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Cationic rhodium(I)-diolefin complexes containing an optically active C_2-symmetric bis(sulfoximine) ligand: Synthesis and catalytic activity

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Abstract

A series of cationic rhodium(I) complexes [Rh(diene)(N^N)][BF_4] (diene = 1,5-cyclooctadiene (cod), norbornadiene (nbd), tetrafluorobenzobarralene (tfb)), containing the optically pure bis(sulfoximine) ligand 1,2-bis(*S*-methyl-*S*-phenylsulfonimidoyl)benzene, have been synthesized and fully characterized. The structure of the *R,R* enantiomer of the ligand, and that of its cyclooctadiene-Rh(I) complex, were confirmed by means of single-crystal X-ray diffraction techniques. Studies on the catalytic activity of these complexes in acetophenone hydrosilylation and dimethyl itaconate hydrogenation are also reported.

Keywords: Rhodium complexes; Sulfoximine ligands; Hydrogenation; Hydrosilylation; X-ray molecular structures

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1. Introduction

Sulfoximines, the monoaza analogues of sulfones discovered by H. R. Bentley and co-workers in 1950s [1], are nowadays recognized as versatile reagents in synthetic organic chemistry [2]. In particular, enantiopure derivatives are widely employed as chiral auxiliaries in the stoichiometric preparation of a diverse range of optically active compounds [2]. Recent works, mainly from C. Bolm´s group, have also demonstrated the utility of sulfoximines in asymmetric catalysis [3-4]. In this context, several *N,N*- [5], *N,O*- [6] and *N,P*-donor [7] ligands containing chiral sulfoximidoyl cores have been designed and successfully applied in different enantioselective metal-catalyzed transformations. Among them, C_2-symmetric bis(sulfoximine) derivatives of type **A**-**C** (see Figure 1) proved to be highly effective ligands in asymmetric copper-catalyzed Diels-Alder reactions [5a,d,e,j,l] and palladium-catalyzed allylic alkylation processes [5b,c], affording products with excellent enantiomeric excesses.

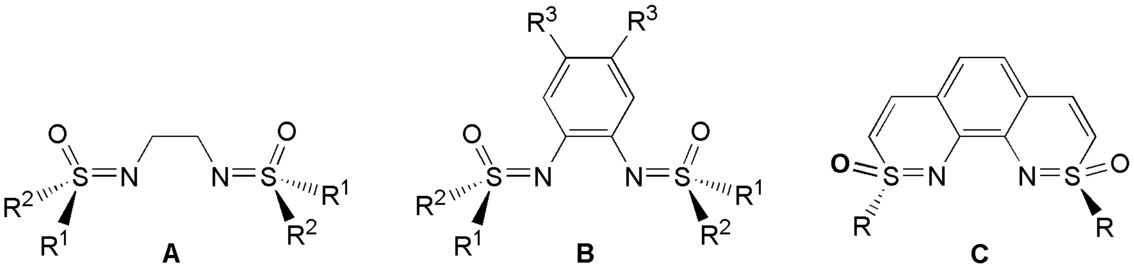


Fig. 1. Generic structures of the C_2-symmetric bis(sulfoximine) ligands used in asymmetric catalysis.

Surprisingly, despite the privileged C_2-symmetry of these ligands which enables their potential use in further catalytic transformations [8], efforts devoted to develop their coordination chemistry have been scarce. In fact, in most of the catalytic studies mentioned above the corresponding metal-complexes were not isolated, the only information presently available on the coordination features of these ligands being restricted to some spectroscopic measurements on Cu(II) derivatives generated *in situ* from **B** [5e,l], and the isolated and X-ray structurally characterized complexes **D** [6f] and **E** [9] (see Figure 2). In all cases the expected *N*-coordination of the sulfoximine units to the metal was observed [10]. We note that, while involvement in catalysis of **E** has not been described, **D** is able to promote the catalytic oxidation of sulfides with cumyl hydroperoxide, giving sulfoxides in very good yields, albeit as racemates [6f].

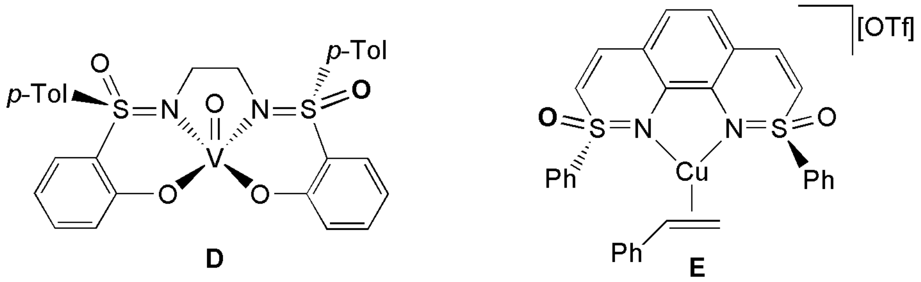
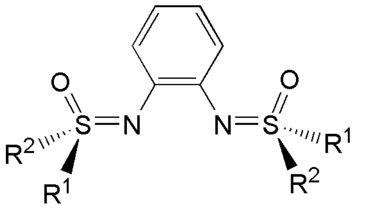


Fig. 2. The only isolated metal-complexes containing chiral C_2-symmetric bis(sulfoximine) ligands.

As a contribution to filling this gap, we decided to explore the suitability of these C_2-symmetric bis(sulfoximines) to act as chelating ligands for rhodium. In particular, using enantiopure 1,2-bis(*S*-methyl-*S*-phenylsulfonimidoyl)benzene **1** in both its (*S*,*S*) and (*R*,*R*) forms as model (see Figure 3), a series of cationic rhodium(I)-diolefin complexes have been synthesized and tested as catalysts in ketone-hydrosilylation and olefin-hydrogenation reactions. Results from this study are presented herein. At this point, we must note that, to the best of our knowledge, no sulfoximine-rhodium complexes have been described to date in the literature [11].



R^1 = Me; R^2 = Ph **[(*S*,*S*)-1]**
R^1 = Ph; R^2 = Me **[(*R*,*R*)-1]**

Fig. 3. The C_2-symmetric bis(sulfoximine) ligand employed in this work.

2. Experimental

2.1. General information

All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of (*R*)-*S*-methyl-*S*-phenylsulfoximine [12], the ligand **(*S*,*S*)-1** [5a], and complexes $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (**2a**) [13], $[\{Rh(\mu\text{-}Cl)(nbd)\}_2]$ (**2b**) [14] and $[\{Rh(\mu\text{-}Cl)(tfb)\}_2]$ (**2c**) [15], which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Optical rotations (α) at 20 ºC at the sodium D-line were measured in a Perkin-Elmer 343 polarimeter. Gas chromatographic measurements were made on a Hewlett-Packard HP6890 equipment using a Supelco Beta-Dex^{TM} 120 (30 m, 250 µm) or a Gamma-Dex^{TM} 225 (30 m, 250 µm) column. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), 282.4 MHz (^{19}F), or 75.4 MHz (^{13}C) using $SiMe_4$ or $CFCl_3$ as standards. DEPT experiments have been carried out for all the compounds reported.

*2.2. Preparation of (R,R)-1,2-bis(S-methyl-S-phenylsulfonimidoyl)benzene (**(R,R)-1**)*

Compound **(*R*,*R*)-1**, isolated as a white solid in 64% yield, was synthetized from 1,2-dibromobenzene and (*R*)-*S*-methyl-*S*-phenylsulfoximine following strictly the same method described by Bolm and Simić for the preparation of its enantiomer **(*S*,*S*)-1** [5a]. Anal. Calcd for $C_{20}H_{20}N_2O_2S_2$ (384.52 g mol^{-1}): C, 62.47; H, 5.24; N, 7.29. Found: C, 62.51; H, 5.19; N, 7.33%; $[\alpha]^{20}_D$ = 170.4º (*c* = 0.001 M in $CHCl_3$).

*2.3. Preparation of complexes [Rh(diene){κ^2(N,N)-**(S,S)-1**}][BF$_4$] (diene = 1,5-cyclooctadiene (**[Rh(cod)(S,S)-1][BF$_4$]**), norbornadiene (**[Rh(nbd)(S,S)-1][BF$_4$]**), tetrafluorobenzobarralene (**[Rh(tfb)(S,S)-1][BF$_4$]**)*

A solution of the appropriate [{Rh(μ-Cl)(diene)}$_2$] dimer **2a-c** (0.4 mmol) in acetone (20 mL) was treated, at room temperature and in the absence of light, with $AgBF_4$ (0.163 g, 0.84 mmol) for 1 h. The AgCl formed was then filtered off (over Kieselgühr) and the resulting solution evaporated to dryness to afford a yellow oily residue. A solution of **(*S*,*S*)-1** (0.308 g, 0.8 mmol) in dichloromethane (20 mL) was then added and the mixture stirred at room temperature overnight. The resulting solution was then filtered over Kieselgühr, the filtrate evaporated to dryness, and the yellow solid residue washed with diethyl ether (3 x 20 mL) and dried in vacuo. **[Rh(cod)(*S*,*S*)-1][BF$_4$]:** Yield: 77% (0.420 g); Anal. Calcd for $RhC_{28}H_{32}F_4N_2O_2S_2B$ (682.42 g mol^{-1}): C, 49.28; H, 4.73; N, 4.11. Found: C, 49.41; H, 4.72; N, 4.02%; Conductivity (acetone, 20°C) 113 Ω^{-1} cm^2 mol^{-1}; $[\alpha]^{20}_D$ = -46.7º (*c* = 0.001 M in $CHCl_3$). IR (KBr) ν = 3553 (m), 3097 (m), 3061 (m), 3019 (m), 2925 (m), 2881 (m), 2835 (m), 1997 (w), 1918 (w), 1830 (w), 1623 (w), 1581 (m), 1478 (s), 1448 (s), 1432 (m), 1405 (m), 1284 (s), 1222 (s), 1066 (s), 1010 (s), 957 (s), 872 (m), 812 (s), 755 (s), 687 (s), 626 (m), 565 (m), 536 (s), 522 (s), 498 (s), 463 (m); ^{1}H NMR (CD_2Cl_2) δ = 1.38, 1.51, 1.90 and 2.17 (m, 2H each, CH_2), 3.35 and 3.99 (br, 2H each, =CH), 3.58 (s, 6H, CH_3), 6.83 (m, 4H, CH_{arom}), 7.68-8.68 (m, 10H, CH_{arom}) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 33.0 and 34.0 (s, CH_2), 42.6 (s, CH_3), 78.4 and 79.1 (d, $^1J_{CRh}$ = 13.5 Hz, =CH), 121.0, 124.8, 128.2, 129.4 and 134.9 (s, CH_{arom}), 138.5 and 141.0 (s, C_{arom}) ppm. **[Rh(nbd)(*S,S*)-1][BF$_4$]:** Yield: 89% (0.474 g); Anal. Calcd for $RhC_{27}H_{28}F_4N_2O_2S_2B$ (666.37 g mol^{-1}): C, 48.67; H, 4.24; N, 4.20. Found: C, 48.55; H, 4.31; N, 4.10%; Conductivity (acetone, 20°C) 98 Ω^{-1} cm^2 mol^{-1}; $[\alpha]^{20}_D$ = -124.0º (c = 0.001 M in $CHCl_3$). IR (KBr) ν = 3547 (m), 3017 (m), 2941 (s), 2862 (s), 2803 (m), 2017 (w), 1617 (w), 1581 (m), 1490 (s), 1447 (s), 1405 (m), 1371 (m), 1307 (m), 1222 (s), 1089 (s), 1058 (s), 1007 (s), 993 (s), 812 (m), 747 (m), 685 (m), 621 (w), 562 (w), 534 (m), 520 (s); ^{1}H NMR (CD_2Cl_2) δ = 1.00 (s, 2H, CH_2), 2.89 (br, 2H, CH), 3.43 and 3.83 (br, 2H each, =CH), 3.66 (s, 6H, CH_3), 6.74 and 6.94 (m, 2H each, CH_{arom}), 7.85 (m, 6H, CH_{arom}), 8.42 (m, 4H, CH_{arom}) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 43.7 (br, CH), 50.7 (s, CH_3), 54.2 and 54.6 (d, $^1J_{CRh}$ = 10.8 Hz, =CH), 62.0 (d, $^3J_{CRh}$ = 7.7 Hz, CH_2), 122.5, 125.2, 129.3, 130.5 and 136.0 (s, CH_{arom}), 136.8 and 140.8 (s, C_{arom}) ppm. **[Rh(tfb)(*S,S*)-1][BF$_4$]:** Yield: 90% (0.575 g); Anal. Calcd for $RhC_{32}H_{26}F_8N_2O_2S_2B$ (799.52 g mol^{-1}): C, 48.07; H, 3.28; N, 3.50. Found: C, 48.12; H, 3.31; N, 3.49%; Conductivity (acetone, 20°C) 115 Ω^{-1} cm^2 mol^{-1}; $[\alpha]^{20}_D$ = -97.3º (c = 0.001 M in $CHCl_3$). IR (KBr) ν = 3619 (m), 3545 (m), 3063 (m), 3027 (m), 2931 (m), 1706 (w), 1635 (w), 1581 (w), 1498 (s), 1448 (m), 1406 (w), 1376 (m), 1320 (w), 1303 (m), 1224 (s), 1122 (s), 1091 (s), 1039 (s), 1007 (s), 999 (s), 948 (m), 893 (m), 855 (m), 815 (m), 753 (s), 686 (m), 629 (w), 535 (m), 521 (m); $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ = -159.8 and -147.2 (d, 2F each, $^3J_{FF}$ = 21.7 Hz, CF_{arom}), -150.8 (s, BF_4^-); ^{1}H NMR (CD_2Cl_2) δ = 2.59 and 3.23 (dd, 2H each, $^3J_{HH}$ = 5.9 and 5.9 Hz, =CH), 3.63 (s, 6H, CH_3), 5.18 (t, 2H, $^3J_{HH}$ = 5.9 Hz, CH), 7.05 and 7.21 (d, 2H each, $^3J_{HH}$ = 3.2 Hz, CH_{arom}), 7.91 (m, 6H, CH_{arom}), 8.46 (m, 4H, CH_{arom}) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 40.6 and 40.7 (d, $^2J_{CRh}$ = 3.7 Hz, CH), 43.9 (s, CH_3), 55.2 and 55.4 (d, $^1J_{CRh}$ = 11.1 Hz, =CH), 123.1, 125.9, 129.5, 131.1 and 136.7 (s, CH_{arom}), 137.2, 141.3 and 142.0 (s, C_{arom}), 138.0 (d, $^1J_{CF}$ = 213.5 Hz, CF), 145.3 (d, $^1J_{CF}$ = 219.1 Hz, CF) ppm.

*2.4. Preparation of complexes [Rh(diene){κ^2(N,N)-**(R,R)-1**}][BF$_4$] (diene = 1,5-cyclooctadiene (**[Rh(cod)(R,R)-1][BF$_4$]**), norbornadiene (**[Rh(nbd)(R,R)-1][BF$_4$]**), tetrafluorobenzobarralene (**[Rh(tfb)(R,R)-1][BF$_4$]**)*

These complexes, isolated as air-stable yellow solids, were prepared through the same procedure starting from the appropriate [{Rh(μ-Cl)(diene)}$_2$] dimer **2a-c** (0.4 mmol) and the optically pure ligand **(*R,R*)-1** (0.308 g, 0.8 mmol). The IR and NMR data obtained were identical to those of their (*S,S*)-enantiomers. **[Rh(cod)(*R,R*)-1][BF$_4$]:** Yield 74% (0.403 g); Anal. Calcd for $RhC_{28}H_{32}F_4N_2O_2S_2B$ (682.42 g mol^{-1}): C, 49.28; H, 4.73; N, 4.11. Found: C, 49.47; H, 4.75; N, 3.97%; Conductivity (acetone, 20°C) 111 Ω^{-1} cm^2 mol^{-1}; $[\alpha]^{20}_D$ = 46.9º (*c* = 0.001 M in $CHCl_3$). **[Rh(nbd)(*R,R*)-1][BF$_4$]:** Yield 91% (0.485 g); $RhC_{27}H_{28}F_4N_2O_2S_2B$ (666.37 g mol^{-1}): C, 48.67; H, 4.24; N, 4.20. Found: C, 48.45; H, 4.37; N, 4.07%; Conductivity (acetone, 20°C) 102 Ω^{-1} cm^2 mol^{-1}; $[\alpha]^{20}_D$ = 123.8º (*c* = 0.001 M in $CHCl_3$). **[Rh(tfb)(*R,R*)-1][BF$_4$]:** Yield 84% (0.537 g); Anal. Calcd for $RhC_{32}H_{26}F_8N_2O_2S_2B$ (799.52 g mol^{-1}): C, 48.07; H, 3.28; N, 3.50. Found: C, 48.16; H, 3.35; N, 3.52%; Conductivity (acetone, 20°C) 116 Ω^{-1} cm^2 mol^{-1}; $[\alpha]^{20}_D$ = 97.2° (*c* = 0.001 M in $CHCl_3$).

2.5. General procedure for the catalytic hydrosilylation of acetophenone

To a solution of acetophenone (0.14 g, 1.2 mmol) and the corresponding rhodium(I) complex (0.012 mmol, 1 mol%) in THF (2.5 mL) a solution of Ph_2SiH_2 (0.25 g, 1.3 mmol) in THF (2.5 mL) was added dropwise under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h and then evaporated to dryness. The degree of conversion was determined by ^{1}H NMR analysis. The resulting residue was dissolved in CH_2Cl_2 and treated with aqueous HCl (2 M, 3 mL) for 2 h, followed by neutralisation with $NaHCO_3$ and dilution with CH_2Cl_2 (10 mL). The organic phase was then separated, the aqueous layer extracted with CH_2Cl_2 (3 x 15 mL), and the combined organic fractions collected and dried over $MgSO_4$. Purification of the resulting 1-phenylethanol from Rh and Si impurities was accomplished by Kugelröhr distillation. The enantiomeric composition of the product was finally determined by chiral GC.

2.6. General procedure for the catalytic hydrogenation of dimethyl itaconate

In a glovebox, a Fischer-Porter reactor (80 mL) was charged with a solution of dimethyl itaconate (0.23 g, 1.45 mmol) and the corresponding rhodium(I) complex (0.003 mmol, 0.2 mol%) in CH_2Cl_2 (4 mL). The vessel was brought outside the glovebox, submitted to four vacuum-hydrogen cycles, and finally pressurized to 4 atm. The reaction mixture was stirred at room temperature for 24 h. Then, the reactor was depressurized, the mixture evaporated to dryness, redissolved in an ethyl acetate-hexane

(1:1) mixture, and passed through a short pad of silica. The resulting residue was analyzed by ^{1}H NMR to determine conversion and by chiral GC for enantiomeric excess.

2.7. X-ray crystallography

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into saturated solutions of **(*R*,*R*)-1** and **[Rh(cod)(*R*,*R*)-1][BF$_4$]** in acetone. The most relevant crystal and refinement data are collected in Table 1. Diffraction data were recorded on a Nonius Kappa CCD single-crystal diffractometer using Cu-Kα radiation with the crystal-to-detector distance fixed at 29 mm, using the oscillation method, with 2° oscillation and 40 s exposure time per frame. The data collection strategy was calculated with the program Collect [16]. Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack [17]. Absorption correction was applied by means of XABS2 [18].

The software package WINGX was used for space group determination, structure solution and refinement [19]. The structures were solved by Patterson interpretation and phase expansion using DIRDIF [20]. Isotropic least-squares refinement on F^2 using SHELXL97 was performed [21]. During the final stages of the refinements, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined (except F atoms of the counteranion in **[Rh(cod)(*R*,*R*)-1][BF$_4$]**; these disordered atoms were located by difference maps and isotropically refined). The H-atoms were geometrically located and their coordinates were refined riding on their parent atoms. The function minimized was $[\Sigma w(F_o^2 - F_c^2)/ \Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (\mathrm{a}P)^2 + \mathrm{b}P]$ (a = 0.0472 and b = 0.4108 for **(*R*,*R*)-1**, and a = 0.0692 and b = 1.1217 for **[Rh(cod)(*R*,*R*)-1][BF$_4$]**) with $\sigma(F_o^2)$ from counting statistics and $P = (\mathrm{Max}\ (F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [22]. Geometrical calculations were made with PARST [23]. The crystallographic plots were made with PLATON [24].

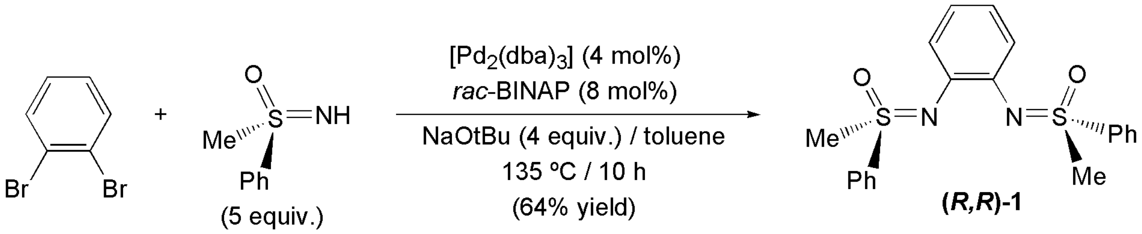
Table 1. Crystal data and structure refinement for **(*R*,*R*)-1** and **[Rh(cod)(*R*,*R*)-1][BF$_4$]**.

	(*R*,*R*)-1	**[Rh(cod)(*R*,*R*)-1][BF$_4$]**
Empirical formula	$C_{20}H_{20}N_2O_2S_2$	$RhC_{28}H_{32}F_4N_2O_2S_2B$
Formula weight	384.50	682.40
Temperature (K)	200(2)	293(2)
Wavelength (Å)	1.5418	1.5418
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit cell dimensions		
a (Å)	7.3744(2)	9.8455(1)
b (Å)	10.4101(3)	19.5481(3)
c (Å)	24.4433(5)	15.1618(2)
α (°)	90	90
β (°)	90	92.924(1)
γ (°)	90	90
Volume (Å^3)	1876.47(8)	2914.25(7)
Z	4	4
Calculated density (g cm^{-3})	1.361	1.555
Absorption coefficient (mm^{-1})	2.708	6.556
F(000)	808	1392
Crystal size (mm)	0.30 x 0.23 x 0.03	0.2 x 0.175 x 0.1
Theta range for data collection (°)	3.62 - 69.65	2.92 - 69.59
Index ranges	$-8 \le h \le 8$	$-11 \le h \le 11$
	$-12 \le k \le 12$	$-23 \le k \le 23$
	$-29 \le l \le 29$	$-18 \le l \le 18$
Reflections collected	27800	105096
Independent reflections	3512 [*R*(int) = 0.0039]	10907 [*R*(int) = 0.0081]
Completeness to theta max.	99.9%	99.8%
Absorption correction	Empirical (XABS2)	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3512/0/237	10907/0/723
Goodness-of-fit on F^2	1.036	1.049
R1[a] $[I > 2\sigma(I)]$	0.0296	0.0392
wR2[a] $[I > 2\sigma(I)]$	0.0760	0.0989
R1 (all data)	0.0305	0.0409
wR2 (all data)	0.0768	0.1006
Absolute structure parameter	-0.003(13)	0.004(6)
Largest difference peak/hole (eÅ^{-3})	0.526 and -0.635	0.926 and -0.641

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$.

3. Results and discussion

The optically pure bis(sulfoximine) ligand (*S*,*S*)-1,2-bis(*S*-methyl-*S*-phenylsulfonimidoyl)benzene [**(*S*,*S*)-1**] was synthesized following the method described by C. Bolm and O. Simić [5a], *i.e.* through a Pd-catalyzed bis-amination of 1,2-dibromobenzene with excess of (*S*)-*S*-methyl-*S*-phenylsulfoximine. Using the same approach, we also succeeded in the preparation of its enantiomer **(*R*,*R*)-1** from (*R*)-*S*-methyl-*S*-phenylsulfoximine (Scheme 1).



Scheme 1. Preparation of the C_2-symmetric bis(sulfoximine) ligand **(*R*,*R*)-1**.

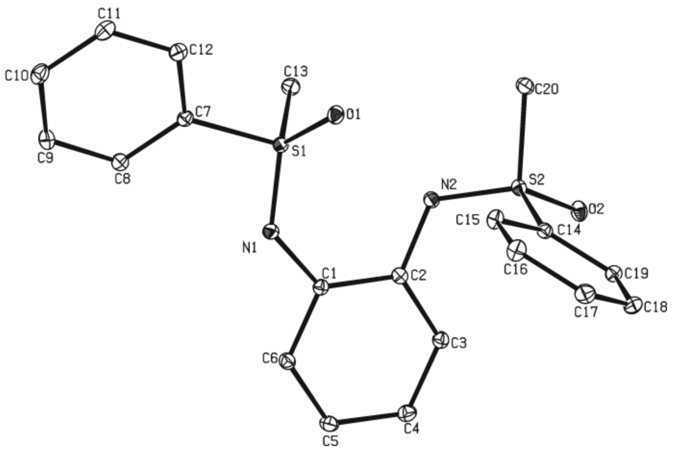
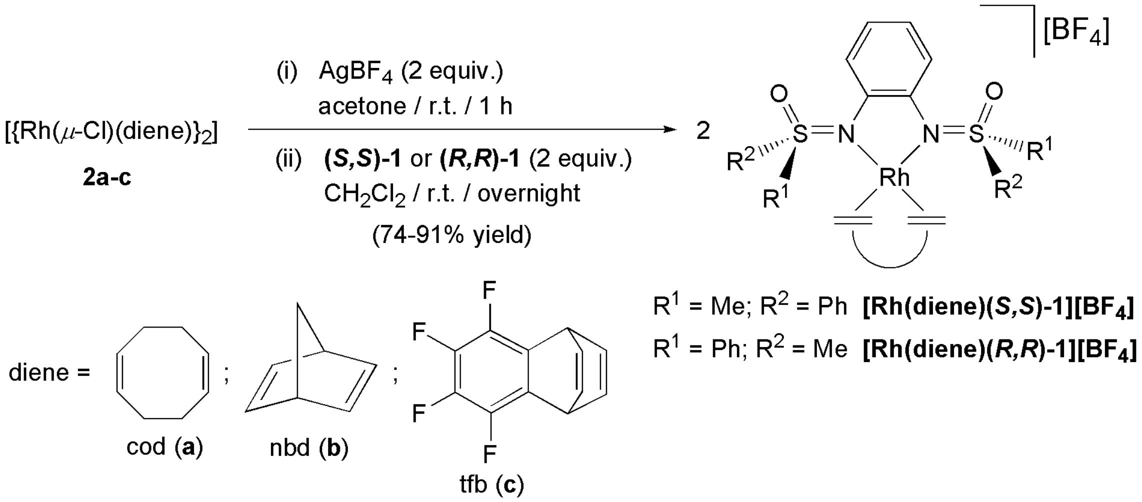


Fig. 4. ORTEP-type view of the structure of the bis(sulfoximine) ligand **(*R*,*R*)-1** showing the crystallographic labelling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): C(1)-C(2) = 1.410(3); C(1)-N(1) = 1.412(2); N(1)-S(1) = 1.5143(16); S(1)-O(1) = 1.4474(12); S(1)-C(7) = 1.7811(18); S(1)-C(13) = 1.777(2); C(2)-N(2) = 1.409(2); N(2)-S(2) = 1.5346(15); S(2)-O(2) = 1.4541(13); S(2)-C(14) = 1.7816(19); S(2)-C(20) = 1.758(2); C(1)-N(1)-S(1) = 132.01(13); N(1)-S(1)-O(1) = 122.84(9); N(1)-S(1)-C(7) = 101.83(9); N(1)-S(1)-C(13) = 113.55(9); O(1)-S(1)-C(7) = 106.68(8); O(1)-S(1)-C(13) = 107.26(9); C(7)-S(1)-C(13) = 102.35(9); N(1)-C(1)-C(2) = 126.78(17); C(1)-C(2)-N(2) = 118.04(16); C(2)-N(2)-S(2) = 120.81(13); N(2)-S(2)-O(2) = 121.42(8); N(2)-S(2)-C(14) = 110.63(9); N(2)-S(2)-C(20) = 102.76(9); O(2)-S(2)-C(14) = 106.73(9); O(2)-S(2)-C(20) = 109.48(9); C(14)-S(2)-C(20) = 104.60(9).

As expected, compound **(*R,R*)-1**, isolated as a white solid in 64% yield, presented identical spectroscopic features (^{1}H and ^{13}C{^{1}H} NMR and IR) to those described by Bolm and Simić for **(*S,S*)-1**. In addition, its identity was unequivocally confirmed by means of X-ray diffraction methods. Single-crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a saturated solution of this compound in acetone. An ORTEP plot of the molecule is shown in Figure 4; selected bond distances and angles are listed in the caption. Bond angles at the sulfur atoms (101.83(9)-122.84(9)°) revealed the stereogenic centers to be in a distorted tetrahedral environment, the S-N (1.5143(16) and 1.5346(15) Å) and S-O (1.4474(12) and 1.4541(13) Å) bond lengths observed lying within the expected range for S=N and S=O double bonds [25]. All these structural features compare well with those previously described in the literature for uncoordinated sulfoximine units [2h]. Slight deviation of the nitrogen atoms N(1) and N(2) from the main aromatic plane was also observed as indicated by the N(1)-C(1)-C(2)-N(2) torsion angle (-6.1(3)°).

Reactions of the acetone-rhodium solvates [Rh(diene)(acetone)$_2$][BF$_4$], generated *in situ* by treatment of the readily available dimers [{Rh(μ-Cl)(diene)}$_2$] (diene = cod (**2a**), nbd (**2b**), tfb (**2c**)) with silver tetrafluoroborate in acetone [26], with **(*S,S*)-1** or **(*R,R*)-1**, in dichloromethane at room temperature, resulted in the high-yield formation (74-91%) of the novel cationic rhodium(I)-diolefin derivatives **[Rh(diene)(*S,S*)-1][BF$_4$]** and **[Rh(diene)(*R,R*)-1][BF$_4$]**, respectively (diene = cod, nbd, tfb), *via* displacement of the coordinated acetone molecules and the selective κ^2(*N,N*)-bidentate coordination of the bis(sulfoximine) ligand to the metal (Scheme 2) [27].



Scheme 2. Preparation of the cationic rhodium(I) complexes **[Rh(diene)(*S,S*)-1][BF$_4$]** and **[Rh(diene)(*R,R*)-1][BF$_4$]**.

Complexes **[Rh(diene)(*S,S*)-1][BF$_4$]** and **[Rh(diene)(*R,R*)-1][BF$_4$]**, isolated as air-stable yellow solids, are soluble in polar solvents, such as acetone, dichloromethane, chloroform and THF, and insoluble in *n*-alkanes and diethyl ether. The formulation proposed for these species is based on analytical data, conductance measurements (1:1 electrolytes; Λ_M = 98-116 Ω^{-1} cm$^2\cdot$mol^{-1}) as well as IR and multinuclear NMR (^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H}) spectroscopy, their NMR spectra showing in all cases the expected resonances for the corresponding diolefin and $\kappa^2(N,N)$-coordinated bis(sulfoximine) ligand (details are given in the Experimental section). Specific optical rotations were also determined and confirmed the enantiopurity of the compounds synthesized.

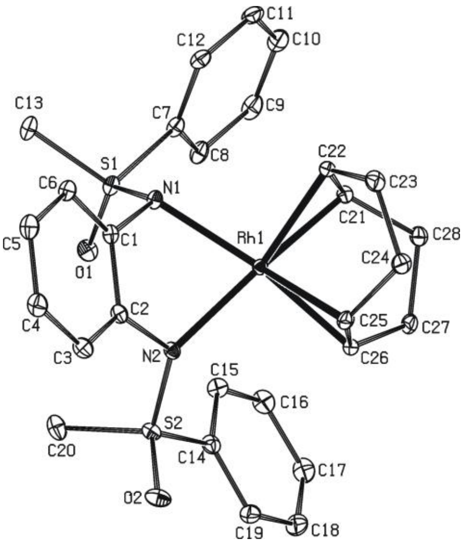
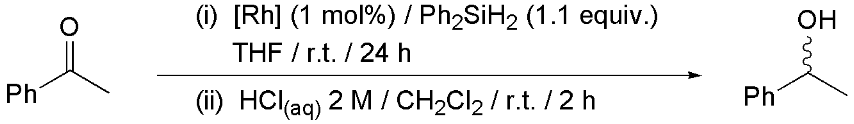


Fig. 5. ORTEP-type view of the structure of complex **[Rh(cod)(*R,R*)-1][BF$_4$]** showing the crystallographic labelling scheme. Tetrafluoroborate anion and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): Rh-N(1) = 2.176(3); Rh-N(2) = 2.131(3); Rh-C* = 2.0011(7); Rh-C** = 2.002(2); C(1)-C(2) = 1.412(6); C(1)-N(1) = 1.440(5); N(1)-S(1) = 1.570(3); S(1)-O(1) = 1.456(3); S(1)-C(7) = 1.766(4); S(1)-C(13) = 1.774(5); C(2)-N(2) = 1.430(5); N(2)-S(2) = 1.565(4); S(2)-O(2) = 1.442(4); S(2)-C(14) = 1.762(5); S(2)-C(20) = 1.763(5); N(1)-Rh-N(2) = 76.75(14); N(1)-Rh-C* = 98.67(15); N(1)-Rh-C** = 165.6(3); N(2)-Rh-C* = 175.0(2); N(2)-Rh-C** = 96.70(10); C*-Rh-C** = 87.32(8); C(1)-N(1)-S(1) = 116.3(3); N(1)-S(1)-O(1) = 119.9(2); N(1)-S(1)-C(7) = 103.16(19); N(1)-S(1)-C(13) = 109.5(2); O(1)-S(1)-C(7) = 109.9(2); O(1)-S(1)-C(13) = 107.8(2); C(7)-S(1)-C(13) = 105.8(2); N(1)-C(1)-C(2) = 117.4(4); C(1)-C(2)-N(2) = 114.8(4); C(2)-N(2)-S(2) = 118.9(3); N(2)-S(2)-O(2) = 119.3(2); N(2)-S(2)-C(14) = 105.71(19); N(2)-S(2)-C(20) = 107.9(2); O(2)-S(2)-C(14) = 109.0(2); O(2)-S(2)-C(20) = 108.5(3); C(14)-S(2)-C(20) = 105.6(2). C* and C** centres of mass of the C=C double bonds of the 1,5-cyclooctadiene ligand (C(21), C(22) and C(25), C(26), respectively).

Moreover, the structure of the cyclooctadiene derivative **[(*R*,*R*)-3a][BF$_4$]** could be unequivocally confirmed by means of X-ray diffraction methods. As in the precedent case, single-crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a saturated solution of the complex in acetone. Two crystallographically independent molecules were found in the asymmetric unit. An ORTEP-type view of one of these molecules, along with selected structural parameters, is shown in Figure 5 (the other does not differ significantly, *i.e.* bond distances ±0.01 Å and bond angles ±1º). The sum of the angles around Rh, formed by the coordinated bis(sulfoximine) nitrogen atoms (N(1) and N(2)) and the centres of mass of the olefinic units (C* and C**) (359.4 º), is in complete accord with the expected square planar geometry about the rhodium center. The observed Rh-to-cod ligand distances and angles fall also within the expected range for this type of compounds [28]. Concerning the bis(sulfoximine) ligand skeleton, its coordination to rhodium is reflected in the elongation of the C-N and N-S bond distances (*ca.* 0.03 and 0.04 Å, respectively) as compared to the structure of the free ligand **(*R*,*R*)-1**, the Rh-N(1) (2.176(3) Å) and Rh-N(2) (2.131(3) Å) bond lengths observed being typical for Rh(I)-N(sp^2) bonds [29]. Unlike the free ligand, the nitrogen atoms N(1) and N(2) lie now exactly within the aromatic plane (N(1)-C(1)-C(2)-N(2) torsion angle = 0.3(5)º). However, we must note that in the second molecule a similar value to that found in **(R,R)-1** was observed (-5.5(6)º).

The transition metal-catalyzed asymmetric hydrosilylation of ketones, followed by hydrolysis of the resulting silyl ethers, provides a useful route to optically active alcohols [30]. Based on the known effectiveness of Rh(I) catalysts with chiral C_2-symmetric *N*,*N*-donor ligands [31], we decided to explore the behaviour of the bis(sulfoximine)-rhodium complexes synthesized in this catalytic transformation. As shown in Table 2, we found that the reactions of acetophenone with diphenylsilane in the presence of complexes **[Rh(diene)(*R*,*R*)-1][BF$_4$]** (1 mol%) for 24 hours at room temperature afford, after the hydrolysis step, the desired 1-phenylethanol in high yields (71-99%) but, in all cases, in complete racemic form (entries 1-3). Similar results were obtained employing directly catalytic systems consisting of 1:2 mixtures of the dimeric precursors [{Rh(μ-Cl)(diene)}$_2$] (diene = cod (**2a**), nbd (**2b**), tfb (**2c**)) and the enantiopure ligand **(*R*,*R*)-1** (1 mol% of Rh; entries 4-6). It is well documented that the enantioselectivity of the hydrosilylation reactions with complexes containing *N*-donor ligands can be enhanced by the use of ligand excess [31]. However, in our case such a benefical effect was not observed, reactions performed with **[Rh(nbd)(*R*,*R*)-1][BF$_4$]** (1 mol%) in the presence of 2 and 4 mol% of **(*R*,*R*)-1** resulting also in the formation of 1-phenylethanol as a racemate (entries 7-8).

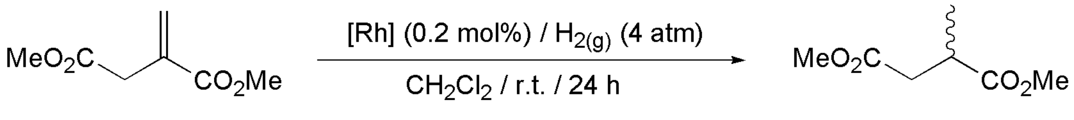
Table 2. Rh-catalyzed hydrosilylation of acetophenone.[a]



Entry	Catalyst	Yield (%)[b]	*ee* (%)[c]
1	**[Rh(cod)(*R*,*R*)-1][BF$_4$]**	71	0
2	**[Rh(nbd)(*R*,*R*)-1][BF$_4$]**	99	0
3	**[Rh(tfb)(*R*,*R*)-1][BF$_4$]**	99	0
4	**2a** (0.5 mol%) / **(*R*,*R*)-1** (1.1 mol%)	99	0
5	**2b** (0.5 mol%) / **(*R*,*R*)-1** (1.1 mol%)	95	0
6	**2c** (0.5 mol%) / **(*R*,*R*)-1** (1.1 mol%)	99	0
7	**[Rh(nbd)(*R*,*R*)-1][BF$_4$]**[d]	99	0
8	**[Rh(nbd)(*R*,*R*)-1][BF$_4$]**[e]	99	0

[a] Reactions were carried out at room temperature in THF (5 mL), under a dry nitrogen atmosphere, using 1.2 mmol of acetophenone and 1.3 mmol of Ph_2SiH_2. [b] Determined by ^1H NMR. [c] Determined by chiral GC. [d] Reaction performed in the presence of 2 mol% of **(*R*,*R*)-1**. [d] Reaction performed in the presence of 4 mol% of **(*R*,*R*)-1**.

Table 3. Rh-catalyzed hydrogenation of dimethyl itaconate.[a]



Entry	Catalyst	Yield (%)[b]	*ee* (%)[c]
1	**[Rh(cod)(*R*,*R*)-1][BF$_4$]**	79	0
2	**[Rh(nbd)(*R*,*R*)-1][BF$_4$]**	94	0
3	**[Rh(tfb)(*R*,*R*)-1][BF$_4$]**	91	0
7	**[Rh(nbd)(*R*,*R*)-1][BF$_4$]**[d]	92	0
8	**[Rh(nbd)(*R*,*R*)-1][BF$_4$]**[e]	90	0

[a] Reactions were carried out at room temperature in CH_2Cl_2 (4 mL) using 1.45 mmol of dimethyl itaconate. [b] Determined by ^{1}H NMR. [c] Determined by chiral GC. [d] Reaction performed in the presence of 0.5 mol% of **(*R*,*R*)-1**. [d] Reaction performed in the presence of 1 mol% of **(*R*,*R*)-1**.

As shown in Table 3, the same disappointing results in terms of enantioselectivity were also observed when complexes **[Rh(diene)(*R*,*R*)-1][BF$_4$]** (0.2 mol%) were used as catalysts for the C=C hydrogenation of the functionalized olefin dimethyl itaconate. In all cases racemic 2-methyl-succinic acid dimethyl ester was formed. Analysis of the crude reaction mixtures by ^{1}H NMR spectroscopy showed in all cases the presence of free **(*R*,*R*)-1**. This fact, along with absence of chiral induction observed, strongly suggests that the bis(sulfoximine) ligand does not remain coordinated to rhodium during the catalytic event.

4. Conclusion

In summary, in this work a series of enantiopure cationic rhodium(I)-diolefin complexes, containing the C_2-symmetric bis(sulfoximine) ligand 1,2-bis(*S*-methyl-*S*-phenylsulfonimidoyl)benzene, have been synthesized and fully characterized. These compounds represent the first examples of isolated sulfoximine-rhodium complexes described to date in the literature [11]. Unfortunately, their use in catalytic asymmetric ketone-hydrosilylation and olefin-hydrogenation reactions only afforded disappointing results.

Appendix A. Supplementary data

CCDC 784405 and CCDC 784406 contain the supplementary crystallographic data for **(*R*,*R*)-1** and **[Rh(cod)(*R*,*R*)-1][BF$_4$]**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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FOR GRAPHICAL ABSTRACT USE ONLY

Cationic rhodium(I)-diolefin complexes containing an optically active C_2-symmetric bis(sulfoximine) ligand: Synthesis and catalytic activity

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Coordination of the (*S*,*S*)- and (*R*,*R*)-enantiomers of the C_2-symmetric bis(sulfoximine) ligand 1,2-bis(*S*-methyl-*S*-phenylsulfonimidoyl)benzene to cationic rhodium(I)-diolefin fragments is described. The catalytic activity of the resulting complexes in hydrosilylation and hydrogenation reactions is also discussed.