Instituto de Investigaciones Químicas.

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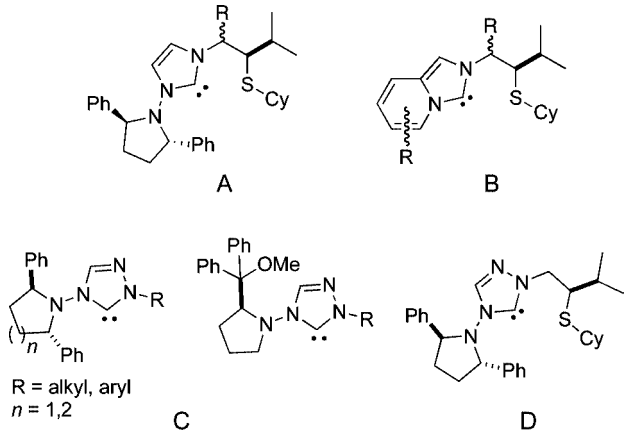


Figure 1. Novel carbene structures.

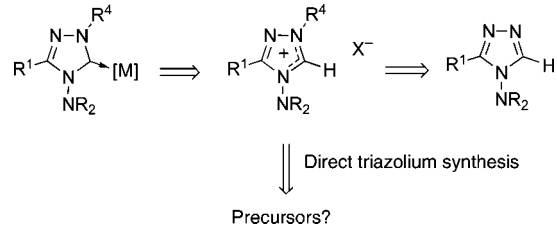
since the pioneering work of Enders,[12] relatively little attention has been devoted to the chemistry of metal 1,2,4-triazol-5-ylidene complexes,[13] a surprising circumstance considering that there are simple routes to access these compounds and that their catalytic activity has been demonstrated,[14] even though 1,2,4-triazol-5-ylidenes are weaker σ donors than conventional imidazol-2-ylidene or imidazolin-2-ylidene ligands.[15] In this context, we now wish to report on the stereoselective synthesis and electronic properties of rhodium(I) complexes bearing *monodentate* (NHC) or *bidentate* (NHC/S) ligands **C** and **D** based on chiral 1-alkyl(aryl)-4-(dialkylamino)-1,2,4-triazol-5-ylidenes as novel carbene structures.[16] The catalytic performance of these rhodium(I) complexes has also been investigated in the asymmetric hydrosilylation of acetophenone.

Results and Discussion

According to our previous experience in the imidazole series, the envisaged retrosynthetic analysis suggests the synthesis of the target complexes by deprotonation of the corresponding triazolium salts. Such salts can be synthesized either by direct methods or, alternatively, by reaction of chiral 4-(dialkylamino)triazoles with the alkylating reagents of choice (Scheme 1).

Previous research in the triazole series revealed that the substitution pattern in the heterocycle has a marked influence on the properties of the ligand.[17] Therefore, we decided to synthesize salts bearing both aliphatic and aromatic substituents at N-1, along with the chiral *N*-dialkylamino groups at N-4.

Scheme 1. Retrosynthetic Analysis for the Synthesis of the Target Complexes



First, essays were made by using the method developed by Boyd[18] and successfully applied by Enders[14a] for the direct synthesis of chiral triazolium salts **3** (Scheme 2). Chiral hydrazines such as (*S*)-1-amino-2-(1,1-diphenyl-1-methoxymethyl)pyrrolidine (**5**; SAPP) and C_2-symmetric hydrazines such as *trans*-(2*S*,5*S*)-1-amino-2,5-diphenylpyrrolidine (**6**) and *trans*-(2*S*,6*S*)-1-amino-2,6-diphenylpiperidine (**7**) were chosen as the amine partner in this reaction. Hydrazine **5**, readily available in both enantiomeric forms, was selected as a representative of proline derivatives, which incorporates an additional coordinating functionality for the eventual synthesis of chelating ligands. C_2-symmetric derivatives such as **6** and **7** were chosen in order to circumvent any issues related to the free rotation around N−N bonds. The excellent asymmetric induction effected by 2,5-/2,6-disubstituted pyrrolidines/piperidines in related contexts was also taken into account.[19] Unfortunately, the 3-alkyl-1,3,4-oxadiazolium salts **2** (R^1 = alkyl), readily available from *N*,*N*′-diformylhydrazines **1**, did not react with *N*,*N*-dialkylhydrazines **5**−**7**, even under forcing conditions. The lack of reactivity in our case suggests that the acidic conditions required result in the protonation of the more basic hydrazine reagents, thereby preventing the initial nucleophilic attack for the ring opening−ring closure reaction, leading to products **4**.

A second methodology for the direct synthesis of the 1,4-disubstituted triazolium salts consists of the reaction of imidoyl chlorides **8** with *N*-formyl hydrazines.[14a] The analogous reaction of *N*-(dialkylamino)imidoyl chlorides (**8**; R^4 = NR′R″), prepared in situ from the corresponding hydrazides **9**, was also investigated, but only decomposition of the starting hydrazides was observed under a variety of conditions.

Therefore, we decided to focus on the alternative synthesis of *N*-(dialkylamino)triazoles **11**−**13** as precursors of the required triazolium salts (Scheme 3). In spite of the apparent simplicity of these structures, a literature search reveals that only a few such compounds have been prepared by a reductive amination/alkylation sequence starting from 4-amino-1,2,4-triazole,[20] a method clearly inappropriate for the introduction of complex, chiral *N*-dialkylamino groups. Therefore, we tried to apply

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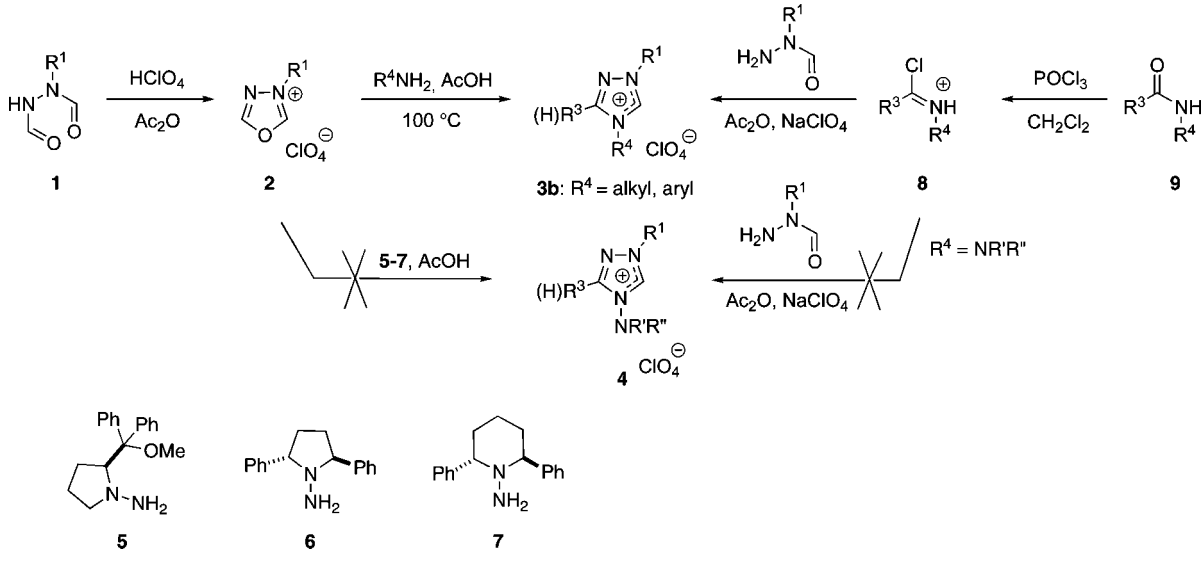
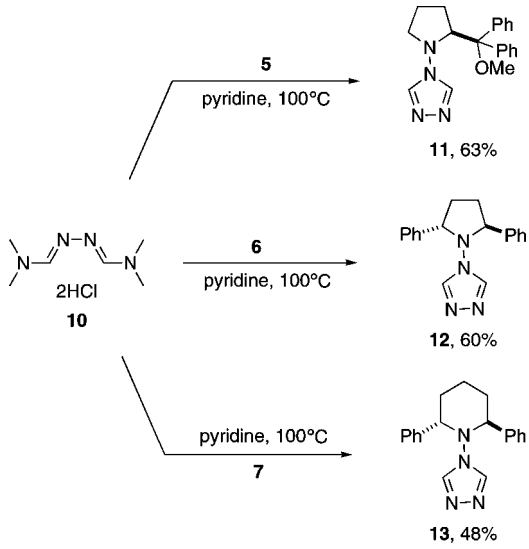
Scheme 2. Attempted Direct Synthesis of Chiral 4-(Dialkylamino)triazolium Salts 4



Scheme 3. Synthesis of Chiral 4-(Dialkylamino)-1,2,4-triazoles 11−13



available methods for the synthesis of 4-substituted 1,2,4-triazoles from primary amines, just by replacing the amine by a chiral *N,N*-dialkylhydrazine. The reaction of *N,N*-dimethylformamidazine dihydrochloride (**10**) with anilines in pyridine provides a straightforward synthesis of 4-aryl-1,2,4-triazoles.[21] Fortunately, the reaction of **10** with *N,N*-dialkylhydrazines **5**−**7** proceeds in a similar way to afford the desired 4-(dialkylamino)-1,2,4-triazoles **11**−**13** in moderate 48−63% yields.

The structure of 4-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-1,2,4-triazole (**12**) was confirmed by single-crystal X-ray diffractometry (Figure 2), the most remarkable feature being the N(1)−N(2) bond distance of 1.397(2) Å, the dihedral angles C(1)−N(1)−N(2)−C(18) = −37.5(3)° and C(4)−N(1)−N(2)−C(18) = 94.9(2)°, and the considerable pyramidalization degree at N(1), all parameters indicating the absence of effective n→π conjugation between the amino lone pair and the heterocycle (Figure 2).

With compounds **11**−**13** in hand, the corresponding 1-alkyl-1,2,4-triazolium salts **14**−**17** were easily prepared by reaction with alkylating reagents such as *i*-PrI and MeOTf (Scheme 4).

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As previously observed in the case of *N*-(dialkylamino)-imidazoles,[6b] the alkylation took place with complete regioselectivity (in all cases, no alkylation at the sp^3 amino nitrogen was observed, in spite of its higher basicity), and the 1-alkyl-triazolium salts **14**−**17** were selectively obtained in excellent yields. The ^{1}H and ^{13}C spectra of these compounds showed characteristic peaks at 10.1−12.5 (H-5), 7.6−8.4 (H-3), and 143 ppm (C-5), similar to those reported for related *N*-alkyl(aryl)-triazolium salts.[14c,16]

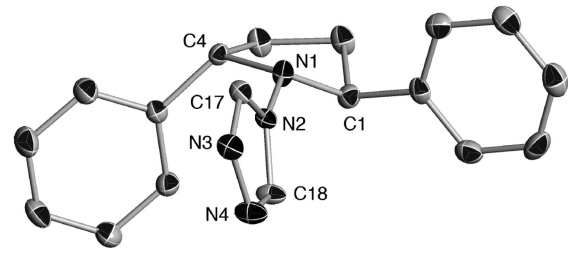
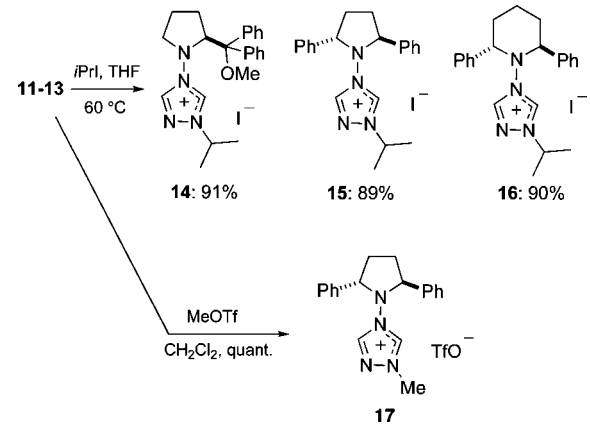
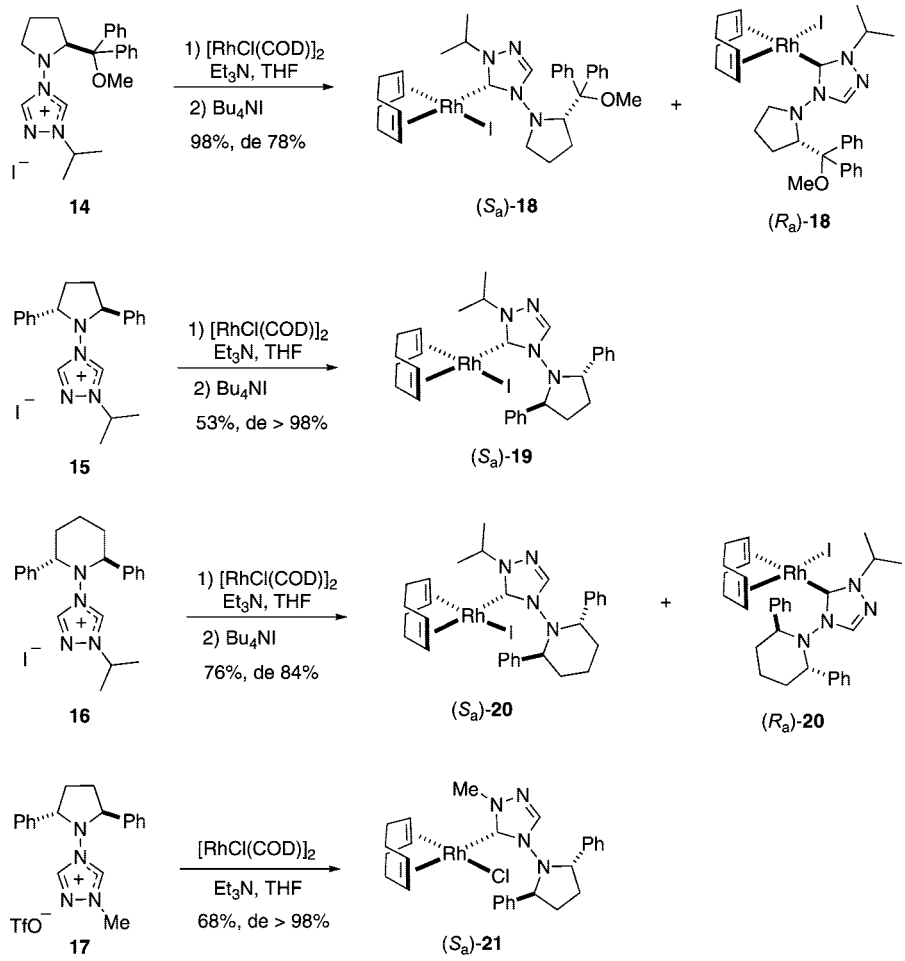


Figure 2. X-ray structure of **12**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): N(1)−N(2) = 1.397(2), C(1)−N(1) = 1.472(3), N(1)−C(4) = 1.503(2), C(17)−N(2) = 1.359(2), C(18)−N(2) = 1.366(3); N(2)−N(1)−C(4) = 115.92(15), N(2)−N(1)−C(1) = 115.36(16), C(1)−N(1)−C(4) = 111.18(16), C(1)−N(1)−N(2)−C(18) = −37.5(3), C(4)−N(1)−N(2)−C(18) = 94.9(2).

Scheme 4. Synthesis of 1-Isopropyltriazolium salts 14−16 and 1-Methyltriazolium salt 17



Scheme 5. Synthesis of Neutral Rhodium(I) Complexes 18−21



Salts **14**−**17** were then used as precursors for the synthesis of a series of Rh(I) complexes. Thus, complexes **18**−**20** were prepared by reaction of iodides **14**−**16** with $[RhCl(COD)]_2$ in the presence of Et_3N as base, while complex **21** was obtained from **17** under the same conditions (Scheme 5). These complexes could be purified by chromatography on silica gel and isolated in moderate to excellent yields (53−98%), and they proved to be robust, air-stable yellow solids unaltered for extended periods even in solution. In the case of complexes **18**−**20** the formation of mixtures with different Cl/I halide ligands was observed. The addition of 1.0 equiv of tetrabutylammonium iodide to the reaction mixture allowed the isolation of the [Rh(NHC)I(COD)] complexes without traces of chloride ligands.

Variable-temperature ^1H NMR studies confirmed that complexes **18**−**21** feature a restricted C−Rh bond rotation[22] and, therefore, two atropoisomers (S_a and R_a) could in principle be formed. It is worth noting that the reactions from salts **15** and **17** proceeded with complete diastereoselectivity,[23] leading to the formation of (S_a)-**19** and (S_a)-**21** as single isomers. The reactions from salts **14** and **16** proceeded also in a diastereoselective way, but small amounts of the minor diastereomers (R_a/S_a)-**18** and (R_a)-**20** were observed in these cases (dr = 89:11 and 92:8, respectively). Orange-yellow crystals of (S_a)-**21**, suitable for single crystal X-ray diffraction analysis, were grown by slow diffusion of hexane in a solution of the complex in CH_2Cl_2. The structure exhibits the expected square-planar coordination at the Rh(I) center, with the triazole ring nearly perpendicular to the coordination plane, as deduced from the torsional Cl(1)−Rh(1)−C(1)−N(1) and Cl(1)−Rh(1)−C(1)−N(3) angles of −83.59(12) and 97.87(11)°, respectively (Figure 3). The Rh−C(carbene) bond length of 2.0112(13) Å is in the range of single Rh−NHC bonds, and the mean C(COD)−Rh bond distances are 2.107 Å (trans to chlorine) and 2.205 Å (trans to the triazol-5-ylidene ligand), the difference of ca. 0.1 Å being a consequence of the higher trans influence associated with the excellent σ-donor ability of the latter. The pyramidalization degree at N(4) and the torsional angles C(4/7)−N(4)−N(3)−C(2) indicate, as in the case of triazole **12**, that there is no efficient conjugation between the *N*-dialkylamino group and the heterocycle in the solid state.[10]

The X-ray structure determination of (S_a)-**21** was also useful for the unambiguous assignment of the S_a absolute configuration of the Rh−C(1) chiral axis. The absolute configuration of (S_a)-

(22) The high steric bulk inhibits the C−Rh bond rotation even for the less hindered complex **21**. For related examples of hindered Rh−C(CNH) bonds, see: (a) Ku, R. Z.; Huang, J. C.; Cho, J. Y.; Kiang, F. M.; Reddy, K. R.; Chen, Y. C.; Lee, K. J.; Lee, G. H.; Peng, S. M.; Liu, S. T. *Organometallics* **1999**, *18*, 2145. (b) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. J. *J. Organomet. Chem.* **1997**, *547*, 357. (c) Westkamp, T.; Schattenmann, W. C.; Spiegler, M. J.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490. (d) Özdemir, I.; Yigit, B.; Çetinkaya, B.; Ülkü, D.; Tahir, M. N.; Arici, C. *J. Organomet. Chem.* **2001**, *633*, 27. (e) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663. (f) See ref 9c,d and 14a,c.

(23) A similar result was observed in the reaction of *N*-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-*N*′-alkylimidazol-2-ylidene silver carbenes with $[RhCl(COD)]_2$ or $[IrCl(COD)]_2$.[6b]

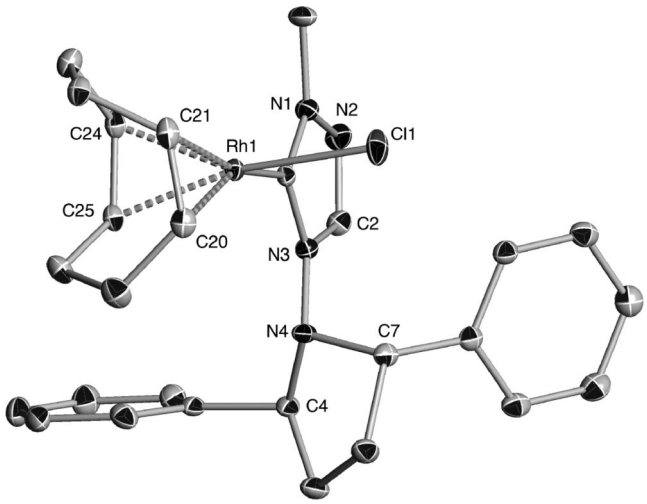
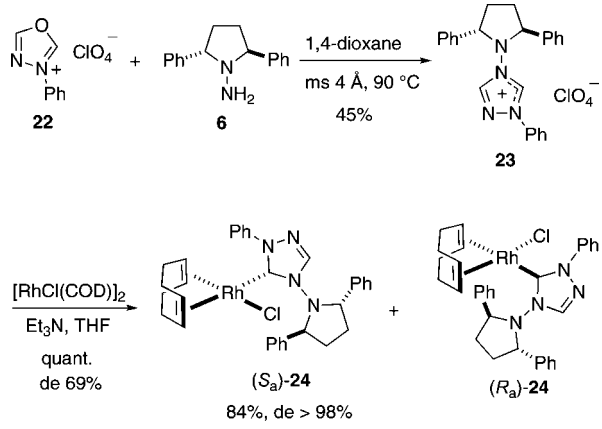


Figure 3. ORTEP-like drawing of the complex (S_a)-**21**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Rh(1)−C(1) = 2.0112(13), N(1)−C(1) = 1.3382(16), N(3)−C(1) = 1.3638(17), Rh(1)−C(20) = 2.1826(13), Rh(1)−C(21) = 2.2276(14), Rh(1)−C(24) = 2.0963(14), Rh(1)−C(25) = 2.1172(13); C(1)−Rh(1)−Cl(1) = 91.12(4), N(1)−C(1)−N(3) = 102.36(11), C(4)−N(4)−C(7) = 108.15(11), N(3)−N(4)−C(7) = 112.93(10), N(3)−N(4)−C(4) = 114.72(11), Cl(1)−Rh(1)−C(1)−N(1) = −83.59(12), Cl(1)−Rh(1)−C(1)−N(3) = 97.87(11), C(2)−N(3)−N(4)−C(7) = 88.59(16), C(2)−N(3)−N(4)−C(4) = −35.96(18).

Scheme 6. Synthesis of 1-Phenyl-1,2,4-triazolium Perchlorate (23) and Rhodium(I) Complex 24



19 and that of the major isomer (S_a)-**20** were assigned by analogy, while, unfortunately, the absolute configuration for the major isomer of (R_a/S_a)-**18** could not be assigned on this basis due to the different topology of the proline-derived *N*-dialkylamino group.

An alternative route was required for the synthesis of 4-(dialkylamino)-1-phenyl-1,2,4-triazoles. In contrast with the 1-alkyl case, a modification of Boyd's[17,18] procedure was successfully applied in this case for the direct synthesis of the desired triazolium salt. Thus, the reaction of **6** with freshly prepared 3-phenyl-1,3,4-oxadiazolium perchlorate **22** afforded 4-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-1,2,4-triazolium perchlorate (**23**) in 45% yield as a white solid (Scheme 6).

Colorless crystals of **23** suitable for single-crystal X-ray diffraction analysis were grown from a toluene/EtOAc mixture. The geometry of one of the independent cations[24] of **23** (Figure 4) shows a noticeable coplanarity of the triazolium and phenyl rings, with a torsional C(2)−N(1)−C(19)−C(20) angle of

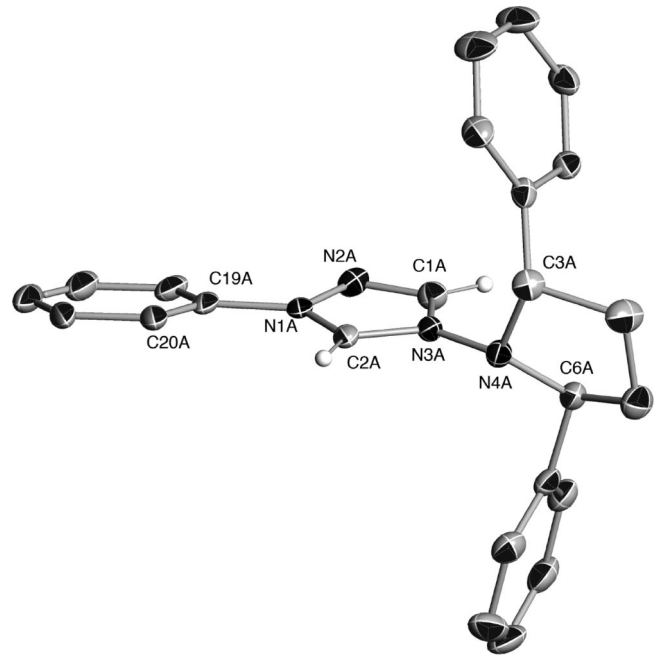


Figure 4. ORTEP-like drawing of one of the independent triazolium cations in the crystal structure of **23**. Most H atoms and the ClO_4 counteranion are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): N(3A)−N(4A) = 1.403(5), N(3A)−C(2A) = 1.329(5), N(1A)−C(2A) = 1.313(6); N(3A)−N(4A)−C(3A) = 114.9(3), C(6A)−N(4A)−C(3A) = 111.7(4), N(3A)−N(4A)−C(6A) = 115.4(3), C(1A)−N(3A)−N(4A)−C(3A) = 94.9(5), C(1A)−N(3A)−N(4A)−C(6A) = −37.3(6), C(2A)−N(1A)−C(19A)−C(20A) = 10.4(6).

10.4(6)°. As in the case of compounds **12** and **21**, the *N*-dialkylamino group does not appear to be efficiently conjugated with the triazolium ring, according to the observed pyramidalization degree at N(4) and the torsional angles C(1A)−N(3A)−N(4A)−C(3A) and C(1A)−N(3A)−N(4A)−C(6A) of 94.9(5) and −37.3(6)°, respectively.

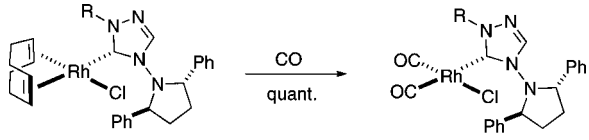
In contrast with the behavior of 1-alkyl-4-(2,5-diphenylpyrrolidin-1-yl)-1,2,4-triazolium salts **15** and **17**, the phenyl-substituted derivative **23** reacted with $[RhCl(COD)]_2$ in the presence of Et_3N to give the rhodium(I) complex **24** as a 85:15 mixture of diastereomers, though in an almost quantitative yield. In this case, nevertheless, a simple chromatographic purification afforded the pure major isomer (S_a)-**24** in 84% yield.[25] The absolute configuration of the chiral axis was assigned by analogy with **21**.

In order to gain further knowledge about the electronic properties of the chiral synthesized 1-alkyl(aryl)-4-(dialkylamino)-1,2,4-triazol-5-ylidene ligands, complexes **21** and **24** were made to react with carbon monoxide to afford dicarbonyl derivatives **25** and **26** in excellent yields (Scheme 7), and their carbonyl stretching frequencies were used to evaluate the

(24) The asymmetric unit of the structure is formed by four symmetrically independent perchlorate salts, with similar geometries for the triazolium cations. Each pair of cations shows strong face-to-face aromatic-stacking interactions between the 1-phenyl rings of both triazoliums and edge-to-face interactions between the 1-phenyl ring of one triazolium and a phenyl ring of the pyrrolidin-1-yl group of another triazolium cation.

(25) The separation of the pure major isomer confirms the configurational stability of the complex, as no trace of the minor isomer was observed after chromatography.

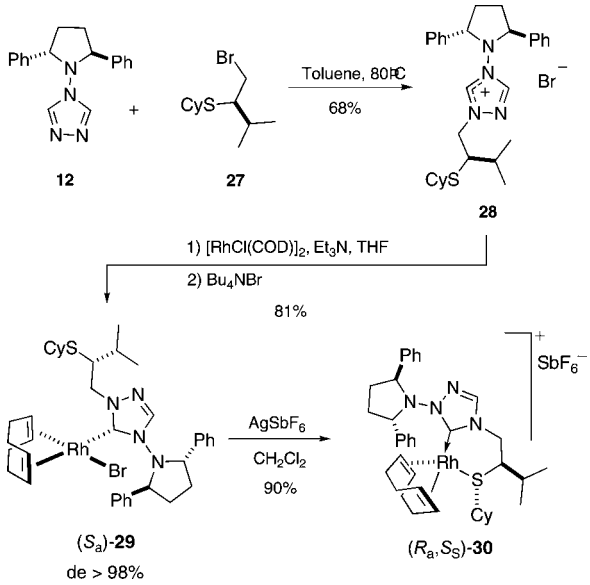
Scheme 7. Synthesis of Rhodium Dicarbonyl Complexes 25 and 26



(S_a)-**21**: R = Me
(S_a)-**24**: R = Ph

25: R = Me
26: R = Ph

Scheme 8. Synthesis of Triazolium Salt 28 and the Rhodium Complexes (S_a)-29 and (R_a,S_S)-30



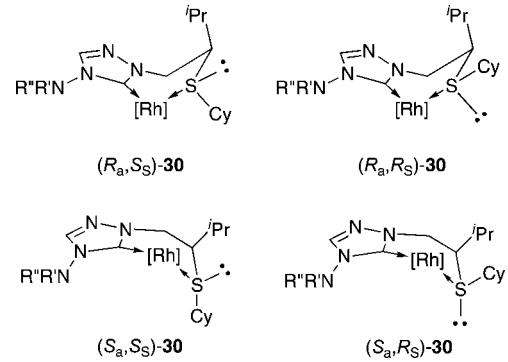
12 **27** **28**

(S_a)-**29**
de > 98%

(R_a,S_S)-**30**

σ-donor ability of the ligands.[26] The observed ν_{CO} stretching frequencies (**25**, ν_{CO} (cm^{-1}) 2003, 2081, average 2042; **26**, ν_{CO} (cm^{-1}) 2006, 2081, average 2043) indicate a considerable effect by the 2,5-diphenylpyrrolidine, making the carbene clearly a better donor than related triazol-5-ylidene ligands.[16] Though in the solid state there is apparently no n→π conjugation between the dialkylamino group and the heterocycle, these results suggest a considerable electronic interaction of the pyrrolidino group with the carbene, a phenomenon that has also been observed in 1,3-bis(1-pyrrolidinoyl)imidazolin-2-ylidenes.[10]

Having established the route for the synthesis of this new chiral NHC ligand class and collected some information on their electronic properties, we decided to explore their potential application in the asymmetric rhodium-catalyzed hydrosilylation of ketones. Inspired by previous works from our group,[6b,c] we decided to prepare also cationic rhodium(I) complexes based on heterobidentate NHC(triazole)/S(thioether) ligands and to include them in reactivity/selectivity screenings. For this purpose, triazole **12** was alkylated with (*R*)-1-bromo-2-(cyclohexylthio)-3-methylbutane (**27**)[6b,c] to afford the 1,2,4-triazolium salt **28** in 68% yield (Scheme 8). This compound was made to react with $[RhCl(COD)]_2$ in the presence of Et_3N to afford the corresponding [RhCl(NHC)(COD)] complex (S_a)-**29** in 81% yield. As for the analogues (S_a)-**19** and (S_a)-**21**, this compound was isolated as a single atropoisomer, thanks to the high induction effected by the 2,5-diphenylpyrrolidino group. Abstraction of the bromide ligand with $AgSbF_6$ enabled coordination of the neighboring sulfur atom to afford the cationic $[Rh(COD)(carbene)(thioether)]^+$ complex (R_a,S_S)-**30** in an excellent 90% yield.



(R_a,S_S)-**30** (R_a,R_S)-**30**

(S_a,S_S)-**30** (S_a,R_S)-**30**

Figure 5. Possible stereoisomers in the formation of **30**. [Rh] denotes Rh(COD).

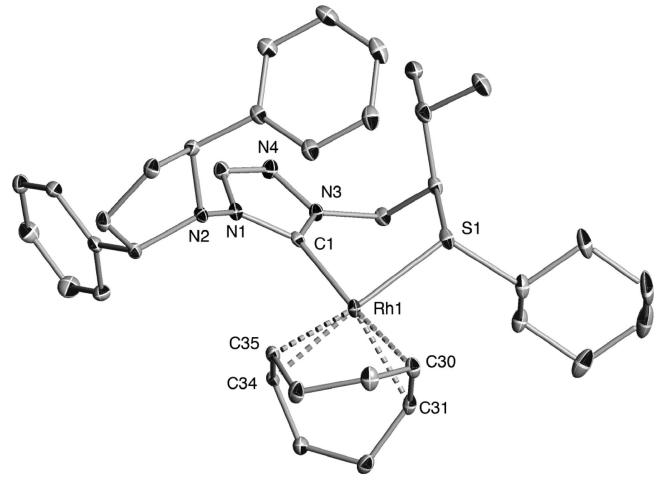
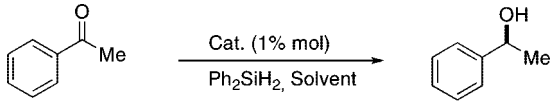


Figure 6. ORTEP drawing of the complex (R_a,S_S)-**30**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the SbF_6^- counteranion are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Rh(1)−C(1) = 2.040(2), N(1)−C(1) = 1.378(3), N(3)−C(1) = 1.347(3), N(1)−N(2) = 1.409(2), Rh(1)−C(30) = 2.229(2), Rh(1)−C(31) = 2.238(2), Rh(1)−C(34) = 2.174(2), Rh−C(35) = 2.180(2); N(3)−C(1)−N(1) = 101.78(19), C(1)−Rh(1)−S(1) = 88.10(6), S(1)−Rh(1)−C(1)−N(3) = 48.12(18).

Four possible stereoisomers, combinations of the possible configurations of the Rh−C axis and the sulfur center, can be a priori formed (Figure 5). It is worth noting, however, that **30** was obtained as a single R_a,S_S stereoisomer, and its structure was determined by single-crystal X-ray diffraction analysis. Suitable orange-yellow crystals of the complex were grown by slow diffusion of diethyl ether into a $CHCl_3$ solution of the complex at room temperature. The complex exhibits the usual square-planar coordination (the C(1)−Rh−S angle is 88.10(6)°) and is arranged in a boatlike conformation, where the sulfur atom binds the rhodium from the upper face of the heterocycle plane (the torsional N(3)−C(1)−Rh−S angle is 48.1°), thereby fixing the R_a absolute configuration of the chiral C(1)−Rh axis (Figure 6). The S_S configuration at sulfur is a consequence of the relative cyclohexyl−isopropyl trans configuration, necessary to avoid severe repulsive steric interactions. In this structure, the COD ligand is placed at the bottom face of the heterocycle plane, avoiding contacts with one of the phenyl groups on the pyrrolidine ring which is shielding the opposite face. The S_a configuration for the chiral axis would be associated with a

(26) (a) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219. (b) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663. (c) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.

Table 1. Hydrosilylation of Acetophenone Catalyzed by Rhodium(I) Triazol-5-ylidene Complexes[a]



entry	catalyst	solvent	temp (°C)	yield (%)[b]	ee[c]
1	(S_a)-**19**	toluene	25	40[d]	8
2	(S_a)-**21**	toluene	25	92	24
3	(S_a)-**21**	toluene	0	86	34
4	(S_a)-**21**	toluene	−20	85	37
5	(S_a)-**21**	toluene	−40	82	38
6	(S_a)-**24**	toluene	25	83	20
7	(S_a)-**24**	Et_2O	25	88	20
8	(S_a)-**24**	toluene	0	78	34
9	(S_a)-**24**	Et_2O	0	85	31
10	(R_a,S_S)-**30**	toluene	25	85	56
11	(R_a,S_S)-**30**	Et_2O	25	88	62
12	(R_a,S_S)-**30**	toluene	0	72[d]	52
13	(R_a,S_S)-**30**	Et_2O	0	79	46
14	(R_a,S_S)-**30**	toluene	−20	66[d]	51
15	(R_a,S_S)-**30**	Et_2O	−20	88	31

[a] Reactions were performed on a 0.5 mmol scale using 1 mol % of catalyst and 2 equiv of Ph_2SiH_2. [b] Isolated yield after column chromatography. [c] Determined by chiral HPLC. [d] Unreacted starting material observed.

second possible boatlike conformation, where the isopropyl and the cyclohexyl groups would be again in a trans relative configuration, but with the sulfur atom binding the rhodium center from the bottom face of the heterocycle. In this case, however, there would be strong steric interactions between the aforementioned phenyl group and the COD ligand, now forced to stay in the upper face of the heterocycle plane. On the other hand, the mean Rh−C(COD) bonds trans to the carbene ligand is 2.234 Å in this case, while the Rh−C(COD) bond trans to the S atom is 2.177 Å, reflecting the stronger trans influence of the carbene.

The asymmetric hydrosilylation of acetophenone has been previously performed with neutral[9c,d,27] and cationic[9a,b] variants of NHC−rhodium and −iridium complexes, generally with low to moderate levels of enantioselectivity (2−60% ee) except in punctual cases (>90% ee).[9a,b,28] Given these precedents, we decided to test compounds (S_a)-**19**, (S_a)-**21**, (S_a)-**24**, and (R_a,S_S)-**30** in the catalytic hydrosilylation of acetophenone with diphenylsilane. First, experiments performed with monodentate (S_a)-**19** were disappointing in view of the relatively low activity and almost negligible selectivity observed. Thus, incomplete reactions were observed after 22 h at room temperature using 1% catalyst loading (Table 1, entry 1). Interestingly, however, the less sterically demanding catalyst (S_a)-**21** exhibited a much better performance, leading to complete conversions under the above conditions and affording moderate selectivities (entries 2−5). The reaction proceeded similarly in a variety of solvents (toluene, Et_2O, THF, CH_2Cl_2), with slightly better results corresponding to the reactions performed in toluene. It was possible to perform reactions at lower temperatures with good catalytic activity, but unfortunately, the enantioselectivity improves only moderately at 0 or −20 °C (entries 3 and 4) and remains at the same level at −40 °C (entry 5). The *N*-phenyl-substituted catalyst (S_a)-**24** exhibited a comparable performance in toluene or Et_2O, with similar activity and selectivity (entries 6−9). Finally, the cationic C/S complex (R_a,S_S)-**30** exhibits activity at room temperature in toluene and Et_2O (entries 11 and 12) similar to that of the neutral complexes (S_a)-**21** and (S_a)-**24**, but with better enantioselectivities (ee of 56 and 62% in toluene and Et_2O, respectively). The catalytic activity dropped at lower temperatures in toluene (probably due to the low solubility of the cationic catalyst) but was maintained in Et_2O (entries 12−15). Unfortunately, however, the enantioselectivity decreased in this last case to 46% and 31% ee in the reactions performed at 0 and −20 °C, respectively.

Conclusions

In summary, rhodium(I) complexes with NHC monodentate or NHC/S heterobidentate ligands based on chiral 1-alkyl(aryl)-4-(dialkylamino)-1,2,4-triazol-5-ylidenes and thioether functionalities can be readily prepared from the corresponding azolium salts by direct reaction with $[RhCl(COD)]_2$ in the presence of Et_3N as the base. It is worth noting that the asymmetric induction effected by the chiral dialkylamino group results in a high stereoselectivity in the formation of the configurationally stable Rh−C(carbene) bond, which reaches very high levels in the aliphatic series (de > 98%) for 2,5-diphenylpyrrolidine derivatives. The analysis of the CO stretching frequencies of the $RhCl(NHC)(CO)_2$ derivatives indicates a relatively high σ-donating ability of the ligand, suggesting a certain degree of n→π dialkylamino/triazolylidene interaction.

The neutral Rh(NHC)X(COD) (X = Cl, I) and cationic Rh(COD)(carbene-S) complexes were active catalysts in the asymmetric hydrosilylation of ketones by diphenylsilane, and the sense of the selectivity was slightly dependent on the nature of the N-heterocyclic carbene and strongly dependent on the solvent and reaction temperature. The most selective catalyst was cationic (R_a,S_S)-**30**, which catalyzed the reaction in Et_2O at room temperature to give the product in 88% yield and with 62% ee.

Experimental Section

Solvents were purified and dried by standard procedures. Flash chromatography was carried out on silica gel (0.040−0.063 or 0.015−0.040 mm). Melting points were recorded in a metal block and are uncorrected. ^1H NMR spectra were recorded at 300, 400, or 500 MHz; ^{13}C NMR spectra were recorded at 75, 100, or 125 MHz, with the solvent peak used as the internal reference. (2*S*,5*S*)-1-Amino-2,5-diphenylpyrrolidine,[19f] (2*S*,6*S*)-1-amino-2,6-diphenylpiperidine,[19f] (*S*)-1-amino-2-(1,1-diphenyl-1-methoxymethyl)pyrrolidine,[29] and (2*R*)-1-bromo-2-(cyclohexylthio)-3-methylbutane[6b,c] were prepared by following previously described procedures. Enantiomeric excesses (ee) were determined by HPLC on chiral stationary phases with *i*-PrOH/hexane mixtures as the eluent.

General Procedure for the Synthesis of 4-(Dialkylamino)-1,2,4-triazoles 11−13. To solutions of hydrazines **5**−**7** (1 mmol) in pyridine (2 mL) was added *N*,*N*-dimethylformamidazine dihydrochloride (**10**; 325 mg, 1.5 mmol), and the reaction mixture was stirred for 4 h at 100 °C. The solvent was then removed in vacuo, the residue was dissolved in a 1/1 H_2O/saturated $NaHCO_3$ mixture, and this solution was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried ($MgSO_4$) and concentrated and the residue purified by flash chromatography (EtOAc). Starting materials, yields, and spectral and analytical data for compounds **11**−**13** are as follows.

4-[(*S*)-2-(1,1-Diphenyl-1-methoxymethyl)pyrrolidin-1-yl]-1,2,4-triazole (11). From **5** (282 mg, 1 mmol), flash chromatography gave 210 mg (63%) of **11** as a yellow oil. $[\alpha]^{20}_D = -109.9°$ (*c* 1.0,

(27) (a) Chianese, A. R.; Crabtree, R. H. *Organometallics* **2005**, *24*, 4432. (b) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913.

(28) Duan, W. L.; Shi, M.; Rong, G. B. *Chem. Commun.* **2003**, 2916.

$CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (s, 2H), 7.46−7.31 (m, 5H), 7.22 (s, 5H), 4.36 (dd, 1H, J = 9.9, 3.3 Hz), 3.12−3.06 (m, 1H), 3.04−2.96 (m, 1H), 2.63 (s, 3H), 2.30−2.24 (m, 1H), 1.94−1.87 (m, 1H), 1.58−1.50 (m, 1H), 1.26−1.20 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2, 139.5, 138.7, 130.0, 129.7, 128.1, 128.0, 127.9, 127.8, 86.4, 71.7, 59.8, 51.5, 28.1, 23.5, 14.5. HRMS: *m/z* calcd for $C_{20}H_{22}N_4O$ 334.1794, found 334.1789.

4-[(2*S*,5*S*)-2,5-Diphenylpyrrolidin-1-yl]-1,2,4-triazole (12). From **6** (248 mg, 1 mmol), flash chromatography gave 174 mg (60%) of **12** as a solid. $[\alpha]^{20}_D$ = −194.1° (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (s, 2H), 7.39−7.12 (m, 10H), 4.59 (t, 2H, J = 5.1 Hz), 2.68−2.55 (m, 2H), 2.31−2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 138.6, 129.0, 128.8, 127.9, 67.7, 29.9. Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.30. Found: C, 74.69; H, 5.92; N, 19.11.

4-[(2*S*,6*S*)-2,6-Diphenylpyrrolidin-1-yl]-1,2,4-triazole (13). From **7** (262 mg, 1 mmol), flash chromatography gave 146 mg (48%) of **13** as a colorless oil. $[\alpha]^{20}_D$ = −162.3° (*c* 0.4, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 2H), 7.28−7.20 (m, 10H), 4.59 (t, 2H, J = 5.0 Hz), 2.36−2.27 (m, 2H), 2.19−2.05 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.3, 139.7, 128.9, 128.5, 128.2, 65.5, 32.6, 19.5. Anal. Calcd for $C_{19}H_{20}N_4$: C, 74.97; H, 6.62; N, 18.41. Found: C, 75.03; H, 6.40; N, 18.57.

General Procedure for the Synthesis of 1-Alkyl-4-(dialkylamino)-1,2,4-triazolium Iodides 14−16 and Triflate 17. To solutions of triazoles **11**−**13** (1 mmol) in dry THF (2 mL) was added *i*-PrI (680 mg, 4 mmol), and the mixture was stirred at 60 °C for 2 days. The solvent was then removed in vacuo and the residue purified by flash chromatography. Alternatively, to a solution of triazole **12** (1 mmol) in dry CH_2Cl_2 (1 mL) was added the methyl triflate (128 μL, 1 mmol) and the mixture was stirred at room temperature for 2 h. The solvent was then removed in vacuo and the residue purified by flash chromatography. Starting materials, yields, and spectral and analytical data for compounds **14**−**17** are as follows.

4-[(*S*)-2-(1,1-Diphenyl-1-methoxymethyl)pyrrolidin-1-yl]-1-isopropyl-1,2,4-triazolium Iodide (14). From **11** (334 mg, 1.0 mmol) and *i*-PrI, flash chromatography (10/1 CH_2Cl_2/MeOH) gave 420 mg (91%) of **14** as a light brown oil. $[\alpha]^{20}_D$ = −94.7° (*c* 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 12.46 (s, 1H), 8.36 (s, 1H), 7.43−7.25 (m, 10H), 5.10−4.95 (m, 3H), 3.64−3.58 (m, 1H), 3.32−3.26 (m, 1H), 2.90−2.83 (m, 1H), 2.65 (s, 3H), 1.87−1.81 (m, 1H), 1.62−1.52 (m, 6H), 0.80−0.72 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.6, 144.0, 139.4, 138.6, 130.1, 129.7, 128.5, 128.4, 128.0, 127.8, 87.4, 72.5, 60.4, 58.0, 51.7, 27.6, 23.2, 22.2 (s br). Anal. Calcd for $C_{23}H_{29}N_4IO$: C, 54.77; H, 5.79; N, 11.11. Found: C, 54.39; H, 5.56; N, 11.27.

4-[(2*S*,5*S*)-2,5-Diphenylpyrrolidin-1-yl]-1-isopropyl-1,2,4-triazolium Iodide (15). From **12** (294 mg, 1.0 mmol) and *i*-PrI, flash chromatography (10/1 CH_2Cl_2/MeOH) gave 371 mg (89%) of **15** as a colorless oil. $[\alpha]^{20}_D$ = −62.8° (*c* 0.9, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 11.53 (s, 1H), 7.80 (s, 1H), 7.52 (d, 4H, J = 7.0 Hz), 7.40−7.26 (m, 6H), 5.24 (t, 2H, J = 4.5 Hz), 4.77 (m, 1H, J = 6.6 Hz), 2.70−2.55 (m, 2H), 2.48−2.36 (m, 2H), 1.33 (d, 3H, J = 6.6 Hz), 1.27 (d, 3H, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.2, 142.7, 137.2, 129.7, 129.4, 128.7, 69.2, 57.4, 31.6, 22.5, 21.5. Anal. Calcd for $C_{21}H_{25}N_4I$: C, 54.79; H, 5.47; N, 12.17. Found: C, 55.02; H, 5.89; N, 11.96.

4-[(2*S*,6*S*)-2,6-Diphenylpyrrolidin-1-yl]-1-isopropyl-1,2,4-triazolium Iodide (16). From **13** (304 mg, 1.0 mmol) and *i*-PrI, flash chromatography (20/1 CH_2Cl_2/MeOH) gave 388 mg (90%) of **16** as a light brown oil. $[\alpha]^{20}_D$ = −79.4° (*c* 1.3, MeOH). ^1H NMR (400 MHz, $CDCl_3$): δ 11.00 (s, 1H), 7.57 (s, 1H), 7.51 (d, 4H, J = 6.8 Hz), 7.33 (t, 4H, J = 7.2 Hz), 7.32−7.20 (m, 2H), 4.93 (t, 2H, J = 5.2 Hz), 4.88 (m, 1H, J = 6.4 Hz), 2.45−2.34 (m, 2H), 2.25−2.10 (m, 2H), 2.10−2.00 (m, 2H), 1.28 (d, 3H, J = 6.8 Hz), 1.23 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 142.4, 138.4, 129.5, 129.0, 128.5, 65.4, 56.7, 32.2, 21.9, 21.1, 18.8. Anal. Calcd for $C_{22}H_{27}N_4I$: C, 55.70; H, 5.74; N, 11.81. Found: C, 55.46; H, 5.81; N, 11.76.

4-[(2*S*,5*S*)-2,5-Diphenylpyrrolidin-1-yl]-1-methyl-1,2,4-triazolium Triflate (17). From **12** (290 mg, 1 mmol) and MeOTf, flash chromatography (10/1 CH_2Cl_2/MeOH) gave 450 mg (quantitative) of **17** as a light brown oil. $[\alpha]^{20}_D$ = −79.6° (*c* 0.7, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 10.1 (s, 1H), 7.81 (s, 1H), 7.45−7.27 (m, 10H), 4.96 (t, 2H, J = 7.2 Hz), 3.83 (s, 3H), 2.72−2.64 (m, 2H), 2.40−2.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 142.8, 136.8, 129.5, 129.4, 128.1, 68.5, 39.6, 30.9. Mass spectrum (CI): *m/z* (relative intensity) 305 (100, M^+ − TfO), 222 (50), 84 (92). HRMS: *m/z* calcd for $C_{19}H_{21}N_4$ (M^+ − TfO) 305.1766, found 305.1758.

General Procedure for the Synthesis of [RhCl(COD)(1-alkyl-4-(dialkylamino)-1,2,4-triazol-5-ylidenes)] Complexes 18−21. To suspensions of 1-alkyl-4-(dialkylamino)-1,2,4-triazolium salts **14**−**17** (0.5 mmol) and $[RhCl(COD)]_2$ (123 mg, 0.25 mmol) in dry THF (5 mL) under Ar was added Et_3N (76 μL, 0.55 mmol), and the mixture was stirred for 2 h at room temperature. For **18**−**20**, tetrabutylammoniun iodide (185 mg, 0.5 mmol) was added and the mixture was stirred for another 30 min. The solvent was removed in vacuo and the residue purified by flash chromatography. Starting materials, yields, and spectral and analytical data for compounds **18**−**21** are as follows.

Rhodium(I) Complex 18. From **14** (252 mg, 0.5 mmol), flash chromatography (1/10 EtOAc/hexane) gave 350 mg (98%, de 78%) of **18** as a yellow solid. Mp: 92−94 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (br s, 1H), 7.44−7.26 (m, 10H), 5.73 (m, 1H, J = 6.6 Hz), 5.60 (dd, 1H, J = 10.3, 1.6 Hz), 5.50 (t, 1H, J = 7.5 Hz), 5.25 (q, 1H, J = 7.5 Hz), 4.94 (br s, 1H), 3.72 (t, 1H, J = 6.9 Hz), 3.16−3.15 (m, 1H), 3.02 (t, 1H, J = 7.1 Hz), 2.75−2.67 (m, 1H), 2.61−2.53 (m, 1H), 2.57 (s, 3H), 2.49−2.41 (m, 1H), 2.21−2.17 (m, 2H), 2.03−1.96 (m, 1H), 1.91−1.63 (m, 5H), 1.60 (d, 3H, J = 6.6 Hz), 1.50 (d, 3H, J = 6.6 Hz), 0.44−0.37 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.4 (d, J_{Rh-C} = 48.9 Hz), 146.9, 140.1, 130.4, 129.7, 127.6, 127.5, 127.0, 126.9, 96.4 (d, J_{Rh-C} = 6.9 Hz), 96.0 (d, J_{Rh-C} = 6.9 Hz), 87.0, 75.8 (d, J_{Rh-C} = 14.0 Hz), 71.5 (d, J_{Rh-C} = 13.4 Hz), 66.2, 56.7, 56.2, 51.0, 34.3, 32.1, 29.4, 28.3, 27.3, 23.6, 22.5, 21.7. Mass spectrum (FAB): *m/z* (relative intensity) 737 (10, M^+ + Na), 587 (46), 389 (25), 281 (24), 197 (100). HRMS: *m/z* calcd for $C_{31}H_{40}N_4OIRhNa$ 737.1200, found 737.1176. Anal. Calcd for $C_{31}H_{40}N_4IORh$: C, 52.11; H, 5.64; N, 7.84. Found: C, 52.34; H, 5.87; N, 8.02.

Rhodium(I) Complex 19. From **15** (230 mg, 0.5 mmol), flash chromatography (1/6 EtOAc/hexane) gave 177 mg (53%) of (S_a)-**19** as an orange-yellow solid. Mp: 134−136 °C dec. $[\alpha]^{20}_D$ = −193.3° (*c* 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.60−7.15 (m, 10H), 6.88 (s, 1H), 5.71 (br s, 1H), 5.68−5.60 (m, 1H), 5.30−5.20 (m, 2H), 4.41 (br s, 1H), 3.13 (br s, 1H), 3.01 (br s, 1H), 2.78 (br s, 2H), 2.55−2.30 (m, 3H), 2.30−2.15 (m, 3H), 2.15−2.05 (m, 1H), 1.87−1.78 (m, 1H), 1.73−1.63 (m, 2H), 1.43 (d, 3H, J = 6.5 Hz), 1.36 (d, 3H, J = 6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.8 (d, J_{Rh-C} = 49.1 Hz), 139.4, 129.1 (br s), 128.8, 128.7, 95.9 (d, J_{Rh-C} = 7.1 Hz), 95.8 (d, J_{Rh-C} = 7.1 Hz), 73.2 (d, J_{Rh-C} = 14.0 Hz), 72.2 (d, J_{Rh-C} = 13.4 Hz), 67.0 (br s), 64.3 (br s), 55.3, 33.5, 31.9 (br s), 31.3, 30.1, 29.3, 26.3 (br s), 22.1, 21.9. Anal. Calcd for $C_{29}H_{36}N_4IRh$: C, 51.95; H, 5.41; N, 8.36. Found: C, 52.06; H, 5.32; N, 8.61.

Rhodium(I) Complex 20. From **16** (237 mg, 0.5 mmol), flash chromatography (1/10 EtOAc/hexane) gave 260 mg (76%, de 84%) of **20** as a brown solid. Mp: 138−140 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.60 (br s, 2H), 7.40−7.00 (m, 8H), 6.72 (s, 1H), 5.85−5.60 (m, 2H), 5.33−5.24 (m, 2H), 5.05−4.96 (m, 1H), 4.46

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(br s, 1H), 3.62 (t, 1H, J = 6.6 Hz), 2.80−1.80 (m, 14H), 1.40 (d, 3H, J = 6.6 Hz), 1.22 (d, 3H, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4 (d, J_{Rh-C} = 49.4 Hz), 140.5, 131.0, 128.4, 128.3, 127.7, 95.1 (d, J_{Rh-C} = 7.7 Hz), 94.7 (d, J_{Rh-C} = 6.8 Hz), 64.7 (br s), 61.8 (br s), 55.6, 33.7, 31.4, 30.8, 28.9, 22.6, 20.9, 20.8. Anal. Calcd for $C_{30}H_{38}N_4IRh$: C, 52.64; H, 5.60; N, 8.19. Found: C, 52.86; H, 5.88; N, 8.34.

Rhodium(I) Complex 21. From **17** (227 mg, 0.5 mmol), flash chromatography (1/3 EtOAc/hexane) gave 187 mg (68%) of (S_a)-**21** as an orange-yellow solid. X-ray-quality crystals were grown by slow diffusion of hexane in a solution of (S_a)-**21** in CH_2Cl_2. Mp: 184−186 °C dec. $[\alpha]^{20}_D$ = −215.0° (c 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, 4H, J = 4.5 Hz), 7.26−7.24 (m, 6H), 6.87 (s, 1H), 5.72 (br s, 1H), 5.05 (br s, 2H), 4.41 (br s, 1H), 4.11 (s, 3H), 3.37−3.32 (m, 1H), 3.16−3.11 (m, 1H), 2.82 (br s, 1H), 2.75 (br s, 1H), 2.53−2.46 (m, 2H), 2.44−2.35 (m, 2H), 2.34−2.27 (m, 2H), 2.07−2.03 (m, 1H), 1.95−1.86 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 184.8 (d, J_{Rh-C} = 51.0 Hz), 138.4, 128.6, 128.5, 98.0 (d, J_{Rh-C} = 7.0 Hz), 97.6 (d, J_{Rh-C} = 7.0 Hz), 69.4 (d, J_{Rh-C} = 14.6 Hz), 68.5 (d, J_{Rh-C} = 13.9 Hz), 63.4 (br s), 40.7, 33.4, 32.3, 31.8 (br s), 29.5, 28.8. Mass spectrum (CI): m/z (relative intensity) 550 (69, M^+), 515 (79), 84 (100). HRMS: m/z calcd for $C_{27}H_{32}N_4ClRh$ 550.1371, found 550.1333.

Synthesis of 4-[(2*S*,5*S*)-2,5-Diphenylpyrrolidin-1-yl]-1-phenyl-1,2,4-triazolium Perchlorate (23). A solution of **6** (640 mg, 2.69 mmol) and freshly prepared 3-phenyl-1,3,4-oxadiazolium perchlorate **22**[18] (2.96 mmol, 1.1 equiv) in dry 1,4-dioxane (10 mL) was stirred with 4 Å MS under an argon atmosphere for 7 h at 80 °C. The solvent was then removed in vacuo, and the residue was purified by flash chromatography (1/2 → 2/1 EtOAc/toluene) to afford **23** as a yellow solid (565 mg, 45%). X-ray-quality crystals were grown by slow diffusion of hexane in a solution of **23** in a toluene/EtOAc mixture. Mp: 178−180 °C. $[\alpha]^{22}_D$ = −81.1° (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.31 (s, 1H), 8.00 (s, 1H), 7.63−7.28 (m, 15H), 5.19 (t, 2H, J = 7.1 Hz), 2.79−2.75 (m, 2H), 2.49−2.44 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 140.7, 137.0, 134.3, 131.2, 130.3, 129.6, 129.4, 128.2, 120.3, 68.8, 31.1. IR (film): 3118, 1680, 1498, 1108, 918, 759 cm^{-1}. Mass spectrum (CI): m/z (relative intensity) 367 (100, $M^+ - ClO_4$), 223 (6), 146 (17). HRMS: m/z calcd for $C_{24}H_{23}N_4$ 367.1923, found 367.1927.

Rhodium(I) Complex 24. To a suspension of **23** (233 mg, 0.5 mmol) and $[RhCl(COD)]_2$ (123 mg, 0.25 mmol) in dry THF (5 mL) under Ar was added Et_3N (76 μL, 0.55 mmol), and the mixture was stirred for 2 h at room temperature. The solvent was removed in vacuo and the residue (de 69%) purified by flash chromatography (1/6 EtOAc/hexane) to give 257 mg (84%) of pure major isomer (S_a)-**24** as a yellow solid. Mp: 104−107 °C. $[\alpha]^{20}_D$ = −145.2° (c 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ 8.76 (d, 1H, J = 12.5 Hz), 7.75−7.01 (m, 15H), 6.62−6.46 (m, 1H), 5.80−5.73 (m, 1H), 5.71−5.58 (m, 1H), 4.42−4.20 (m, 1H), 3.12−3.06 (m, 1H), 2.80−2.70 (m, 1H), 2.68−2.48 (m, 2H), 2.45−2.18 (m, 3H), 2.15−1.91 (m, 2H), 1.89−1.69 (m, 4H), 1.61−1.52 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 187.3 (d, J_{Rh-C} = 86.3 Hz), 140.6, 139.3, 129.3, 128.6, 128.3, 128.2, 128.1, 127.9, 127.8, 127.4, 124.2, 97.4 (d, J_{Rh-C} = 12.5 Hz), 97.1 (d, J_{Rh-C} = 12.5 Hz), 70.5 (d, J_{Rh-C} = 23.7 Hz), 67.3 (d, J_{Rh-C} = 22.5 Hz), 67.2, 64.5, 32.8, 32.4, 32.0, 29.9, 29.6, 28.6. Mass spectrum (CI): m/z (relative intensity) 612 (5, M^+), 504 (5). HRMS: m/z calcd for $C_{32}H_{34}N_4RhCl$ 612.1527, found 612.1501.

General Procedure for the Synthesis of Rhodium Dicarbonyl Complexes 25 and 26. CO was bubbled through a solution of (S_a)-**21** and (S_a)-**24** (0.05 mmol) in $CDCl_3$ (0.5 mL) for 15 min. The solvent was then concentrated, and the residue was dried under vacuum to give the dicarbonyl complexes in quantitative yields. Starting materials and spectra and analytical data for compounds **25** and **26** are as follows.

Complex 25. From (S_a)-**21** (275 mg, 0.5 mmol). $[\alpha]^{20}_D$ = −138.8° (c 0.17, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (br s, 1H), 7.42−7.27 (m, 10H), 4.94 (br s, 2H), 3.91 (s, 3H), 2.76−2.70 (m, 2H), 2.34−2.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 185.2 (d, J_{Rh-C} = 55.3 Hz), 182.3 (d, J_{Rh-C} = 73.6 Hz), 178.6 (d, J_{Rh-C} = 44.0 Hz), 139.3, 137.9, 128.9, 128.7, 128.6, 128.4, 66.5 (br s), 40.8, 29.7. IR (film): 2081, 2003, 1653, 1558, 1540, 1457 cm^{-1}. ESIMS: m/z 435.0 [100, $M^+ - Cl - CO$].

Complex 26. From (S_a)-**24** (306.2 mg, 0.5 mmol). $[\alpha]^{20}_D$ = −29.1° (c 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08−8.06 (m, 2H), 7.54−7.30 (m, 14H), 2.81−2.80 (m, 2H), 2.38−2.37 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 185.4 (d, J_{Rh-C} = 56.2 Hz), 181.7 (d, J_{Rh-C} = 73.8 Hz), 179.1 (d, J_{Rh-C} = 44.1 Hz), 140.1, 139.0, 138.1, 129.0, 128.9, 128.8, 128.7, 128.5, 123.8, 66.6 (br s), 29.7. IR (film): 2924, 2853, 2081, 2006, 1495, 1455, 756, 703 cm^{-1}. ESIMS: m/z 497.0 [100, $M^+ - Cl - CO$].

Synthesis of Heterobidentate NHC(triazole)/S(thioether) Bromide 28 and Rh(I) Complexes 29−30. Triazolium Bromide 28. To a solution of **12** (148 mg, 0.51 mmol) in dry toluene (1.5 mL) was added **27** (204 mg, 0.77 mmol) in dry toluene (1 mL). The reaction mixture was stirred at 80 °C for 2 days. The solvent was then removed in vacuo and the residue purified by flash chromatography (1/10 MeOH/CH_2Cl_2) to afford the triazolium salt **28** as a light brown waxy solid (192 mg, 68% yield). $[\alpha]^{20}_D$ = −25.1° (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.10 (s, 1H), 8.07 (s, 1H), 7.55 (d, 4H, J = 7.5 Hz), 7.32 (t, 4H, J = 7.5 Hz), 7.25 (t, 2H, J = 7.5 Hz), 5.23 (t, 2H, J = 7.2 Hz), 4.42 (dd, 1H, J = 13.8, 9.3 Hz), 4.20 (dd, 1H, J = 13.8, 6.3 Hz), 2.88−2.80 (m, 1H), 2.70−2.58 (m, 2H), 2.54−2.48 (m, 1H), 2.42−2.30 (m, 2H), 2.10−1.40 (m, 5H), 1.24−1.00 (m, 6H), 0.84 (br s, 3H), 0.74 (d, 3H, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8, 142.9, 137.3, 129.6, 129.3, 128.8, 69.0, 55.5, 49.5, 44.4, 34.2, 34.0, 31.8, 31.7, 28.6, 26.2, 25.8, 20.8, 17.5. Mass spectrum (FAB): m/z (relative intensity) 477 (6, $M^+ + 2$), 476 (21, $M^+ + 1$), 475 (59, M^+), 281 (10), 73 (100). HRMS: m/z calcd for $C_{29}H_{39}N_4S$ 475.2895, found 475.2917.

Rhodium(I) Complex 29. To a suspension of $[RhCl(COD)]_2$ (49 mg, 0.1 mmol) and the triazolium salt **28** (111 mg, 0.2 mmol) in dry THF (1 mL) under argon was added Et_3N (32 μL, 0.2 mmol) and the reaction mixture was stirred for 2 h at room temperature. Then tetrabutylammoniun bromide (32 mg, 0.1 mmol) was added and the mixture was stirred for another 30 min. The solvent was removed in vacuo and the residue purified by flash chromatography (1/6 EtOAc/hexane) to afford the rhodium(I) complex (S_a)-**29** as a yellow solid (124 mg, 81% yield). $[\alpha]^{20}_D$ = −154.3° (c 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.25 (m, 10H), 6.89 (s, 1H), 5.80−5.70 (br s, 1H), 5.30−5.15 (m, 1H), 5.09−5.01 (m, 1H), 4.93 (dd, 1H, J = 13.6, 4.4 Hz), 4.43 (br s, 1H), 4.12 (t, 1H, J = 13.6 Hz), 3.92−3.76 (m, 1H), 3.04−2.93 (m, 3H), 2.87−2.56 (m, 2H), 2.59−2.45 (m, 1H), 2.28−2.15 (m, 6H), 1.86−1.68 (m, 6H), 1.67−1.24 (m, 8H), 1.12 (d, 3H, J = 6.8 Hz), 0.82 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6 (d, J_{Rh-C} = 49.0 Hz), 137.9, 129.1, 128.6, 128.5, 120.1, 96.9 (d, J_{Rh-C} = 7.0 Hz), 71.0 (d, J_{Rh-C} = 13.9 Hz), 69.9 (d, J_{Rh-C} = 13.6 Hz), 67.5 (br s), 64.0 (br s), 56.6, 50.5, 44.2, 34.9, 34.7, 33.5, 31.7, 29.9, 29.7, 28.8, 26.6, 26.5, 26.2, 25.8, 20.9, 15.6. HRMS: m/z calcd for $C_{37}H_{50}BrN_4RhS$ 765.6942, found 765.6951.

Cationic Rhodium(I) Complex 30. To a solution of (S_a)-**29** (60 mg, 0.08 mmol) in dry CH_2Cl_2 (0.5 mL) under argon was added $AgSbF_6$ (13.5 mg, 0.08 mmol), and the mixture was stirred in the dark at room temperature for 1 h. The reaction mixture was then filtered through Celite and washed with CH_2Cl_2 (3 × 2 mL), and the solvent was removed in vacuo to give a yellow oil. Treatment with Et_2O gave (R_a,S_S)-**30** as an orange-yellow solid (66 mg, 90% yield). X-ray-quality crystals were grown by slow diffusion of diethyl ether into a solution of (R_a,S_S)-**30** in $CHCl_3$. Mp: 172−174 °C dec. $[\alpha]^{20}_D$ = +11.1° (c 0.3, $CHCl_3$). ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.43 (br s, 2H), 7.35−7.22 (m, 6H), 7.13 (br s, 2H), 6.82 (br s, 1H), 5.47 (br s, 1H), 4.87−4.78 (m, 1H), 4.64 (dd, 1H, J = 14.8, 7.6 Hz), 4.57−4.49 (m, 1H), 4.43 (d, 2H, J = 7.6 Hz), 2.80−2.63 (m, 1H), 2.61−2.42 (m, 4H), 2.40−2.03 (m, 8H), 1.92−1.81 (m, 2H), 1.62−1.50 (m, 6H), 1.48−1.15 (m, 6H), 0.85 (d, 3H, J = 6.7 Hz), 0.81 (d, 3H, J = 6.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.4 (d, J_{C-Rh} = 51.0 Hz), 140.9, 136.9, 136.7, 129.7, 128.9, 128.8, 128.6, 128.1, 127.1, 96.4 (br s), 95.0 (br s), 86.0 (br s), 85.6 (br s), 68.9, 66.8, 57.7, 50.9 (br s), 48.0 (br s), 34.3, 33.3, 32.6 (br s), 30.9, 30.6, 29.6, 29.0, 27.3, 26.6, 26.3, 24.9, 20.6, 19.3. Mass spectrum (FAB): m/z (relative intensity) 685 (67, M^+), 577 (100). HRMS: m/z calcd for $C_{37}H_{50}N_4SRh$ 685.2811, found 685.2840. Anal. Calcd for $C_{37}H_{50}F_6N_4RhSSb$: C, 48.22; H, 5.47; N, 6.08. Found: C, 48.29; H, 5.52; N, 6.15.

General Procedure for the Catalytic Hydrosilylation Reaction. In a small Schlenk tube, the catalyst (0.005 mmol) was dissolved in dry solvent (0.25−1.0 mL) under argon. After addition of acetophenone (58 μL, 0.5 mmol) at room temperature, the reaction mixture was cooled to the required temperature and diphenylsilane (105−380 μL, 0.55−2.0 mmol) was added dropwise over a period of 2 min. The bright yellow reaction mixture was stirred for 22 h, and then MeOH (1 mL) and aqueous HCl (2M, 0.1 mL) were added. The resulting mixture was stirred for 30 min, diluted with H_2O (5 mL), and extracted with Et_2O (3 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated, and the residue was purified by flash chromatography (4/1 pentane/Et_2O) to afford the pure alcohol as a colorless oil. The absolute configuration of the enantiomerically enriched alcohol was determined by comparing the sign of its optical rotation with literature data. The enantiomeric excess of the product was determined by HPLC using an OB chiral stationary phase and 95/5 hexane/*i*-PrOH as eluent, 1 mL/min flow rate, and T = 30 °C. t_r = 7.14 min (minor isomer *R*), and t_r = 9.87 min (major isomer *S*).[30]

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Supporting Information Available: CIF files giving crystallographic data for compounds **12**, (S_a)-**21**, **23**, and (R_a,S_S)-**30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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