Chiral Phosphino(sulfinylmethyl)triarylphosphonium Ylide Ligands: Rhodium Complexes and Catalytic Properties

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A novel phosphine−phosphonium ylide ligand bearing a chiral sulfinyl moiety was prepared by reaction of (*o*-diphenylphosphinophenyl)diphenylphosphonium methylide with (*S*)-menthyl *p*-tolylsulfinate. Reaction of this ylide with $[Rh(cod)_2][PF_6]$ gave stable cationic disymmetrically P,C-chelated rhodium complexes with an asymmetric ylidic carbon atom anchored to the metal center. The configuration of this carbon is controlled by the *S*-configuration of the adjacent sulfinyl group. The stereoselectivity of the complexation is reversed from 9:1 at 20 °C to 1:9 at −45 °C. An X-ray diffraction analysis of the thermodynamic complex shows that the stereoselectivity is not directed by chelation of the SO group which lies at a nonbonding distance from the rhodium center. In the presence of triethylamine, epimerization occurs via a putative neutral P,C-chelated complex bearing an yldiide ligand. In the presence of HPF_6 and PPh_3, cleavage of the ylidic carbon−rhodium bond takes place simultaneously with displacement of the phosphino−phosphonium ligand by PPh_3. The phosphine end of the ligand is intended to preserve at least one phosphine−rhodium bond, which is a common feature of all the rhodium catalysts derived from the Wilkinson complex. Indeed, we found that the phosphino−phosphonium ylide complexes are active—though poorly enantioselective—as catalysts for hydrogenation of (*Z*)-α-acetamidocinnamic acid and hydrosilylation of acetophenone.

Introduction

Both the persistency of phosphorus−metal bonds and the relative weakness of carbon−transition metal bonds largely contribute to the possibility of catalytic processes. Nevertheless catalytic processes with persistent carbene−metal bonds have recently attracted much interest,[1] including from an enantioselective point of view.[1b,c] Along the same line, beyond the imidazolylidene ligands, one may envisage other ligands providing persistent carbon−metal bonds. In particular, while much efforts have been recently devoted to catalytic applications of chiral iminophosphorane[2a−d] and phosphine oxide ligands,[2e−l] and whereas the coordination chemistry of phosphonium ylide C-ligands is widely documented,[3] catalytic applications thereof are scarce.[4] Let us mention Grey's report on olefin hydrogenation catalyzed by a phosphonium diylide−rhodium complex[5] and Starzewski's report on olefin polymerization catalyzed by phosphonium ylide−(phosphinoenolate)nickel complexes.[6] To the best of our knowledge, there are only a few examples of asymmetric catalysis using chiral phosphonium ylide ligands in rhodium and palladium complexes (Scheme 1).[7,8] These hybrid P,C

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(3) (a) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. (b) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1. (c) Belluco, U.; Michelin, R. A.; Mozzon, M.; Bertani, R.; Facchin, G.; Zanotto, L.; Pandolfo L. *J. Organomet. Chem.* **1998**, *557*, 37. (d) Bricklebank, N. *Organophosphorus Chemistry*; The Royal Society of Chemistry: 1999; Vol. 29, Chapter 6, p 231.

(4) It is well established from Keim's work that stabilized phosphonium ylides are merely *precursors* of the actual phosphinoenolate ligands of the catalytically active nickel species for olefin oligomerization (SHOP process): Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466.

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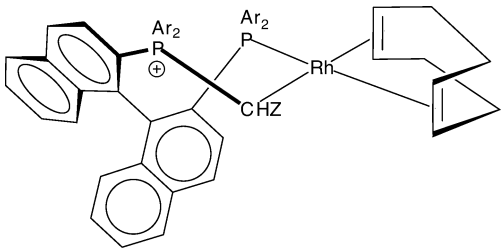
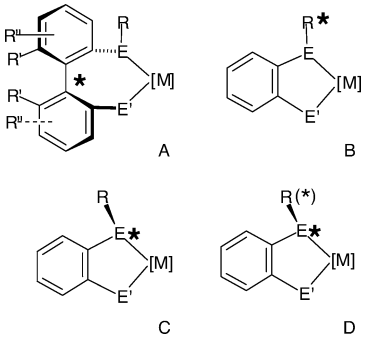
Scheme 1. Chiral Rhodium Catalysts with Binaphthium Methylide Derivatives as Ligands (Ar = Ph, Z = H; Ar = *p*-Tol, Z = CO_2Et, CO_2t-Bu, CN)



Scheme 2. Patterns for Assessing Chirality in Transition Metal Complexes from Chelating Ligands with an Aromatic Bridge



chelating ligands are actually phosphino−phosphonium ylide ligands with the same binaphthyl bridge as that of (*R*)-binap.[11a] For (2′-di(*p*-tolyl)phosphinyl-1,1′-binaphth-2-yl)di(*p*-tolyl)phosphonium carboxymethylide ligands ("yliphos"), the stabilized nature of the free ylide favors decoordination from the catalytic metal centers.[7] This hemilabile character may account for the poor enantioselectivity observed.[7a] By contrast, the nonstabilized (*R*)-binapium methylide ligand was shown to give a stable chelated rhodium complex.[8,9]

In the latter complex, however, the atropochirality results in a poor control (ca. 4 kcal mol^{-1}) of the chiral configuration of the flexible eight-membered rhodacycle.[8,10] We reasoned that a less flexible six-membered rhodacycle would maintain a more stable chiral conformation. As a shorter aromatic bridge, 1,2-phenylene was selected to replace the 2,2′−1,1′-binaphthylene bridge of binap. Contrary to the latter however, the 1,2-phenylene bridge is intrinsically achiral. The optimal way to introduce chirality was designed from the following considerations. Several topological patterns can be distinguished to assess chirality in the coordination sphere of the metal (Scheme 2). The pattern A, where the (atropo)chirality is carried by the ligand bridge, encompasses binap,[11a] X-MOP,[11b] biphemp,[11c] and related ligands.[2e,11d] The chirality element here belongs to the metallacycle and is able to directly control its geometrical features, e.g., the λ/δ configuration in the case of a C_2 symmetric ligand. Reetz's diiminophosphorane (E′ = ER = N═PPh_3) refers to this pattern.[2a] The binapium methylide rhodium complexes shown in Scheme 1 provide C_1-symmetric examples of pattern A (E′ = PAr_2, ER = Ph_2P^+-CHZ). The pattern B, where the appending chirality element remains outside the metallacyle, corresponds to Burk's R-Duphos-type ligands (ER = E′ = 2,5-dialkylphospholanyl),[12] but was also exemplified in C_1 versions (E′ = PPh_2, ER* = 4(*S*)-*i*-Pr-1,3-oxazolinyl).[13] The pattern C occurs as soon as the complexing atom is stereogenic and corresponds to the case of diphosphines with resolved asymmetric phosphorus atoms. It has been exemplified in both C_2 symmetric (e.g., E′ = E*−R = P*PhMe)[14] and C_1 symmetric versions (e.g., E′ = PPh_2, E*−R = S*(O)−Ar).[15] In the hybrid pattern D, the stereogenic center E* is created simultaneously with the complexation process, while its configuration could be controlled by an appending chiral substituent R(*). The substituent R(*) then plays a secondary role in assessing the chirality of the metal environment.

The pattern D is here envisionned for E′ = PPh_2 and E−R* = $Ph_2P^+-CH-S^*(O)Ar$. The presence of an asymmetric ylidic carbon directly bound to the metal center would bring the chiral information inside the metallacycle and as close as possible to the metal center. To the best of our knowledge, enantiomerically pure chiral complexes containing an asymmetric ylidic carbon−transition metal unit have not been reported.

Results and Discussion

Ligand Synthesis. Although a few (sulfinylmethyl)-phosphoniums had been previously prepared by Trippett[16a] and Aitken,[16b,c] optically active α-sulfinylphosphonium ylides with a stereogenic sulfur center have been described only recently by Mikolajczyk.[17] The preparation of (*S*)-(*p*-tolylsulfinyl)methyl)triphenylphosphonium ylide **4a** was based on the reaction of (methyl)triphenylphosphonium ylide **1a** with menthyl (*S*)-*p*-tolylsulfinate **2** (Scheme 1). The semistabilized ylide **4a** can be used in situ for the preparation of chiral (*E*)-alkenyl sulfoxides through classical Wittig reaction with α,β-unsaturated aldehydes or protonated to the corresponding ((*p*-tolylsulfinyl)methyl)triphenylphosphonium salt **4aH**$^+$.[17]

The above method was thus envisioned for the preparation of more functional derivatives such as (2-diphenylphosphinophenyl)((*p*-tolylsulfinyl)methyl)diphenyl-

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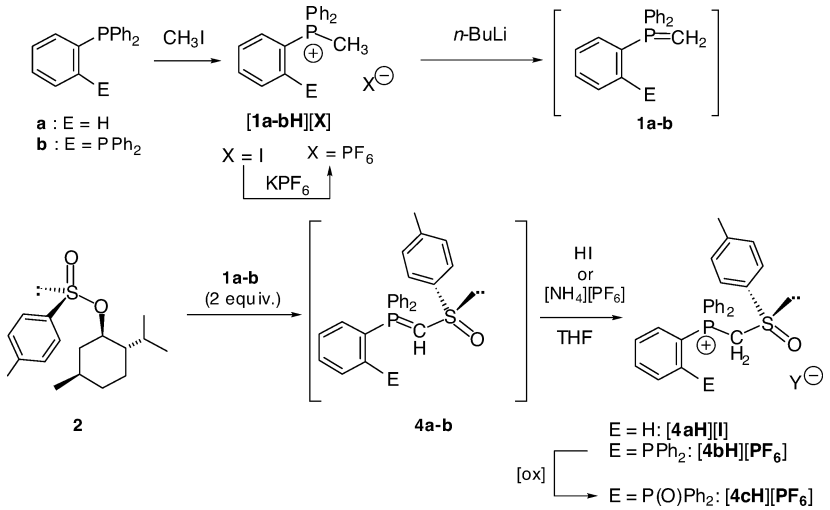

Figure 1. Preparation of ((*S*)-sulfinylmethyl)triphenylphosphonium derivatives.

phosphonium ylides (ligand pattern D, Scheme 1). The starting (2-diphenylphosphinophenyl)diphenylphosphonium methylide **1b** was prepared by deprotonation of the corresponding phosphino−phosphonium **1bH**$^+$, itself selectively prepared from methyl iodide and 1,2-diphenylphosphinobenzene.[9,18] The phosphino−phosphonium iodide [**1bH**][**I**] was first converted to the hexafluorophosphate [**1bH**][**PF$_6$**]. Deprotonation of **1bH**$^+$ and subsequent addition of optically pure menthyl (*S*)-*p*-tolylsulfinate **2** lead to the semistabilized (2-diphenylphosphinophenyl)(sulfinylmethyl)diphenylphosphonium ylide **4b** (Figure 1).

As in the case of **4aH**$^+$,[17] the initial (sulfinylmethyl)-phosphonium **4bH**$^+$ is in situ deprotonated to the semistabilized ylide **4b** by the yet unreacted unstabilized ylide **1b**. After removal of [**1bH**][**PF$_6$**] by filtration, protonation of **4b** with [NH_4][PF_6] led to (sulfinylmethyl)-(2-(diphenylphosphinophenyl)diphenylphosphonium-hexafluorophosphate [**4bH**][**PF$_6$**] in 50% yield. No oxygen transfer from the sulfur atom to the phosphorus atom was observed,[19] but incidental oxidation of **4bH**$^+$ allowed for the isolation of the corresponding phosphine oxide **4cH** (Figure 1).

The ^{31}P NMR characteristics of the phosphinyl− and phosphinoyl−phosphoniums **4bH**$^+$ and **4cH**$^+$ are consistent with reported data on the unfunctional phosphonium **4aH**$^+$ (Table 1) and with further data on *o*-$Ph_2P-C_6H_4-(Ph)_2P$ = X phosphazenes (X = NH, $NSiMe_3$, NBn, $NP(O)(OPh)_2$)[20] and phosphine oxides (X = O).[21]

Rhodium Complexes. Until recently, most of rhodium complexes with either independent phosphine and phosphonium ylide ligands[22] or chelating phosphino−phosphonium ylide ligands[23] were rhodium(III) complexes. Since most common catalyst precursors for hydrogenation or hydrosilylation (see below) are rhodium(I) complexes, the rhodium(I) complexes of **4b** were targeted.[7,9,10,24] The chiral phosphoniophosphine **4bH**$^+$ was thus deprotonated back to the ylide **4b** with *n*-BuLi and in situ reacted with [$Rh(cod)_2$][PF_6] at room temperature. The ^{31}P NMR specrum of the crude material exhibits two sets of three signals corresponding to a 9:1 mixture of epimeric complexes [**5a**][**PF$_6$**] and [**5b**][**PF$_6$**], which could be separated by chromatography over silica gel (Figure 2). 1D and 2D ^{1}H, ^{31}P, ^{13}C, and ^{103}Rh NMR data (see Experimental Section) are consistent with a P,C chelating behavior of the ligand. While stabilized phosphonium ylides $R_3P{=}CH-CO_2R'$ were reported to react with [$PdCl_2$(cod)] and [$PtCl_2$(cod)] at an sp^2 carbon atom of the cyclooctadiene ligand,[25] the cyclooctadiene ligand remains intact in complexes **5**$^+$. When the complexation reaction of the ylide is carried out at low temperature (−45 °C), the phosphino−phosphonium ylide complex **5**$^+$ is formed in 85% yield but with a reversed diastereoselectivity: **5a**$^+$:**5b**$^+$ = 1:9 (Figure 2). This suggests that **5a**$^+$ is the thermodynamic epimer, while **5b**$^+$ is the kinetic one (see below).

Table 1. Comparative ^{31}P NMR Data for Methyltriarylphosphonium Salts, Ylides, and Ylide Complexes

	Ph_2P	$^1J_{RhP}$	Ph_2P^+	J_{PP^+}	$^2J_{RhP^+}$	$PF_6{}^-$[a]
[**4aH**][**I**]			19.80			
[**4bH**][**PF$_6$**]	−7.69		23.30	23.5		−141.60
[**4cH**][**PF$_6$**]	35.34		28.51	6.5		−141.45
[**1b**][b]	−11.40		27.30	29.9		
[**4a**][c]			23.30			
[**4b**][c]	−10.60		27.90	21.6		
[(binapCH_2)-Rh(cod)][BF_4][d]	25.65	155.0	34.18	5.3	5.2	
[**5a**][**PF$_6$**]	28.51	154.8	26.41	24.1	6.9	−141.70
[**5b**][**PF$_6$**]	22.75	151.5	20.41	43.5	≈0	−141.68

[a] Septet, $^1J_{PF}$ ≈ 713 Hz. [b] In Et_2O at 81 MHz. [c] In THF at 81 MHz. [d] Refs 9 and 10.

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(21) The reduced $^3J_{PP^+}$ coupling constant in the phosphonium−phosphine oxide **4cH**$^+$ (ca. 7 Hz) is consistent with data reported for the related derivatives *o*-O=PPh(R)−C_6H_4−(Ph)(R)P$^+$−Me (R = Me: $^3J_{PP^+}$ = 9 Hz; R = Ph: $^3J_{PP^+}$ < 3 Hz).[18]
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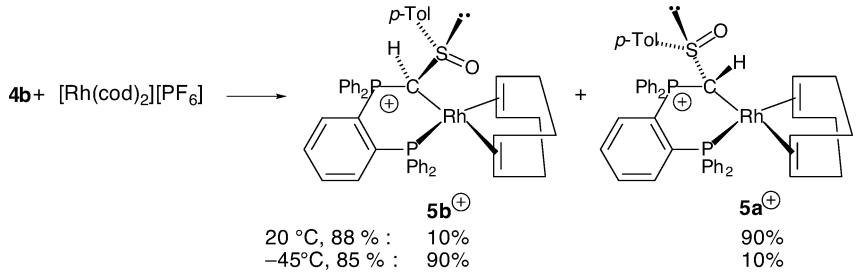

Figure 2. Diastereoselective preparation of both epimers of complex $\mathbf{5}^+$.

Table 2. Crystal Data and Structure Refinement for Complex [5b][PF$_6$]

empirical formula	$C_{46}H_{44}F_6OP_3SRh$
fw	954.69
temperature	180(2) K
wavelength (Mo, Kα)	0.71073 Å
cryst syst	orthorhombic
space group	$P2_12_12_1$
unit cell dimens	a = 14.561(5) Å
	b = 14.596(5) Å
V	8421(4) Å^3
Z, calcd density	8, 1.506 mg·m^{-3}
absorp coeff	0.632 mm^{-1}
F(000)	3904
cryst size	(0.42 × 0.35 × 0.14) mm
cryst form	parallelepiped
cryst color	orange
2θ range	3.3−52.1°
d(hkl) range	12.453−0.809 Å
range for data collection	3.47−28.28°
index ranges	$-19 \le h \le 19$, $-19 \le k \le 16$, $-52 \le l \le 52$
no. of reflns collected/unique	68 906/10 449 [R(int) = 0.0693]
completeness to 2θ = 56.56°	99.5%
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	0449/0/528
goodness-of-fit on F^2	1.091
final R indices [$I > 2(I)$]	R1 = 0.0451, wR2 = 0.0877
R indices (all data)	R1 = 0.0486, wR2 = 0.0897
absolute struct param	0.01(3)
largest diff peak and hole	0.715 and −0.495 e·Å^{-3}

IR data suggest that the sulfinyl group is not, or at least not strongly, bonded to the rhodium atom. Indeed, the stretching S=O vibration occurs at roughly the same frequency in complexes $\mathbf{5a}^+$ (ν_{S-O} = 1034 cm^{-1}) and $\mathbf{5b}^+$ (ν_{S-O} = 1040 cm^{-1}) as in the free (sulfinylmethyl)-phosphonium $\mathbf{4H}^+$ (ν_{S-O} = 1052 cm^{-1}). The most striking variation in the IR spectra concerns the C−P$^+$ vibration: with respect to the free ligand $\mathbf{4bH}^+$ (ν_{P^+-C} = 1111 cm^{-1}), it takes place at lower frequency in $\mathbf{5b}^+$ (ν_{P^+-C} = 1096 cm^{-1}) and at higher frequency in **5a** (ν_{P^+-C} = 1118 cm^{-1}). The NMR characteristics of both the epimeric complexes are listed in Table 1. They compare well with those of the [((*R*)-binapCH$_2$)Rh(cod)]$^+$ complex. In particular, the $^2J_{RhP}$ coupling constant reaches ca. 5 Hz is both $\mathbf{5a}^+$ and [((*R*)-binapCH$_2$)Rh(cod)]$^+$ and vanishes for $\mathbf{5b}^+$. The ylidic CH unit occurs at shielded ^{1}H and ^{13}C chemical shifts. The deshielding of the proton corresponds to a shielding of the carbon in $\mathbf{5a}^+$ (δ^1_H = 4.2 ppm, δ^{13}_C = 38.4 ppm) by comparison with $\mathbf{5b}^+$ (δ^1_H = 3.5 ppm, δ^{13}_C = 45.4 ppm). The ^{103}Rh chemical shifts of $\mathbf{5b}^+$ (+261.3 ppm) and $\mathbf{5a}^+$ (+170.0 ppm) fall in the classical range for Rh(olefin)(P)(X) complexes. For comparison, the related orthometalated P,C complex (*o*-R$_2$PC$_6$H$_4$)Rh(cod) occurs at δ^{103}_{Rh} = +22 ppm.[26] However, the rhodium atom is slightly more deshielded in $\mathbf{5b}^+$ than in $\mathbf{5a}^+$, and this might result in different catalytic behaviors.

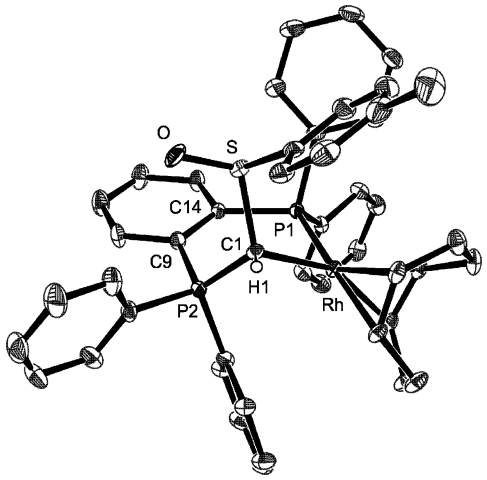

Figure 3. ORTEP view of the X-ray crystal structure of the complex [**5a**][**PF$_6$**], with 50% probability displacement ellipsoids for non-hydrogen atoms. Selected bond lengths (Å): Rh−C(1) = 2.152(3); S(1)−O(1) = 1.495(3); P(2)−C(1) = 1.764(4); P(2)−C(9) = 1.808(4); C(1)−H(1) = 0.85(4); S(1)−C(1) = 1.806(4); C(9)−C(14) = 1.414(5); Rh−P(1) = 2.2730(10); P(1)−C(14) = 1.835(3). Selected bond angles (deg): C(1)−Rh−P(1)=92.26(10); S(1)−C(1)−Rh=111.41(16); P(2)−C(1)−Rh = 100.76(16); C(14)−P(1)−Rh = 116.70(12); C(1)−P(2)−C(9) = 109.91(17); C(9)−C(14)−P(1) = 122.9(3); C(14)−C(9)−P(2) = 123.8(3); O(1)−S(1)−C(1) = 111.07(17).

The structure and purity level of both complexes (to be tested in catalytic experiments: see below) were established by accurate HRMS, sharp melting points, and NMR spectra (see Experimental Section and Supporting Information). Furthermore, crystals of the $\mathbf{5a}^+$ epimer deposited from a dichloromethane−diethyl ether solution and allowed for an X-ray diffraction analysis (Table 2, Figure 3). The ylidic carbon of $\mathbf{5a}^+$ has the *R*-configuration. The six-membered metallacycle adopts an envelop conformation where the rhodium atom lies in the plane defined by both the phosphorus atoms and the phenylene carbon atoms (Rh−(P1,C14,C9,P2) = 0.043 Å). The ylidic carbon (C1) is tilted out by the dihedral angle (C1, P2, Rh, P1) = 69.51°, namely, 1.122 Å above the plane (P1,C14,C9,P2). A similar tilting of the methylide unit from the RhP$_2$ plane was calculated in a DFT model of the related rhodium complex [((*R*)-binapCH$_2$)Rh(cod)] (Scheme 1).[9] Despite the long known coordinating ability of the sulfinyl group toward rhodium(I) centers, and especially when chelating,[27] both the sulfur and oxygen atoms occur at nonbonding distances

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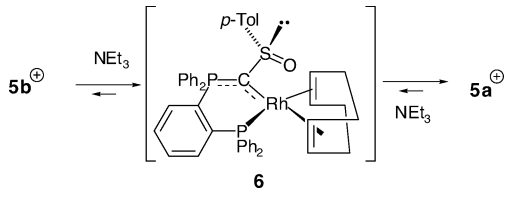

Figure 4. Reversible deprotonation of epimeric complexes $\mathbf{5a}^+$ and $\mathbf{5b}^+$, through the putative intermediate **6**.

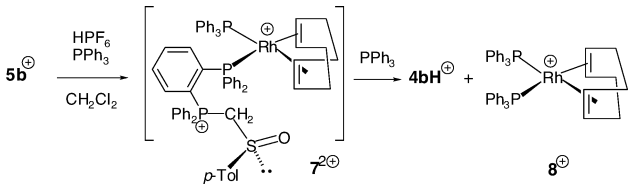

Figure 5. Acidic cleavage of the ylidic carbon−rhodium bond by HPF_6 in the presence of triphenylphosphine.

from the rhodium center (Rh···O = 4.6041(30) Å, Rh···S = 3.2761(13) Å). This is in accordance with the IR data discussed above.

Other structural features of the complex $\mathbf{5a}^+$ qualitatively compare with those of Cavell's homologous (but achiral) phosphino−phosphazene rhodium(I) complex (P,N-η^2-*o*-Ph_2P-C_6H_4−Ph_2P = *N*$SiMe_3$)RhCl(CO).[20] In particular, the critical bonds have the same order of magnitude: Rh−C = 2.152(3) Å in $\mathbf{5a}^+$ versus Rh−N = 2.146(6) Å in Cavell's complex. The main difference qualifying the ylidic carbon−nitrogen analogy resides in a 10° difference between the critical angles: P−C−Rh = 100.76(16)° in $\mathbf{5a}^+$ versus P−N−Rh = 109.9(4)° in Cavell's complex.[20]

The ylidic carbon is substituted by an unusual set of substituents H, P^+, S, and Rh. To the best of our knowledge, this is the first example of a transition metal ylide complex containing an asymmetric ylidic carbon of definite absolute configuration. Let us, however, mention Spannenberg's doubly zwitterionic palladium(II) complex, where the relative configuration of two ylidic carbons is spontaneously controlled during the complexation of the achiral stabilized bisphosphonium diylide ligand PhCO−CH=PPh_2−CH_2CH_2−Ph_2P=CH−COPh at a $PdCl_2$ center: the racemic *dl* isomer formed selectively at the expense of the *meso* isomer.[28]

The configuration of the ylidic carbon of the pure complexes $\mathbf{5a}^+$ ($[\alpha]_D^{20}$ = +58.4°) and $\mathbf{5b}^+$ ($[\alpha]^{24}{}_D$ = +106°) is stable. *In basic medium*, however, epimerization of $\mathbf{5b}^+$ to the thermodynamically more stable isomer $\mathbf{5a}^+$ takes place. After heating complex [**5b**][$\mathbf{PF_6}$] in the presence of triethylamine for 10 h in THF at 50 °C, the final ratio $\mathbf{5b}^+$:$\mathbf{5a}^+$ = 1:9 is identical to the crude diastereoisomeric ratio obtained when [**5**][$\mathbf{PF_6}$] is directly prepared at room temperature. The epimerization likely proceeds through deprotonation of the secondary asymmetric ylidic carbon to give a rhodaylide intermediate **6** (Figure 4). Similar complexes containing an yldiide ligand,[29] namely, an R_3P=C(R′)−[M] unit, are known.[3,30] The adjacent sulfinyl group then controls the approach of the proton and determines the thermodynamic diastereoisomeric ratio. In terms of free enthalpy at 25−50 °C, the S_S,R_C isomer $\mathbf{5a}^+$ is therefore more stable than the S_S,S_C isomer $\mathbf{5b}^+$ by ca. 1.4 kcal·mol^{-1}.

In acidic medium, the ylidic carbon−rhodium bond is cleaved. No clean product could be identified from the reaction of [**5b**][$\mathbf{PF_6}$] with aqueous HCl in chloroform at either 25 or −55 °C. In the presence of triphenylphosphine however, the noncoordinating anion of hexafluorophosphoric acid (1 equiv of HPF_6) allowed for the formation of the free protonated ligand [**4bH**][$\mathbf{PF_6}$] along with the known complex [**8**][$\mathbf{PF_6}$] (Figure 5).[31] The likely intermediate $\mathbf{7}^{2+}$ was not detected: the electrostatic repulsion of the cationic charges must indeed favor the displacement of the phosphoniophosphine ligand by a second neutral triphenylphosphine ligand (Figure 5).

Catalytic Properties. As emphasized in the Introduction, few catalytic studies of phosphonium ylide transition metal complexes are available.[5−7,9,10] The challenge of the discovery of catalytic reactions catalyzed by complexes bearing such persistent carbon ligands is here tackled with complexes $\mathbf{5a}^+$ and $\mathbf{5b}^+$. Since diaminocarbenes behave as efficient persistent carbon ligands in rhodium-catalyzed hydrosilylation of ketones,[1b,c] hydrosilylation was first selected as a trial reducing process. From a conceptual standpoint, beyond the effect of the persistent Rh−C bond, the course of the catalysis should be influenced by the (chiral) electrostatic field generated by the phosphonium center and embedding the rhodium center.[32] Within a more general prospect, it is worth noting that rhodium(I) complexes of nondeprotonated phosphino−phosphonium ligands were shown to be active in olefin hydrogenation in biphasic media,[33] and more recently in homogeneous hydroformylation of 1-hexene[34] and asymmetric hydrogen transfer to (*Z*)-α-acetamidocinnamic acid.[35]

Catalytic Hydrosilylation. Both epimers of the complex $\mathbf{5}^+$ in 1% catalytic ratio were found to separetely catalyze hydrosilylation of acetophenone **9** by Ph_2SiH_2 over a 20−40 h period at room temperature (Figure 6). As shown in Table 3, complex $\mathbf{5a}^+$ is definitely much more selective than complex $\mathbf{5b}^+$. Various solvents were used, and the catalytic efficiency increases in the order CH_2Cl_2 < no < THF. No "CCl_4 effect" was observed.[36]

Regarding the enantioselectivity, complex $\mathbf{5b}^+$ is slightly more enantioselective than complex $\mathbf{5a}^+$. In THF, while $\mathbf{5b}^+$ produces a 8% excess of (*S*)-(−)-phenylethanol **12**, $\mathbf{5a}^+$ produces a 5% excess of the opposite enantiomer. Although not high in absolute value, this reversal of enantioselectivity suggests that

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Table 3. Catalytic Hydosilylation of Acetophenone Catalyzed with Complexes 5a$^+$ and 5b$^+$

catalyst	solvent	time (h)	% conv[a]	% yield[b]	% selectivity[c]	$[\alpha]_D^{25}$	% ee[d]
5b$^+$	THF	20	nd	nd (60)		−3.5°	8
5b$^+$	CH_2Cl_2	40	quant.	66 (52)	66	−0.9°	2
5b$^+$	CH_2Cl_2:CCl_4, 3:1	40	95	50 (39)	53	−1.4°	3
5b$^+$	no	40	99	75 (60)	76	−1.8°	4
5a$^+$	THF	40	97	95 (79)	98	+2.3°	5
5a$^+$	CH_2Cl_2	40	91	82 (70)	90	−0.3°	1

[a] % conv = (**10** + **11**)/**9** × 100. [b] After hydrolysis. Isolated yields of **12** are given in parentheses. [c] In hydrosilylation product: **11**/(**9** + **10** + **11**) × 100. [d] Determined from the optical rotation of pure (*R*)-**12**: $[\alpha]_D^{20}$ +45° (*c* 5, MeOH).

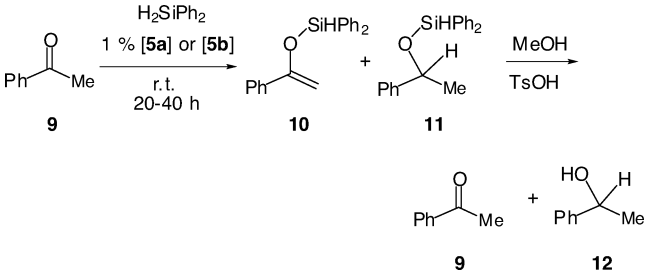

Figure 6. Hydrosilylation of acetophenone catalyzed by complexes **5a**$^+$ and **5b**$^+$.

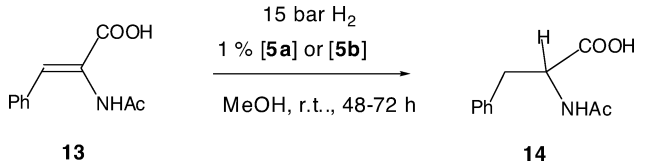

Figure 7. Hydrogenation of (*Z*)-α-acetamidocinnamic acid catalyzed by complexes **5a**$^+$ and **5b**$^+$.

5a$^+$ and **5b**$^+$ behave as pseudoenantiomeric catalysts. As anticipated in the Introduction, the sulfinyl chiral center plays a secondary role in the chirality of the rhodium coordination sphere.

It is worth noting that the catalytic propensity of phosphinophosphonium ylide rhodium complexes for hydrosilylation of acetophenone seems to be quite general. Such an activity and 10% ee were indeed provided by the homologous binapium methylide rhodium complex.[10]

The catalytic properties were then evaluated in another reducing catalytic process: hydrogenation.

Catalytic Hydrogenation. The ylidic carbon−rhodium bond of complexes **5a**$^+$ and **5b**$^+$ is stable under up to 15 bar of hydrogen atmosphere. This rather surprising observation prompted us to test these complexes for the hydrogenation of (*Z*)-α-acetamidocinnamic acid **13**, a reference substrate.[37] Under 15 bar H_2, each epimer **5a**$^+$ and **5b**$^+$ was found to be catalytically active in 1% catalytic ratio (Figure 7). The stability of the complex was confirmed by the absence of metallic rhodium even after a 72 h, the required reaction time to reach quantitative conversion. The enantioselectivity in *N*-acetyl-(*R*)-phenylalanine **14** remained low (ca. 2% with **5a**$^+$ and 4% with **5b**$^+$). The addition of one catalytic equivalent of triphenylphosphine did not improve the activity nor the enantioselectivity (Table 4).

Conclusion

It has been shown that chiral phosphino(sulfinylmethyl)phosphonium ylides constitute a novel class of hybrid P,C chelating ligands of rhodium(I). In these complexes, a resolved asymmetric ylidic carbon atom is bound to the metal center. The reducing catalytic efficiency of these complexes has been demonstrated and dramatically fills the paucity of reported examples of catalytically active phosphonium−ylide transition metal complexes. The enantioselectivity of these catalytic processes remains to be improved. The flexibility and/or the absence of C_2 symmetry of the (C,P,Rh,C,P$^+$,C) six-membered metallacycle might be responsible for the lack of enantioselectivity. This challenge will be the goal of future investigations.

Table 4. Catalytic Hydrogenation of (*Z*)-α-Acetamidocinnamic Acid 13 with Complexes 5a$^+$ and 5b$^+$[a]

catalyst	time (h)	PH_2 (bar)	conv (%)	$[\alpha]_D^{25}$	ee (%)[b]
5b$^+$	48	1	0		
5b$^+$	48	15	71	−1.8°	4
5b$^+$ + PPh_3	72	15	66	−0.7°	1
5a$^+$	72	15	100	−1.2°	2

[a] See Experimenttal Section. [b] Estimated from the optical rotation with respect to the reported value for pure (*R*)-**14**: $[\alpha]_D^{26}$ −51.8° (*c* 1, EtOH).[46]

Experimental Section

Reactions were carried out under a nitrogen atmosphere using Schlenk tube and vacuum line techniques. THF and ether were distilled over Na/benzophenone. Ethanol was distilled over Drierite. Dichloromethane was distilled over P_2O_5. Butyllithium was purchased from Aldrich as a 1.6 M solution in hexane. 1,2-Diphenylphosphinobenzene and methyl iodide were purchased from Fluka. Ammonium tetrafluoroborate was purchased from Aldrich. $[Rh(cod)_2][BF_4]$ was prepared from $[RhCl(cod)]_2$,[38] itself prepared from cyclooctadiene and $RhCl_3 \cdot 3H_2O$ (Johnson-Matthey) according to a modified procedure (no carbonate was added).[39] $[Rh(cod)_2][BF_4]$ was converted to the $[Rh(cod)_2][PF_6]$ by anion metathesis with 13 equiv of KPF_6 in a $CH_2Cl_2-H_2O$ mixture. NMR spectra were recorded in $CDCl_3$ solution, on Bruker AC 200 and AMX 400 spectrometers. Positive chemical shifts at low field are expressed in ppm by internal reference to TMS for ^1H and ^{13}C and by external reference to 85% H_3PO_4 in D_2O for ^{31}P. ^{103}Rh chemical shifts are given to high frequency of $\Xi(^{103}Rh) = 3.16$ MHz. Optical rotations were measured in a 1 dm cell with a Perkin-Elmer 241 photopolarimeter.

Crystallographic Studies. Data were collected at low temperature (T = 180 K) on a STOE diffractometer using graphite-monochromated Mo K radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems cryostream cooler jet cooler device. The final unit cell parameters were obtained by means of a least-squares refinement performed on a set of 8000 well-measured reflections. A crystal decay was monitored, and no significant fluctuations of intensities were observed during

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the data collection. Structure was solved by direct methods using SIR92[40] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97[41] included in WinGX version 1.63.[42] The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[43] Hydrogens atoms were located on difference Fourier maps, but introduced in the process of the refinement in idealized positions using a riding model. The C−H distances were fixed at 0.93 Å for C sp^2 atoms and 0.96 Å for C sp^3 atoms, with an isotropic parameter at 20% higher than the U_{eq} value of the C sp^2 atom to with they were attached and 50% higher for the C sp^3 atom. Methyl groups were refined by using a rigid group with the torsion angle refined as a free variable. All nonhydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. The absolute configuration was assigned on the basis of the refinement of the Flack's enantiopole parameter, X, which is the fractional contribution of $F(-h)$ to the observed structure amplitude,[44] as depicted in the following formula: $F_o^2 = (1 - x)F(h)^2 + xF(-h)^2$. This parameter is sensitive to the polarity of the structure. The Flack's parameter was found close to 0, which clearly indicated the good choice of the enantiomer refined. Least-squares refinements were carried out by minimizing the function $w(F_o - F_c)^2$,where F_o and F_c are the observed and calculated structure. The criteria for a satisfactory complete analysis were the ratios of root-mean-square shift standard deviation being less than 0.1 and no significant features in final difference Fourier maps. Drawings of molecules are performed by using the program ORTEP3 with 50% probability displacement ellipsoids for non-hydrogen atoms.[45][46]

(*S*)-[2-(Diphenylphosphino)phenyl][(*p*-tolylsulfinyl)methyl]diphenylphosphonium Hexafluorophosphate [4bH][PF$_6$]. To a stirred suspension of [2-(diphenylphosphino)-phenyl] (methyl)diphenylphosphonium hexafluorophosphate [**1bH**][**PF$_6$**] (1.0 g, 1.65 mmol) in diethyl ether (70 mL) at −20 °C was added dropwise a solution of *n*-BuLi (1.1 mL of 1.5 M solution in hexane, 1.65 mmol). The cooling bath was removed, and the mixture was allowed to warm to room temperature. After 30 min the mixture was cooled to −20 °C and (*S*)-(−)-menthyl *p*-toluenesulfinate (0.243 g, 0.83 mmol) was added. After 10 min stirring at −20 °C and 30 min at room temperature a precipitate of [2-(diphenylphosphino)phenyl]methyldiphenylphosphonium hexafluorophosphate, insoluble in Et_2O, was filtered off, and the mixture was quenched with a solution of ammonium hexafluorophosphate (0.26 g, 1.65 mmol) in THF (30 mL). Then, the solvents were evaporated, water (30 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography on silica gel using dichloromethane−acetone (20:0.5) as the eluent. Yield: 0.31 g (50%). Mp: 119 °C. $[\alpha]^{22}_D$ +61.8 (*c* 2.0, CH_2Cl_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 23.30 (d, $J_{PP^+} = 23.5$ Hz, P^+), −7.69 (d, $J_{PP^+} = 23.5$ Hz, P), −141.60 (septet, $J_{PF} = 712.7$ Hz, PF_6^-). ^1H NMR (400 MHz, $CDCl_3$): δ 7.87−6.84 (m, 28 H), 5.04−4.98 (m, 2 H, CH_2), 2.43 (s, 3 H, CH_3). $^{13}C\{^1H, ^{31}P\}$ NMR (100.6 MHz, $CDCl_3$): δ 143.74, 143.41, 139.36, 139.23, 137.79, 135.95, 135.59, 135.42, 135.33, 134.70, 134.14, 133.58, 132.81, 132.05, 131.83, 131.18, 130.90, 30.58, 130.37, 129.61, 129.43, 129.33, 125.14, 124.57, 118.79, 118.11, 54.60 (P^+CH_2), 22.00 (CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 143.74, 143.41 (dd, $J_{CP^+} = 15.2$ Hz, $J_{CP} = 11.8$ Hz), 139.35 (d, $J_{CP^+} = 12.8$ Hz), 139.23 (d, $J_{CP^+} = 10.4$ Hz), 137.78 (dd, $J_{CP^+} = 13.5$ Hz, J_{CP} =10.5 Hz), 135.95 (d, $J_{CP^+} = 2.9$ Hz), 135.58 (d, $J_{CP^+} = 3.0$ Hz), 135.42 (d, $J_{CP^+} = 2.3$ Hz), 135.33 (d, $J_{CP^+} = 11.0$ Hz), 134.70 (d, J_{CP} = 4.6 Hz), 134.14 (d, $J_{CP} = 20.1$ Hz), 133.58 (d, $J_{CP^+} = 11.1$ Hz), 132.81 (d, $J_{CP} = 16.5$ Hz), 132.06 (d, $J_{CP} = 3.9$ Hz), 131.82 (d, $J_{CP^+} = 13.3$ Hz), 131.18, 130.90 (d, $J_{CP^+} = 13.2$ Hz), 130.58 (d, J_{CP^+} =13.6 Hz), 130.37, 129.61, 129.42 (d, $J_{CP} = 8.3$ Hz), 129.33 (d, $J_{CP} = 6.5$ Hz), 125.15 (dd, $J_{CP^+} = 88.3$ Hz, $J_{CP} = 37.6$ Hz), 124.57, 118.79 (dd, $J_{CP^+} = 89.4$ Hz, $J_{CP} = 2.7$ Hz), 118.11 (d, $J_{CP^+} = 86.9$ Hz), 54.61 (dd, $J_{CP^+} = 50.5$ Hz, $J_{CP} = 21.0$ Hz, P^+CH_2), 22.00 (CH_3). IR (KBr): 3052, 2920, 1640, 1483, 1440, 1111, 1052, 840, 741, 557 cm^{-1}. FAB-MS *m*/*z* (rel int): 599 (62) ([**4bH**$^+$]), 460 (15), 459 (44), 383 (100), 154 (24). HRMS calcd for $C_{38}H_{33}OSP_2^+$ 599.1727, found 599.1722. The purity of the compound was established by its NMR spectra (see Supporting Information).

Spectroscopic Characteristics of [4cH][PF$_6$]. [4cH]-[PF$_6$] was obtained by incidental oxidation upon prolonged exposure to air during chromatography. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 35.39 (d, $J_{PP^+} = 6.5$ Hz, P(O)), 28.51 (d, $J_{PP^+} = 6.5$ Hz, P^+), −141.42 (septet, $J_{PF} = 712.9$ Hz, PF_6^-). ^1H NMR (400 MHz, $CDCl_3$): δ 7.85−7.15 (m, 28 H), 5.40 (dd, 1 H, $^2J_{HH} \approx 13.5$, $^2J_{PH} = 15.1$ Hz; C*H*HP$^+$), 4.70 (dd, 1 H, $^2J_{HH} = 13.5$ Hz, $^2J_{PH} = 4.4$ Hz; C*H*HP$^+$), 2.46 (s, 3 H, CH_3). $^{13}C\{^1H, ^{31}P\}$ NMR (100.6 MHz, $CDCl_3$): δ 143.44, 140.34, 139.86, 137.81, 137.38, 137.27, 135.75, 135.43, 135.32, 134.96, 134.68, 133.91, 133.62, 133.23, 132.48, 131.59, 131.03, 130.97, 130.12, 129.61, 129.58, 128.76, 128.65, 124.47, 121.38 ($J_{P^+C} = 86.4$ Hz, J(O)-PC = 6.9 Hz), 120.32 ($^1J_{P^+C} = 85.2$ Hz), 119.33 ($^1J_{P^+C} = 94.6$ Hz), 56.66 ($^1J_{P^+C} = 54.4$ Hz), 22.00. (+)-ES-MS *m*/*z*: 615.2 ([**4cH**$^+$]). (−)-ES-MS *m*/*z*: 144.9 ([**PF$_6^-$**]). The purity of the compound was established by its NMR spectra (see Supporting Information).

Rhodium Complexes [5][PF$_6$]. To a stirred solution of [**4bH**][**PF$_6$**] (100 mg, 0.134 mmol) in THF (8 mL) at −20 °C was added *n*-BuLi (84 μL of 1.6 M solution in hexane, 0.134 mmol). The cooling bath was removed, and the mixture was allowed to warm to room temperature (orange solution). After 15 min bis(1,5-cyclooctadiene)rhodium(I) hexafluorophosphate (61 mg, 0.132 mmol) was added, and the stirring was continued for an additional 2 h. The solvent was evaporated, and the crude mixture of two diastereomeric rhodium complexes (in the ratio **5a**$^+$:**5b**$^+$ = 9:1) was purified by flash column chromatography (dichloromethane−acetone gradient), giving 104 mg (81%) of **[5a][PF$_6$]** and 9 mg (7%) of **[5b][PF$_6$]**.

In a similar experiment, addition of equimolar amounts of bis(1,5-cyclooctadiene)rhodium(I) hexafluorophosphate to ylide **4** at −45 °C led to the mixture of diastereoisomeric rhodium complexes in the opposite ratio (**5a**$^+$:**5b**$^+$ = 1:9). Purification of crude products by flash column chromatography gave 9 mg (7%) of [**5a**][**PF$_6$**] and 100 mg (78%) of [**5b**][**PF$_6$**] as orange solids.

Complex [5b][PF$_6$] ($(S)_S(S)_C$ Epimer). Mp: 155−156 °C. $[\alpha]^{20}_D$ +63.1 (*c* 2.0, CH_2Cl_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.75 (dd, $^1J_{PRh} = 151.5$ Hz, $^3J_{PP^+} = 43.5$ Hz, P), 20.41 (d, $^3J_{PP^+} = 43.5$ Hz, P^+), −141.68 (septet, $^1J_{PF} = 713.2$ Hz, PF_6^-). ^{103}Rh NMR (12.6 MHz, $CDCl_3$): δ 261.29 (d, $J_{PRh} = 152.2$ Hz). ^1H NMR (400 MHz, $CDCl_3$, $T = 253$ K): δ 7.98−6.86 (m, 28 H), 5.23 (br s, 1 H, cod-C*H*), 3.53 (br s, 1 H, P$^+$C*H*), 3.45−3.36 (m, 3 H, cod-C*H*), 2.51−2.26 (m, 2H, cod-CH_2), 2.48 (s, 3 H, CH_3), 2.24−2.05 (m, 1H, cod-CH_2), 2.02−1.58 (m, 5H, cod-CH_2). $^{13}C\{^1H, ^{31}P\}$ NMR (100.6 MHz, $CDCl_3$): δ 143.37, 141.81, 139.81, 139.00, 136.61, 136.06, 135.83, 134.90, 134.84, 133.96, 133.39, 132.41, 131.89, 131.58, 131.16, 131.10, 130.69, 130.59, 130.13, 129.49, 129.29, 128.59, 126.61, 123.89, 123.32, 120.73, 99.60 (d, $J_{CRh} = 10.2$ Hz, cod-*C*H), 94.75 (d, $J_{CRh} = 8.4$ Hz, cod-*C*H),

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91.52 (d, J_{CRh} = 6.7 Hz, cod-*C*H), 83.17 (d, J_{CRh} = 9.0 Hz, cod-*C*H), 45.44 (d, J_{CRh} = 26.2 Hz, P^+*C*H), 32.52 (cod-*C*H_2), 32.91 (cod-*C*H_2), 28.52 (cod-*C*H_2), 27.86 (cod-*C*H_2), 2.07 (*C*H_3). ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 143.37 (d, J_{CP^+} = 14.8 Hz), 141.80, 139.81 (dd, J_{CP} = 31.0 Hz, J_{CP^+} = 7.5 Hz), 139.00 (dd, J_{CP} = 9.3 Hz, J_{CP^+} = 9.3 Hz), 136.61 (d, J_{CP^+} = 8.6 Hz), 136.05 (d, J_{CP} = 3.6 Hz), 135.84 (d, J_{CP} = 14.0 Hz), 134.90 (d, J_{CP^+} = 3.0 Hz), 134.85 (d, J_{CP^+} = 3.0 Hz), 133.97 (d, J_{CP^+} = 8.0 Hz), 133.40 (d, J_{CP} = 10.5 Hz), 132.41 (d, J_{CP^+} = 9.8 Hz), 131.88 (d, J_{CP^+} = 13.0 Hz), 131.58 (dd, J_{CP} = 41.3 Hz, J_{CP^+} = 9.6 Hz), 131.15, 131.09, 130.68 (d, J_{CP^+} = 11.8 Hz), 130.59, 130.13 (d, J_{CP^+} = 12.7 Hz), 129.49 (d, J_{CP} = 10.4 Hz), 129.29 (d, J_{CP} = 9.4 Hz), 128.60 (dd, J_{CP} = 34.2 Hz, J_{CP^+} = 19.1 Hz), 126.62 (dd, J_{CP^+} = 61.4 Hz, J_{CP} = 5.0 Hz), 123.89, 123.33 (dd, J_{CP^+} = 70.4 Hz, J_{CP} = 19.1 Hz), 120.74 (dd, J_{CP^+} = 79.5 Hz, J_{CP} = 7.0 Hz), 99.61 (dd, J_{CRh} = 10.1 Hz, J_{CP} = 4.0 Hz, cod-*C*H), 94.74 (d, J_{CRh} = 9.0 Hz), 91.53 (dd, J_{CP} = 17.7 Hz, J_{CRh} = 7.0 Hz, cod-*C*H), 83.17 (d, J_{CRh} = 9.1 Hz, cod-*C*H), 45.44 (ddd, J_{CRh} = 26.2 Hz, J_{CP^+} = 23.0 Hz, J_{CP} = 7.0 Hz, P^+*C*H), 35.51 (cod-*C*H), 32.90 (d, J_{CP} = 5.0 Hz, cod-*C*H), 28.52 (cod-*C*H), 27.87 (cod-*C*H_2), 22.03 (*C*H_3). IR (KBr): 3054, 2920, 1638, 1481, 1437, 1096, 1040, 837, 742, 693, 557 cm^{-1}. FAB-MS *m*/*z* (rel int): 809 (84) [$C_{46}H_{44}OSRhP_2^+$], 701 (58), 670 (26), 549 (100), 460 (18), 459 (43), 154 (38). HRMS calcd for $C_{46}H_{44}OSRhP_2^+$: 809.1636, found 809.1635.

The purity of the compound (to be used in catalysis) was established by its NMR spectra (see Supporting Information).

Complex [5a][PF$_6$] ((*S*)$_s$(*R*)$_c$ Epimer). Mp: 149−151 °C. $[\alpha]^{24}_D$ +106.4 (*c* 1.1, CH_2Cl_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.51 (dd, J_{PRh} = 154.8 Hz, J_{PP^+} = 24.1 Hz, *P*), 26.41 (dd, J_{PP^+} = 24.1 Hz, J_{P^+Rh} = 6.9 Hz, P^+), −141.70 (septet, J_{PF} = 712.7 Hz, PF_6^-). ^{103}Rh NMR (12.6 MHz, $CDCl_3$): δ 170.02 (d, J_{PRh} = 153.2 Hz). ^{1}H NMR (400 MHz, $CDCl_3$, *T* = 253 K): δ 7.96−7.10 (m, 28 H), 4.75 (br s, 1 H, cod-C*H*), 4.18 (q, *J* = 2.8 Hz, 1 H, P^+C*H*), 3.65 (br s, 1 H, cod-C*H*), 3.57 (br s, 1 H, cod-C*H*), 3.40 (br s, 1 H, cod-C*H*), 2.40 (s, 3 H, CH3), 2.10−1.46 (m, 7 H, cod-CH_2), 1.31−1.17 (m, 1 H, cod-CH_2). ^{13}C{^{1}H, ^{31}P} NMR (100.6 MHz, $CDCl_3$): δ 144.63, 143.26, 138.91, 138.03, 137.10, 136.59, 135.95, 134.57, 134.29, 134.09, 133.39, 133.32, 132.38, 131.84, 131.82, 131.73, 130.65, 130.43, 129.99, 129.91, 129.81, 129.65, 126.16, 125.87, 125.75, 123.47, 103.73 (d, J_{CRh} = 6.9 Hz, cod-*C*H), 101.51 (d, J_{CRh} = 6.8 Hz, cod-*C*H), 89.24 (d, J_{CRh} = 8.6 Hz, cod-*C*H), 88.60 (d, J_{CRh} = 9.1 Hz, cod-*C*H), 38.36 (d, J_{CRh} = 23.3 Hz, P^+*C*H), 31.40 (cod-*C*H_2), 30.37 (cod-*C*H_2), 30.10 (cod-*C*H_2), 29.35 (cod-*C*H_2), 22.27 (*C*H_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 144.63 (d, J_{CP^+} = 11.1 Hz), 143.25, 138.89 (d, J_{CP^+} = 9.3 Hz), 138.02 (dd, J_{CP^+} = 12.1 Hz, J_{CP} = 9.9 Hz), 137.10 (br s), 136.59 (dd, J_{CP} = 35.8 Hz, J_{CP^+} = 7.2 Hz), 135.95 (d, J_{CP} = 3.8 Hz), 134.56, 134.27, 134.09 (d, J_{CP} = 11.3 Hz), 133.39 (d, J_{CP^+} = 12.1 Hz), 133.32 (d, J_{CP} = 10.3 Hz), 132.38 (d, J_{CP^+} = 9.6 Hz), 131.84, 131.82, 131.73 (dd, J_{CP^+} = 13.1 Hz, J_{CP} = 38.3 Hz), 130.64, 130.42 (d, J_{CP^+} = 12.8 Hz), 129.99 (d, J_{CP^+} = 9.5 Hz), 129.89 (d, J_{CP} = 9.7 Hz), 129.81 (dd, J_{CP^+} = 12.1 Hz, J_{CP} = 24 Hz), 129.65 (d, J_{CP} = 10.0 Hz), 126.17 (d, J_{CP^+} = 100.0 Hz), 125.87, 125.75 (d, J_{CP^+} = 71.9 Hz), 123.48 (dd, J_{CP^+} = 87.5 Hz, J_{CP} = 20.1 Hz), 103.71 (ddd, J_{CRh} = 7.0 Hz, J_{CP} = 9.1 Hz, J_{CP^+} = 3.0 Hz, cod-*C*H), 101.52 (dd, J_{CP} = 10.1 Hz, J_{CRh} = 7.0 Hz, cod-*C*H), 89.23 (d, J_{CRh} = 9.3 Hz, cod-*C*H), 88.63 (d, J_{CRh} = 8.7 Hz, cod-*C*H), 38.36 (ddd, J_{CRh} =23.3 Hz, J_{CP^+} = 24.8, J_{CP} = 6.4 Hz, P^+*C*H), 31.37 (cod-*C*H_2), 30.35 (cod-*C*H_2), 30.10 (cod-*C*H_2), 29.36 (cod-*C*H_2), 22.28 (*C*H_3). IR (KBr): 3060, 2919, 1637, 1482, 1438, 1118, 1034, 837, 742, 715, 693, 558 cm^{-1}. FAB-MS *m*/*z* (rel int): 809 (100) [$C_{46}H_{44}OSRhP_2^+$], 701 (28), 670 (38), 549 (76), 459 (20), 307 (36), 154 (92). HRMS calcd for $C_{46}H_{44}OSRhP_2^+$: 809.1636, found 809.1636. The purity of the compound (to be used in catalytic experiments) was established by its NMR spectra (see Supporting Information).

Single crystals of [**5a**][**PF$_6$**] suitable for X-ray diffraction analysis were obtained by crystallization from CH_2Cl_2−Et_2O. It allowed for the assignment of the $(S)_s(R)_c$ configuration for the epimer **5a**$^+$. The configuration of the epimer **5b**$^+$ is therefore $(S)_s(S)_c$.

Reaction of [5b][PF$_6$] with HPF$_6$ and PPh$_3$. Formation of Complex [8][PF$_6$]. To a stirred solution of rhodium complex $(S)_S(S)_C$ isomer, **5b**$^+$ (15 mg, 0.016 mmol) and triphenylphosphine (4.1 mg, 0.016 mmol) in dichloromethane (1 mL) at −20 °C was added hexafluorophosphoric acid (2 μL of 65% HPF_6 in water, 0.016 mmol). After 20 min at −20 °C and 30 min at room temperature the solvent was evaporated and the ^{31}P NMR spectrum was recorded. Signals from starting ligand [**4bH**][**PF$_6$**] and complex $[(PPh_3)_2Rh(cod)][PF_6]$, [**8**][**PF$_6$**], were observed.[26] Crude product [**8**][**PF$_6$**] was purified by column chromatography. ^{31}P NMR (81 MHz, $CDCl_3$): δ 26.57 (d, $^1J_{RhP}$ = 145.3 Hz); −144.04 ppm (sept, $^1J_{PF}$ = 712.7 Hz).

Asymmetric Hydrogenation of (*Z*)-α-Acetamidocinnamic Acid. To (*Z*)-α-acetamidocinnamic acid (0.1 g, 0.49 mmol) and the rhodium complex (4.6 mg, 0.005 mmol, 1 mol %) was added methanol (4 mL), and the mixture was stirred under reaction conditions specified in Table 2. After the quoted time, the solution was evaporated to dryness and the conversion was determined by ^{1}H NMR spectroscopy. Depending on the conversion, one of the following procedures was used to remove the catalyst: (A) In the case of 100% conversion the catalyst was removed by extracting the residue with dichloromethane (3 × 0.5 mL). (B) In the case of partial conversion the residue was dissolved in 0.5 M NaOH and extracted with ether (3 × 20 mL). The aqueous phase was acidified with dilute HCl, extracted with ether (3 × 20 mL), and washed with brine. The ethereal phase was dried over $NaSO_4$ and evaporated to dryness.

Asymmetric Hydrosilylation of Acetophenone. To a stirred solution of rhodium complex (8 mg, 0.008 mmol, 1 mol %) and acetophenone (0.1 g 0.83 mmol) in appropriate solvent (1 mL) (see Table 3) was added diphenylsilane (0.16 g, 0.87 mmol). Stirring was continued for the quoted period. To determine the chemical and hydrosilylation yield, a sample was taken and a ^{1}H NMR spectrum was recorded. The reaction mixture was quenched by addition of methanol (0.5 mL) containing 1% of *p*-toluenesulfonic acid. After srirring at room temperature for 30 min the solvents were evaporated in vacuo, and the crude product was purified by column chromatography using diethyl ether−pentane (1:3) as the eluent.

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Supporting Information Available: Full listings of crystallographic data, atomic parameters, atomic coordinates, bond distances, and bond angles for [**5a**][**PF$_6$**] and ^{1}H, ^{31}P, and ^{13}C NMR spectra of compounds [**4bH**][**PF$_6$**], [**4cH**][**PF$_6$**], [**5a**][**PF$_6$**], and [**5b**][**PF$_6$**]. This material is available free of charge via the Internet at http://pubs.acs.org.

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