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Chiral rhodium complexes containing bidentate ligands derived from (*R*,*R*)-1,2-diaminocyclohexane for catalytic enantioselective hydrosilylation of acetophenone

Carmela G. Arena[a,*], Roberto Pattacini[b]

[a] *Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone, 31 Villaggio S. Agata, 98166 Messina, Italy*
[b] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parco Area delle Scienze 17A, 43100 Parma, Italy*

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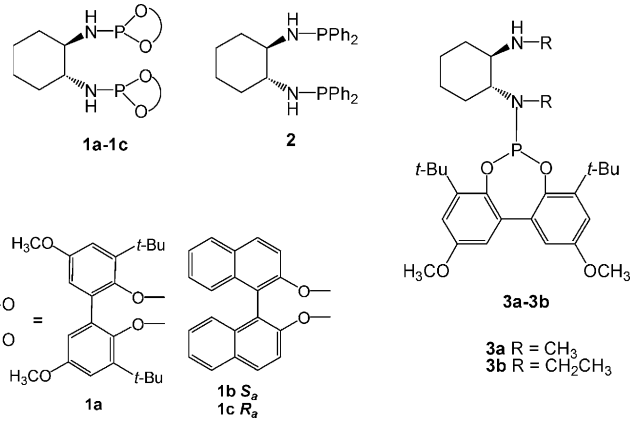
Abstract

Bidentate P,P- and N,P-ligands derived from inexpensive and commercially available chiral source (*R*,*R*)-1,2-diaminocyclohexane, have been tested in the asymmetric Rh-catalyzed addition of diphenylsilane to acetophenone. Studies on the reactivity of these ligands towards the rhodium precursor $[Rh(cod)Cl]_2$ (cod = cycloocta-1,5-diene) have shown that either monomeric, or dinuclear complexes, or both can be found in the solution. The structure of the cationic complex $[Rh(cod)(\mathbf{3a})]PF_6$ (**12**), has been elucidated by X-ray analysis. The presence in the reaction mixture of different rhodium complexes which act as precatalysts, influences the activity and stereoselectivity of the process.

Keywords: Rhodium; P ligands; N,P ligands; Enantioselectivity; Hydrosilylation

1. Introduction

The hydrosilylation of prochiral ketones catalyzed by enantioselective transition metal complexes has become an attractive method for the synthesis of optically active secondary alcohols [1]. In particular, rhodium(I) complexes that contain chiral ligands act as highly active catalysts for a wide variety of aryl alkyl and dialkyl ketones [2]. A large number of homo- or mixed bidentate donor ligands have been screened in Rh-catalyzed addition of silanes to ketones. Many of them yielded promising results in terms of asymmetric induction and catalytic activity [3]. We have recently published a new series of bisphosphoroamidite **1a**–**1c** and amino-phosphoroamidite **3a**–**3b** ligands. They were derived from the economical, commercial chiral source (*R*,*R*)-1,2-diaminocyclohexane. They have been used in the Cu-catalyzed asymmetric conjugate addition of diethylzinc to 2-cyclohexenone [4].



In order to evaluate whether this new series of P,P- and N,P-chiral ligands could be used in other transition-metal

* Corresponding author. Tel.: +39 906765722; fax: +39 90393756.
E-mail address: c.arena@chem.unime.it (C.G. Arena).

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catalyzed enantioselective transformations, we decided to employ the bisphosphororamidite ligand **1a** and the amino-phosphoroamidite ligand **3a** in the Rh-catalyzed hydrosilylation. Moreover, we wondered if the stereoselectivity of the process would be different using the (*R*,*R*)-1,2-bis(diphenylphosphinamino)cyclohexane (**2**). The phenyl groups on the phosphorus atom take a helical conformation in this ligand when it is chelated to a rhodium center [5]. We also decided to investigate the reactivity of these ligands towards the rhodium precursor $[Rh(cod)Cl]_2$ (cod = cycloocta-1,5-diene).

2. Experimental

All syntheses were performed under purified nitrogen using standard Schlenk techniques. Solvents were dried by standard procedures. Unless otherwise indicated, all materials were commercially available and were used without further purification. NMR experiments were carried out using the Bruker AMX R300 spectrometer. ^{1}H NMR spectra were referenced to internal tetramethylsilane and $^{31}P\{^1H\}$ spectra to external 85% H_3PO_4 (δ = 0 ppm). Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano. Gas chromatographic analyses were run on a Fisons GC 8000 Mega series instrument equipped with a J&W β-Dex capillary column (30 m × 0.32 mm i.d., 0.25 μm film).

2.1. *[RhCl(**1a**)]$_2$ (**4**)*

Ligand **1a** (177 mg, 0.2 mmol) was added to a stirred solution of $[Rh(cod)Cl]_2$ (49 mg, 0.1 mmol) in toluene (2 mL). After 20 min, the complex **4** was obtained, as yellow–orange solid, by precipitation with hexane (10 mL). Yield (85%, 192 mg). Anal. Calc. for $C_{50}H_{68}ClN_2O_8P_2Rh$: C, 58.57; H, 6.68; Cl, 3.46; N, 2.73. Found: C, 58.81; H, 6.75; Cl, 3.41; N, 2.46. ^{1}H NMR (C_6D_6): δ = 0.92 (m, 2H, CH_2); 1.25 (m, 4H, CH_2), 1.7 (m, 2H, CH_2) 1.88 (s, 18H, $C(CH_3)_3$), 2.30 (s, 18H, $C(CH_3)_3$), 2.53 (s, 2H, NH), 2.88 (s br, 2H, CH), 3.18 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 6.37 [d, $^4J_{H,H}$ = 3.0 Hz, 2H, CH], 6.78 [d, $^4J_{H,H}$ = 3.0 Hz, 2H, CH], 7.13 [d, $^4J_{H,H}$ = 3.0 Hz, 4H, CH]. ^{31}P NMR (C_6D_6): δ = 145.7 [d, $^1J_{P,Rh}$ = 292 Hz].

2.2. *[Rh(cod)(**2**)]BF$_4$ (**9**)*

Ligand **2** (48.2 mg, 0.1 mmol) was added to a stirred solution of $[Rh(cod)]_2BF_4$ (40.5 mg, 0.1 mmol) in dichloromethane (2 mL). After 10 min, the compound **9** was obtained by precipitation with hexane. Yield (83%, 74 mg). Anal. Calc. for $C_{38}H_{44}BF_4N_2P_2Rh$: C, 58.48; H, 5.68; N, 3.59. Found: C, 58.25; H, 5.77; N, 3.51. ^{1}H NMR ($CDCl_3$): δ = 0.81 (m, 2H, CH_2); 1.25–2.38 (m, 14H, CH_2), 1.71 (m, 2H, CH_2); 2.5 (s br, 2H, NH), 3.29 (s br, 2H, CH), 4.24 (m br, 2H, =CH), 4.85 (m br, 2H, =CH), 6.90–7.80 (m, 20H, CH). ^{31}P NMR ($CDCl_3$): δ = 66.0 [d, $^1J_{P,Rh}$ = 161 Hz].

2.3. *[Rh(cod)(**3a**)]PF$_6$ (**12**)*

Ligand **3a** (106 mg, 0.2 mmol) was added to a stirred solution of $[Rh(cod)Cl]_2$ (49 mg, 0.1 mmol) in toluene (5 mL). The yellow solution was stirred for 30 min, and NH_4PF_6 (42.4 mg, 0.26 mmol) was added. After stirring overnight, the inorganic salts were filtered and the filtrate was reduced (2 mL). Addition of hexane (10 mL) precipitated complex **12** as yellow solid (88%, 156 mg). Anal. Calc. for $C_{38}H_{57}F_6N_2O_4P_2Rh$: C, 51.59; H, 6.49; N, 3.17. Found: C, 51.48; H, 6.54; N, 3.01. ^{1}H NMR (C_6D_6): δ = 1.25 (m, 2H, CH_2); 1.39 (s, 9H, $C(CH_3)_3$), 1.55 (m, 6H, CH_2); 1.67 (s, 9H, $C(CH_3)_3$), 1.80 (m, 4H, CH_2), 2.13 [d, $^3J_{P,H}$ = 7.0 Hz, 3H, CH_3], 2.36 (m, 6H, CH, CH_2), 2.74 (s br, 3H, CH_3), 3.49 (s br, 1H, NH), 3.79 (s, 3H, OCH_3), 3.8 (s, 3H, OCH_3), 4.09 (s br, 1H, =CH), 4.62 (s br, 1H, =CH), 5.32 (s br, 1H, =CH), 5.62 (s br, 1H, =CH), 6.52 [d, $^4J_{H,H}$ = 3.0 Hz, 1H, CH], 6.70 [d, $^4J_{H,H}$ = 3.0 Hz, 1H, CH], 6.95 [d, $^4J_{H,H}$ = 3.0 Hz, 1H, CH], 7.00 [d, $^4J_{H,H}$ = 3.0 Hz, 1H, CH]. ^{31}P NMR (C_6D_6): δ = 129.2 [d, $^1J_{P,Rh}$ = 251 Hz], −141.1 [sept. $^1J_{P,F}$ = 712 Hz, PF_6^-]).

2.4. *General procedure for asymmetric hydrosilylation of acetophenone*

The ligand (0.01 mmol) was added to a solution of $[Rh(cod)Cl]_2$ (0.005 mmol) in toluene (2 mL). After 20 min, acetophenone (1 mmol) and Ph_2SiH_2 (1.1 mmol) were added. The mixture obtained, was then stirred at room temperature for 20 h. The solution was quenched with MeOH (7 mL) and 2.5 M aqueous NaOH (5 mL). The conversions (conv.) and ee values were determined using GC with a J&W β-dex column [3a].

2.5. *X-ray data collection, structure solution and refinement for complex **12***

When a $CHCl_3$ solution of complex **12** underwent slow evaporation, suitable crystals for the X-ray analysis were obtained. The intensity data were collected at room temperature on an AXS Smart 1000 single crystal diffractometer (using a graphite monochromated Mo Kα radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in Table 1. The raw frame data was processed using SAINT and SADABS to yield the reflection data file. The Bruker software was used for the absorption correction [6] (maximum and minimum effective transmission value 1.000 and 0.8477). The structure was solved by direct and Fourier methods and refined by full-matrix least-square procedures (based on F_o^2) (SHELX-97) [7], first with isotropic thermal parameters, and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen. The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms, apart from the hydrogen atom bound to N(1), which was identified and isotropically refined. CCDC

Table 1
Crystal data and structure refinement for complex **12**

Formula	$C_{38}H_{57}F_6N_2O_4P_2Rh$
FW	884.71
Crystal system	Orthorhombic
Space group	*P*212121
a (Å)	10.557(5)
b (Å)	17.406(5)
c (Å)	22.125(5)
V (Å^3)	4066(2)
Z	4
D_{calcd} (g cm^{-3})	1.445
F(0 0 0)	1840
Crystal size	0.19 × 0.15 × 0.23
μ (cm^{-1})	0.567
Reflections collected	23814
Reflections unique	9050 (R_{int} = 0.033)
Observed reflections [$I > 2\sigma(I)$]	5214
Parameters	487
R indices [$I > 2\sigma(I)$]	R_1 = 0.0498, wR_2 = 0.0804
R indices (all data)	R_1 = 0.1148, wR_2 = 0.0944

$$R1 = \sum||F_o| - |F_c||/\sum|F_o|,\ wR_2 = \left[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\right]^{1/2}.$$

reference number 234032 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

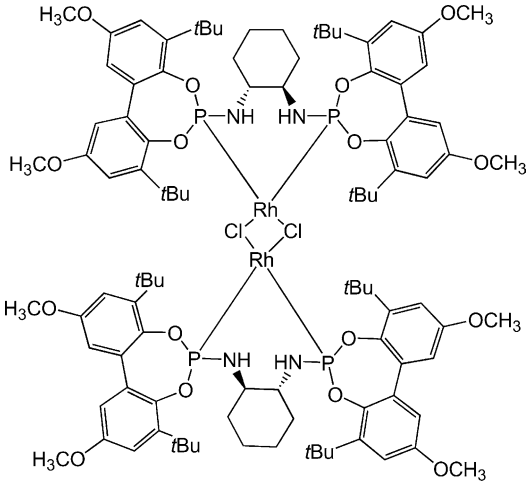
3. Results and discussion

3.1. Coordination studies

Generally, the Rh-catalyst for the enantioselective hydrosilylation of ketones is prepared in situ using L* (chiral bidentate ligand) and $[Rh(cod)Cl]_2$ [2]. However, little information regarding Rh(I)-complexes, which form in solution and act as precatalyst, is available. It is well known that the reaction of $[Rh(cod)Cl]_2$ with bidentate ligands can give both chelating monomeric or bridged dinuclear complexes. This depends on the metal–ligand ratio, steric and electronic factors of the ligand and on the nature of solvent [8].

Hence our interest in studying the chemical behavior of ligands **1a**–**3a** towards the dimeric complex $[Rh(cod)Cl]_2$. We expected a different reactivity among ligands **1a**–**3a** owing to the different electronic nature of donor atoms.

The reaction of bisphosphoroamidite **1a** in toluene, with $[Rh(cod)Cl]_2$ in a 2:1 molar ratio afforded, almost exclusively, the binuclear Cl-bridged complex $[RhCl(\mathbf{1a})]_2$ (**4**). The $^{31}P\{^1H\}$ spectrum (C_6D_6) of the crude solution shows a doublet centered at δ = 145.7 ($^1J_{P,Rh}$ = 292 Hz). This is due to the equivalent phosphorus atoms of the bisphosphoroamidite being chelated to the rhodium center. Very low intensity resonances were also present, but could not be identified. The addition of pyridine to the reaction mixture [9] formed the monomeric complex **5** supporting the assignment of a symmetrical chloro bridged dinuclear structure for complex **4**. The two non-equivalent phosphorus atoms of the compound **5** display two doublets of doublets at δ = 142.0 ($^1J_{P,Rh}$ = 235 Hz; $^2J_{P,Rh,P}$ = 67 Hz) and at δ = 151.8 ($^1J_{P,Rh}$ = 258 Hz; $^2J_{P,Rh,P}$ = 67 Hz) in the $^{31}P\{^1H\}$ spectrum (C_6D_6). Compound **4**, as a yellow–orange air stable powder, was also isolated.



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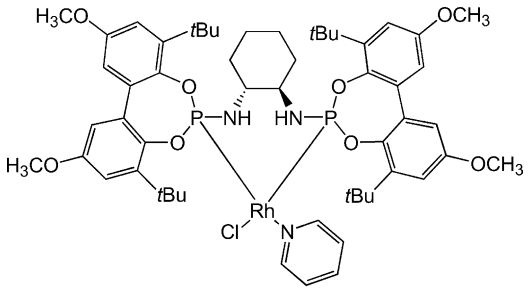

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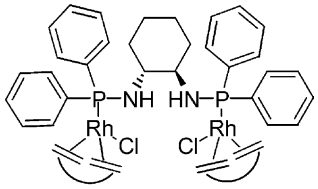
Reaction of **2** [10] with $[Rh(cod)Cl]_2$ in toluene, in a 2:1 molar ratio, afforded three products. The $^{31}P\{^1H\}$ spectrum (C_6D_6) of the mixture featured three doublets at δ = 58.3 ($^1J_{P,Rh}$ = 157 Hz); 63.9 ($^1J_{P,Rh}$ = 159 Hz) and 83.7 ($^1J_{P,Rh}$ = 213 Hz) whose peak areas were in the 1:0.5:0.25 ratio, respectively. Due to probable oxidation products of ligand **2**, additional signals were observed in the range δ = 20–24.5. The doublet at δ = 83.7 was assigned to the chloro-bridged complex $[RhCl(\mathbf{2})]_2$ (**6**), being that the addition of pyridine had led to the formation of the monomeric complex $[Rh(C_6H_5N)Cl(\mathbf{2})]$ (**7**) [δ = 75.0 (dd, $^1J_{P,Rh}$ = 88 Hz; $^2J_{P,R,hP}$ = 56 Hz); δ = 86.5 ($^1J_{P,Rh}$ = 104 Hz; $^2J_{P,Rh,P}$ = 56 Hz)].

In a separate experiment, the addition of $NaBF_4$ to the crude solution allowed us to assign the doublet at δ = 63.9 to the cationic compound $[Rh(cod)(\mathbf{2})]Cl$ (**8**). The sodium salt addition led to the exchange of Cl^- for BF_4^- giving the complex $[Rh(cod)(\mathbf{2})]BF_4$ (**9**) with a doublet at δ = 66 ($^1J_{P,Rh}$ = 161 Hz) in the $^{31}P\{^1H\}$ spectrum ($CDCl_3$), as confirmed

by the analysis of a pure sample of **9** (see Section 2).

Finally, we identified the component at δ = 58.3, as the binuclear complex {[Rh(cod)Cl]$_2$(**2**)} (**10**) in which the two metal atoms are bridged by only one ligand.



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In agreement with this assignment, the reaction of **2** with [Rh(cod)Cl]$_2$, in an equimolar ratio, gave a mixture of complexes **8** and **10** in the 0.2:1 ratio. Moreover, in the ^{1}H NMR spectrum the olefin proton resonances of compounds **10** were observed at δ = 4.30, 4.92, 5.80 and 5.88. Unfortunately, all attempts to obtain **10** as a pure compound were unsuccessful.

Differently from ligands **1a**–**2**, the reaction between the amino-phosphoroamidite ligand **3a** and [Rh(cod)Cl]$_2$ caused exclusively the splitting of the chloro bridge and the formation of the [Rh(cod)(**3a**)]Cl (**11**). The exchange of Cl^- for PF_6^- allowed us to obtain the cationic complex [Rh(cod)(**3a**)]PF_6 (**12**), which displayed a doublet at δ = 129.2 ($^1J_{P,Rh}$ = 251 Hz) in the $^{31}P\{^1H\}$ spectrum (C_6D_6). Slow evaporation of a $CHCl_3$ solution of **12** yielded yellow crystals suitable for X-ray analysis.

A view of the structure of the cation of **12** is shown in Fig. 1, together with the atom numbering system; selected bond distances and angles are given in Table 2. The Rh atom displays a slightly distorted square planar coordination, which involves both the P1 and N1 atoms from the chelating ligand **3a** (Rh1–P1 and Rh1–N1 are 2.236(1) and 2.176(5) Å, respectively) and the M1 and M2 midpoints of the two double bonds of the cod ligand (Rh1–M1 and Rh–M2 are 2.1778(6) and 2.0404(5) Å, respectively). The two phenyl rings of the ligand are not coplanar (the dihedral angle between them is 50.8°(1)), and the C19, C22, C29 and C32 atoms are not collinear (the C10···C22···C32 angle involving non-bonded atoms is 168.4°(2)), probably due to the steric hindrance of the *tert*-butyl groups. The absolute configuration at C9, C14 and N1 is *R*,*R*,*R*.

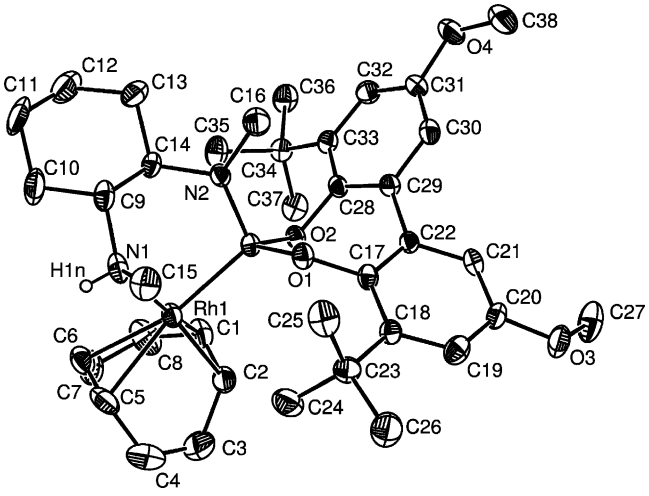


Fig. 1. Ortep view of compound **12** with thermal ellipsoids drawn at the 30% probability level.

Table 2
Selected distances and angles for complex **12**

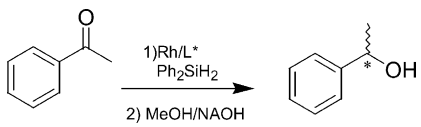
Bond lengths			
Rh1–P1	2.237(2)	P1–O1	1.616(3)
Rh1–N1	2.178(5)	P1–O2	1.638(3)
Rh1–M1	2.1778(6)	P1–N2	1.635(4)
Rh1–M2	2.0404(5)	N1–C9	1.510(8)
Rh1–C1	2.146(5)	N1–C15	1.469(7)
Rh1–C2	2.154(6)	N2–C14	1.491(6)
Rh1–C5	2.274(7)	N2–C16	1.462(6)
Rh1–C6	2.281(6)		
Bond angles			
P1–Rh1–M1	177.95(4)	O1–P1–N2	99.78(2)
P1–Rh1–M2	96.15(4)	O2–P1–N2	111.19(2)
N1–Rh1–M1	91.01(1)	Rh1–N1–C9	117.51(3)
N1–Rh1–M2	175.10(1)	Rh1–N1–C15	111.90(3)
P1–Rh1–N1	87.24(1)	C9–N1–C15	111.84(4)
Rh1–P1–O1	119.48(1)	P1–N2–C14	116.43(3)
Rh1–P1–O2	113.45(1)	P1–N2–C16	125.15(3)
Rh1–P1–N2	109.50(1)	C14–N2–C16	118.41(4)
O1–P1–O2	102.52(2)		

3.2. Rh-catalyzed hydrosilylation of acetophenone

The P,P-**1a**–**2** and N,P-**3a** ligands were screened in the asymmetric Rh-catalyzed addition of Ph_2SiH_2 to acetophenone (Scheme 1). The results are summarized in Table 3.

Using preformed dimeric rhodium complex [RhCl(**1a**)]$_2$ (**4**) the conversion reached 99% and (*S*)-1-phenylethanol was obtained in 16% ee value (entry 1). The catalytic system [Rh(cod)Cl]$_2$/**1a** gave the same enantiomeric excess value with a slight decrease in the conversion (entry 2). Probably, the presence of by-products in the reaction mixture, as the $^{31}P\{^1H\}$ NMR spectral monitoring revealed (see coordination studies), reduces the activity of the catalyst. [Rh(cod)$_2$]BF_4/**1a** system afforded poorer results (58% conv., 8% ee, entry 3).

Although the catalytic precursor containing ligand **2** gave a higher ee value (25% entry 5 versus 16% entry 1) than [Rh(cod)Cl]$_2$/**1a** system and an inversion in the absolute configuration of the 1-phenylethanol (*R* versus *S*), the conversion was rather low (48%). Vigorous hydrogen evolution was observed during the addition of diphenylsilane and consider-



Scheme 1.

Table 3
Asymmetric hydrosilylation of acetophenone

Entry	L	Rh-complex	Solvent	T (°C)	Conv. (%)[a]	ee (%)[a]
1	**1a**	$[Rh(Cl)(\mathbf{1})]_2$	Toluene	25	99	16 (*S*)
2	**1a**	$[Rh(cod)Cl]_2$	Toluene	25	94	16 (*S*)
3	**1a**	$[Rh(cod)_2]BF_4$	Toluene	25	58	8 (*S*)
4	**1a**	$[Rh(Cl)(\mathbf{1})]_2$	Toluene	0	30	8 (*S*)
5	**2**	$[Rh(cod)Cl]_2$	Toluene	25	48	25 (*R*)
6	**2**	$[Rh(cod)Cl]_2$	Toluene	0	18	5 (*R*)
7	**2**	$[Rh(cod)_2]BF_4$	CH_2Cl_2	25	30	15 (*R*)
8	**3a**	$[Rh(cod)Cl]_2$	Toluene	25	40	0
9	**3a**	$[Rh(cod)_2]BF_4$	CH_2Cl_2	25	50	0
10	**3a**	$[Rh(cod)_2]BF_4$	THF	25	73	0

Reaction conditions: acetophenone (1 mmol), Ph_2SiH_2 (1 mmol), L/Rh = 1, [cat] = 1 mol%, t = 20 h.
[a] Percentage conversions and enantiomeric excesses determined by GC (β-Dex column).

able amounts of silylenol ether $Ph_2HSiOC(Ph)=CH_2$ were detected in the ^1H NMR spectrum. This indicates that silylation of the enol of acetophenone becomes a prominent drawback when employing $[Rh(cod)Cl]_2$/**2** as precatalyst [1].

When the temperature is lowered, hydrogen evolution is reduced, however a decrease in the reaction rate and enantioselectivity was also observed (entry 6).

The catalytic system $[Rh(cod)_2]BF_4$/**2**, was tested in CH_2Cl_2 owing to its low solubility in toluene. The cationic $[Rh(cod)(\mathbf{2})]BF_4$ species formed in solution (as evidenced by the presence of a doublet in the $^{31}P\{^1H\}$ NMR spectrum) displayed a lower performance being that the conv. and ee values were respectively, 30% and 15% (entry 7).

As observed with ligand **1a**, the rhodium cationic complex $[Rh(cod)_2]BF_4$ is also less efficient with the P,P-**2** ligand. The chloride ligand is apparently required for a better activity in active species. Unfortunately, investigations carried out on both the actual reaction mixture and the mixture after catalytic reaction, did not provide useful information about the species present in the solution.

Although many Rh-catalyzed hydrosilylations give a better performance at lower temperatures, the yield and the ee value of 1-phenylethanol dropped dramatically when the Rh/L (L = **1**–**2**) systems were tested at 0 °C [11].

The $[Rh(cod)Cl]_2$/**3a** system showed moderate catalytic activity in the hydrosilylation of acetophenone, but was not stereoselective (entry 8). In this case no hydrogen evolution was observed, and no silylenol was detected in the ^1H NMR spectrum. The reaction between $[Rh(cod)Cl]_2$ and the N,P-**3** ligand afforded the cationic complex $[Rh(cod)(\mathbf{3a})]Cl$ (**11**), as its only product (see above). Thus, we expected similar results when using the catalytic system $[Rh(cod)_2]BF_4$/**3a**. Experiments were conducted in CH_2Cl_2 or THF, owing to the poor solubility of the complex in toluene. As was expected, no asymmetric induction was obtained and the catalytic activity was depended on the solvent employed (entry 9 versus 10). When the temperature was lowered to 0 °C, no influence on enantioselectivity was noticed.

4. Conclusions

We tested P,P-**1a**–**2**, and N,P-**3a**, ligands derived from the economical, commercial chiral source (*R*,*R*)-1,2-diaminocyclohexane, in the asymmetric Rh-catalyzed addition of diphenylsilane to acetophenone. Studies of the reactions of **1a**–**3a** with $[Rh(cod)Cl]_2$ displayed that either monomeric or dinuclear complexes, or both can be found in the solution.

The $[Rh(cod)Cl]_2$/**1a** system and the $[RhCl(\mathbf{1})]_2$ complex showed good catalytic activity (from 94 to 99%) however low enantiomeric excess value was obtained (16%). The lower catalytic activity of the $[Rh(cod)Cl]_2$/**1a** system is probably due to the presence of unidentified Rh-ligand species in solution.

With the catalytic system $[Rh(cod)Cl]_2$/**2** an improvement in the asymmetric induction was observed (25% versus 16%) together with an inversion in the absolute configuration of the 1-phenylethanol (*R* versus *S*), but the conversion was only 48%. The low activity is due to the formation of the by-product silylenol ether $Ph_2SiOC(Ph)=CH_2$. The activity and the stereoselectivity of the process is probably unfavorably influenced by the presence in the solution of three different rhodium complexes acting as precatalysts.

Although many chiral nitrogen–phosphorus ligands/Rh systems have provide secondary alcohols with good-to-excellent selectivity [2,3a,3d] the $[Rh(cod)Cl]_2$/**3a** system, in which only the cationic precatalyst **11** forms in solution, was not stereoselective. Unfortunately, the mechanism and the configuration-determining step for the Rh-catalyzed asymmetric hydrosilylation are not yet well defined [12]. This precludes any rational interpretation of this result.

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