Synthesis and Crystal Structure of a Unique and Homochiral *N,S*-Bonded *N,N′*-Bis(*tert*-butanesulfinyl)amidinate Rhodium(I) Complex

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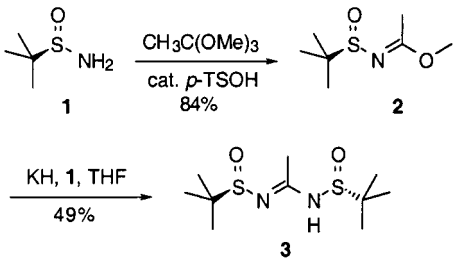
Introduction

Chiral ligands containing both nitrogen and sulfur have recently received considerable attention in asymmetric catalysis.[1] A number of mixed *N,S*-donor ligands and their corresponding complexes have been reported, including 2-pyridinethiazolidines,[2] thioamides,[3] and thioureas.[4] All existing chiral variants of these ligands depend on the chirality about the appended α-carbon centers. A few examples of chirality on sulfur have been reported for alternative ligand scaffolds as exemplified by the neutral sulfoximido cap structure reported by Bolm and Süss-Fink[5] and the *β*-amino sulfoxide ligand reported by Pettinari and co-workers.[6]

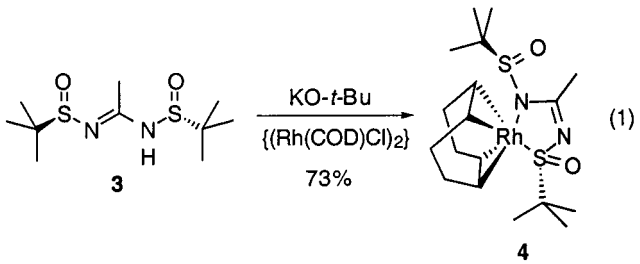
Chiral sulfinamide-containing scaffolds have attractive features as ligands for metal complexation.[7−9] These chiral sulfur moieties have the potential to bind through nitrogen,[7] sulfur, or oxygen[9] to form a number of uniquely bonded motifs. Additionally, they are both structurally and optically stable, and can be rapidly assembled from simple building blocks.[10] Herein, we report a novel homochiral *N,N′*-bis(*tert*-butanesulfinyl)-amidine ligand **3** and its complexation with rhodium(I) to afford a structurally unique nitrogen- and sulfur-bonded organometallic complex **4**. This is the first reported anionic and homochiral *N,S*-bonded bis(sulfinyl)amidinate complex involving any transition metal center. Furthermore, to our knowledge, structure **4** represents the first example of a complex involving any sulfinamide moiety with rhodium(I).

Scheme 1. Synthesis of Ligand **3**



Results and Discussion

The reaction of (*R*)-*tert*-butanesulfinamide[11] **1** with trimethyl orthoacetate leads to a single isomer of the condensation product **2** (Scheme 1). This compound was then used to acylate the potassium salt of a second equivalent of (*R*)-*tert*-butanesulfinamide to afford the *N,N′*-bis(sulfinyl)amidine ligand **3**. This novel pseudo-C_2-symmetric ligand can be isolated in good yield by an aqueous extraction followed by precipitation from hexanes and diethyl ether to afford an analytically pure white powder. After stirring 2 equiv of the potassium salt of **3** with 1 equiv of $(Rh(COD)Cl)_2$, we isolated a fluorescent orange powder as a precipitate, and subsequent trituration in boiling



(1)

hexanes affords the rhodium(I) complex **4** as a single product as observed by ^{1}H NMR spectroscopy (eq 1). The isolated complex is air stable and soluble in most organic solvents. The slow layering of diethyl ether into toluene solutions of **4** affords single crystals suitable for X-ray structure determinations. The molecular structure, including atom labeling, is shown in Figure 1.

Crystallographic Studies. Complex **4** crystallizes in the acentric orthorhombic space group $P2_12_12_1$. The rhodium atom is coordinated by a COD ligand and a *N,N′*-bis(*tert*-butanesulfinyl)amidinate ligand, which is bonded to the rhodium center via a nitrogen (N(2)) and a sulfur atom (S(1)) to form a five-membered heterocyclic metallocycle. Interestingly, the two *tert*-butyl substituents of the metal complex of ligand **3** are both situated on one face of the complex, while the sulfinyl oxygen atoms are positioned in the opposite direction.

An additional and interesting structural feature is the considerable *trans* influence revealed in the rhodium−COD sp^2 carbon bonds. The bonds positioned *trans* to the nitrogen (N(2)) are slightly shorter (2.110(3) and 2.139(3) Å) than those positioned *trans* to the sulfur (2.200(3) and 2.255(4) Å).

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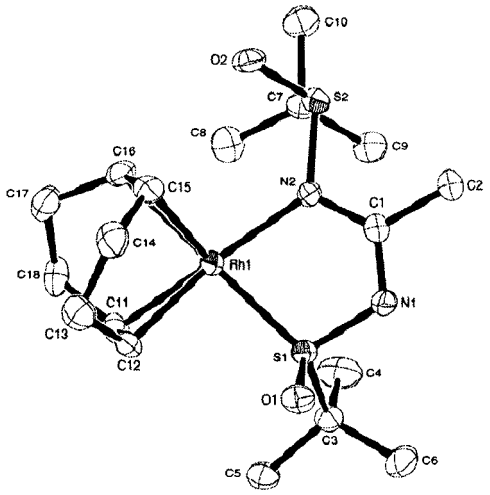

Figure 1. ORTEP drawing of **4** showing the atom labeling scheme. Thermal ellipsoids are shown at 50% probability.

Table 1. Crystallographic Data of the Rh Complex **4**[a]

chem formula $RhS_2O_2N_2C_{18}H_{33}$	fw 476.50
$a = 9.7213(1)$ Å	space group $P2_12_12_1$
$b = 10.9246(2)$ Å	$T = -99$ °C
$c = 19.3747(4)$ Å	$\lambda = 0.71073$ Å
$V = 2057.62(6)$ Å^3	$\rho_{calcd} = 1.54$ g/cm^3
$Z = 4$	$R(F),a = 0.020$
μ(Mo Kα) = 10.45 cm^{-1}	$Rw,b = 0.021$

[a] $R = \Sigma m||F_o| - |F_c||/\Sigma|F_o|$. $Rw = \{[\Sigma w|F_o| - |F_c)^2]/[\Sigma w(F_o^2)]\}^{1/2}$.

Furthermore, the two shortest Rh−C bonds (Rh−C(11), Rh−C(15)) lie on opposite sides of the rhodium coordination plane. The geometry of the metal center is square planar with respect to the coordinating diene, and the C−Rh−C angles above (C(16)−Rh−C(15) = 36.1(1)°) and below (C(11)−Rh−C(12) = 37.6(1)°) the plane of the rhodium(I) center are nearly equal. Finally, the remaining bond lengths and angles in the molecule are apparently normal.

NMR Studies. A single complex is observed by NMR spectroscopy when **4** is dissolved in $CDCl_3$. The ^{1}H NMR of the complex shows four distinct COD alkene proton resonances at 6.68, 6.27, 4.52, and 4.36 ppm. The former two resonances are shifted downfield considerably relative to the remaining COD alkene protons, presumably a result of the *trans* influence from the coordinating nitrogen. Additionally, two distinct *tert*-butyl resonances are observed in the form of broad singlets at 1.20 and 1.27 ppm. In the ^{13}C spectrum, the COD alkene resonances are present between 107.4 and 74.9 ppm, and each resonance has a distinct Rh−C coupling constant. The ^{13}C NMR spectra also reveal the lack of symmetry in the complex by the presence of four distinct COD methylene resonances, as well as two distinct *tert*-butyl peaks at 23.4 and 23.3 ppm.

Experimental Section

General Procedures. The organic solvents were dried by standard procedures. Unless otherwise noted, all reagents were obtained from commercial suppliers and used with no further purification. IR spectra were taken as thin films by dropping a solution of the compound in CH_2Cl_2 on a salt plate and allowing the solvent to evaporate off (only partial data are reported). For all NMR spectra, the samples were dissolved in $CDCl_3$ and chemical shifts are reported in parts per million downfield from an internal solvent peak. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Synthesis of Methyl *N*-[(*R*)-(1,1-Dimethylethyl)sulfinyl]ethanimidate[9] (2). To a 25 mL round-bottom flask charged with 1.55 g of *tert*-butanesulfinamide[11] (12.8 mmol) were added 12.0 mL of trimethyl orthoacetate (94.0 mmol) and 10 mg of *p*-toluenesulfonic acid monohydrate (0.005 mmol). A water-cooled reflux condenser was then attached to the reaction flask, and the mixture was brought to reflux. The solution was stirred for 3 h after which time the reaction was determined to be complete by TLC (neat EtOAc). The volatile material was removed in vacuo, and the crude oil was purified by chromatography (1:1 hexanes:EtOAc) to afford 1.90 g of the title compound in 84% yield: $[\alpha]^{23}_D$ −131° (*c* 1.0, $CHCl_3$); IR 1620, 1281, 1081 cm^{-1}; ^{1}H NMR (300 MHz) δ 3.76 (s, 3H), 2.29 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (75 MHz) δ 174.4, 56.0, 54.2, 22.0, 19.0. Anal. Calcd for $C_7H_{15}NO_2S$: C, 47.42; H, 8.53; N, 7.90. Found: C, 47.46; H, 8.68; N, 7.98.

Synthesis of *N*,*N*′-Bis[(*R*)-1,1-dimethylethyl)sulfinyl]ethanimidamide (3). A flame-dried 250 mL three-neck flask equipped with a 250 mL addition funnel and a stir bar was charged with 3.5 g of KH (35 wt % in mineral oil, 31 mmol, 3 equiv) and 26 mL of THF, and the suspension was cooled to 0 °C in an ice bath. To the stirred suspension was added 1.24 g (10.2 mmol, 1 equiv) of *tert*-butanesulfinamide in portions, and the mixture was allowed to stand until the evolution of gas had ceased (ca. 45 min). After this time, 1.80 g (10.8 mmol) of *tert*-butanesulfinylimidate **2** in 26 mL of THF was added dropwise. After the mixture was stirred and allowed to cool for 2−3 h, the reaction was quenched with 1 M $NaHSO_4$ and the THF was evaporated on a rotary evaporator. The residue was taken up in EtOAc, washed with 1 M $NaHSO_4$, dried over $MgSO_4$, and filtered. Evaporation of the solvents afforded a yellow solid, which was dissolved in Et_2O and precipitated by the addition of hexanes to afford 1.33 g of the title product as a pure white solid (49%): $[\alpha]^{23}_D$ −578° (*c* 1.0, $CHCl_3$); IR 3124 (br), 1605, 1579, 1456, 1093 cm^{-1}; ^{1}H NMR (500 MHz) δ 10.46 (s, 1H), 2.30 (s, 3H), 1.28 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (125 MHz) δ 163.2, 58.5, 57.1, 22.7, 22.2, 22.1. Anal. Calcd for $C_{10}H_{22}N_2O_2S_2$: C, 45.08; H, 8.32; N, 10.51. Found: C, 45.06; H, 8.62; N, 10.39.

Synthesis of [(1,2,5,6-η)-1,5-Cyclooctadiene] {*N*-[(*R*)-(1,1-Dimethylethyl)sulfinyl]-*N*′-[(*R*)-(1,1-dimethylethyl)sulfinyl-κS]ethanimidamidato-κN}rhodium (4). To a 50 mL round-bottom flask was added a suspension of 73.0 mg of 95% KO-*t*-Bu (1.2 equiv, 0.62 mmol) in 5 mL of toluene. After the suspension was cooled to 0 °C, 138 mg of bis(sulfinyl)imidamide **3** (0.520 mmol, 1 equiv) in 5 mL of toluene was added with stirring. The suspension was stirred for an additional 90 min under nitrogen. After this time, the reaction solution was warmed to room temperature, and 127 mg (0.260 mmol, 0.5 equiv) of Rh(COD)-Cl_2 was added as a solid. The suspension immediately turned bright

Table 2. Selected Interatomic Distances for Rhodium Complex **4** Determined from X-ray Single-Crystal Structural Data

atoms	*d*, (Å)	atoms	*d*, (Å)
Rh(1)−S(1)	2.2676	S(1)−C(3)	1.8490
Rh(1)−N(2)	2.1096	S(2)−O(2)	1.4838
Rh(1)−C(11)	2.1391	S(2)−N(2)	1.7008
Rh(1)−C(12)	2.1718	S(2)−C(7)	1.8553
Rh(1)−C(15)	2.2000	N(1)−C(1)	1.3169
Rh(1)−C(16)	2.2549	N(2)−C(1)	1.3582
S(1)−O(1)	1.4791	C(1)−C(2)	1.5085
S(1)−N(1)	1.6581		

Table 3. Selected Bond Angles for Rhodium Complex **4**

atoms	angle (deg)	atoms	angle (deg)
S(1)−Rh(1)−N(2)	79.7191	Rh(1)−N(2)−C(1)	115.8209
Rh(1)−S(1)−O(1)	114.5474	S(2)−N(2)−C(1)	115.4316
Rh(1)−S(1)−N(1)	104.3833	N(1)−C(1)−N(2)	123.8753
Rh(1)−S(1)−C(3)	122.1717	N(1)−C(1)−C(2)	113.7048
O(1)−S(1)−N(1)	107.6763	N(2)−C(1)−C(2)	122.4199
O(1)−S(1)−C(3)	105.8441	S(1)−C(3)−C(4)	108.0558
N(1)−S(1)−C(3)	100.5094	S(1)−C(3)−C(5)	106.8548
O(2)−S(2)−N(2)	108.0535	S(1)−C(3)−C(6)	108.1015
O(2)−S(2)−C(7)	106.4947	S(2)−C(7)−C(8)	1131.5709
N(2)−S(2)−C(7)	101.5342	S(2)−C(7)−C(9)	107.0786
S(1)−N(1)−C(1)	115.3276	S(2)−C(7)−C(10)	103.7155
Rh(1)−N(2)−S(2)	128.7315		

orange. After the suspension was stirred for 8 h, approximately 8 mL of hexanes was added via syringe, and the suspension was cooled to 0 °C. After 20 min at 0 °C, the mixture was quickly filtered to remove the KCl as a yellow crust. The filtrate was evaporated to dryness to afford a deep red powder, which was subsequently triturated with boiling hexanes and filtered (twice) to provide 177 mg (0.375 mmol) of a bright orange powder in 73% yield. NMR analysis revealed the presence of the title compound as a single product: $[\alpha]^{23}_{D}$ −168° (*c* 1.0, $CHCl_3$); IR 1485, 1313, 1108, 1080 cm^{-1}; ^1H NMR (300 MHz) δ 6.68 (s, 1H), 6.27 (s, 1H), 4.52 (s, 1H), 4.36 (s, 1H), 2.60−2.53 (m, 1H), 2.45−2.38 (m, 1H), 2.32 (s, 3H), 2.32−2.30 (m, 1H), 2.20−2.05 (m, 3H), 1.93−1.87 (m, 1H), 1.82−1.76 (m, 1H), 1.27 (s, 9H), 1.20 (s, 9H); ^{13}C NMR (125 MHz) δ 177.0, 107.4 (J_{RHC} = 8.75 Hz), 95.7 (J_{RHC} = 7.5 Hz), 86.3 (J_{RHC} = 15 Hz), 74.9 (J_{RHC} = 11.2 Hz), 64.4, 59.3, 32.9, 31.7, 28.8, 27.5, 23.4, 23.3, 21.2.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of [(1,2,5,6-η)-1,5-COD]{*N*-[(*R*)-NS(O)*t*Bu]-*N*′-[(*R*)-(NS(O)*t*Bu-κS]ethanimidamidato-κN}-rhodium complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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