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Optically Active Transition Metal Complexes 111.[1] Synthesis and Structure of a new thioamidato rhodium(I) complex

Henri Brunner * [a], Jürgen Bügler [a] and Bernhard Nuber [b]

a) Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

b) Institut für Anorganische Chemie, Universität Heidelberg, D-69120 Heidelberg, Germany

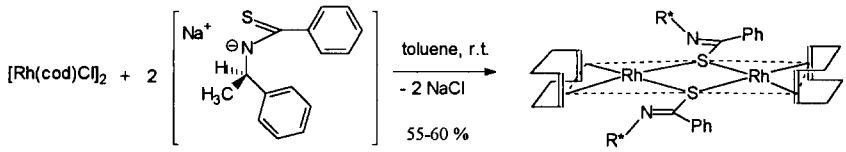
Abstract: The reaction of $[Rh(cod)Cl]_2$ with deprotonated N-[(*R*)-1-phenylethyl]thiobenzamide affords the new complex **1**. In the solid state **1** exists as a binuclear complex with the two sulfur atoms of two thioamidato ligands bridging the Rh atoms. The molecular structure of **1** was determined by X-ray analysis: $C_{46}H_{52}N_2S_2Rh_2$, monoclinic, space group C2, a = 10.564(4), b = 16.864(5), c = 23.548(7), β = 95.05(3)°, Z = 2 × 2, R = 0.046, R_w = 0.039. Complex **1** equilibrates with an isomer in solution at room temperature.

Chiral ligands containing nitrogen and sulfur donor atoms have received considerable attention in asymmetric synthesis,[2] e.g., the 2-pyridinylthiazolidines.[3,4] We examined other optically active N,S ligands, in particular thioamides. Although a number of rhodium complexes with N,S-donors has been reported,[5-8] there are no publications on rhodium(I) compounds dealing with the complexation of thioamides either in their neutral or in their anionic, deprotonated form. Herein we describe the preparation and the structure of a binuclear rhodium(I) complex with a deprotonated, bridging, chirally N-substituted thiobenzamide ligand.

After removal of the amide proton the thiobenzamide moiety can act as anionic monodentate or bidentate chelating or bridging ligand. The structurally similar carboxylato ligands give binuclear rhodium(I) complexes with bridging μ-κ^2O,O' carboxylato groups,[9,10] whereas the pyridine-2-carboxamidato ligand occupies two coordination positions in mononuclear rhodium(I) complexes in pyridine-N/amide-N chelation.[1] A binuclear rhodium(I) complex with the ligand pyridine-2-thiolate was published recently.[11] In this compound the pyridine-2-thiolate systeme acts both as monodentate and as bidentate ligand.

Results and discussion

The proton of N-[(*R*)-1-phenylethyl]thiobenzamide can be conveniently abstracted by the addition of excess NaH to its solution in an anhydrous dichloromethane/THF mixture to give a yellow solution of the sodium salt. Excess NaH is filtered off and the solution is reacted with $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) in toluene at room temperature (Scheme 1). Recrystallisation of the crude reaction product affords the orange, air-stable, crystalline compound **1**.



1 (R* = (*R*)-1-phenylethyl)

Scheme 1.

Well-formed crystals of **1** suitable for X-ray analysis were obtained from toluene/n-pentane at room temperature.[12] Surprisingly, the structure of **1** consists of binuclear molecules with two monodentate, bridging thiobenzamidato ligands. The remaining coordination sites are occupied by cod. A view of the structure with the atomic labelling is depicted in Figure 1. Selected bond distances and angles are given below.

The complex crystallises in the monoclinic system (space group C2) with 2 × 2 almost identical molecules in the unit cell. The individual molecules possess a C_2 axis perpendicular to the Rh1-Rh1a axis and the S1-S1a axis. The main difference of the two molecules in the unit cell is the orientation of the phenyl ring of the thiobenzamide (C7-C12) relative to the plane of the thiobenzamide moiety (S1-C13-N1). The angle between these two planes in the two independent molecules is 32.4° and 22.4°, respectively. The metals are not directly bonded to one another (Rh1-Rh1a = 3.52⊕). The coordination plane is folded along the S1-S1a vector (dihedral angle 142.9°). The structurally related complex $[Rh_2(CO)_2(\mu\text{-}SPh)_2(cod)]$ exhibits a value of 135° for

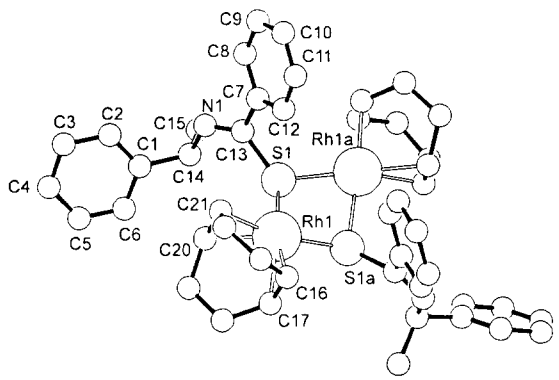


Figure 1: Molecular structure of **1** in the solid state. H atoms are left out. Selected bond distances (⊕) and angles (°): Rh1-S1, 2.370(2); Rh1-S1a, 2.360(2); Rh1-C16, 2.130(8); Rh1-C17, 2.135(8); Rh1-C20, 2.098(8); Rh1-C21, 2.111(8); S1-C13, 1.825(8); C13-N1, 1.254(9); C16-C17, 1.364(12); C20-C21, 1.357(14); S1-Rh1-S1a, 76.3(1); Rh1-S1-Rh1a, 96.4(1); C16-Rh1-C21, 82.8(3); C17-Rh1-C20, 82.1(3); N1-C13-S1, 122.2(6).

this angle.[13] The substituents at the S atoms adopt a *syn* orientation (roof-up) when viewing along the Rh1-Rh1a axis.

The coordination geometry about the rhodium atoms is planar. The S1-Rh1-S1a-angle of 76.3(1)° departs markedly from square plane geometry. Similar angles (78.7° and 78.9°) were found in a (cod)(pyridine-2-carboxamidato)rhodium(I)[1] and a (cod)(pyrrol-2-carbaldiminato)rhodium(I)[14] complex. The C16-Rh1-C21 and C17-Rh1-C20 angles are in accord with those observed for (cod)(carboxylato)rhodium(I) complexes.[9,10] The cod ligands exhibit their characteristic tub conformation and the distance of rhodium to the midpoint of the coordinated double bond is with a mean value of 2.01⊕ in the usual range of dimeric rhodium(I) cod complexes.[15-17]

The Rh1-S1-Rh1a-angle of 96.4(1)° differs from the angle found in the rhodium(I) complex of the bridging, monodentate pyridine-2-thiolato ligand (80.5°).[11] The values for the bond lengths C13-N1 (1.254(9)⊕) and C13-S1 (1.825(8)⊕) reveal that the C13-N1 bond possesses more and the C13-S1 bond less double bond character compared to an uncoordinated thiobenzamide (C-N ≈ 1.32⊕, C-S ≈ 1.71⊕).[18]

The IR-spectrum (KBr) of **1** does not show the ν(N-H) band that is observed at 2310 cm^{-1} for N-[(*R*)-1-phenylethyl]thiobenzamide, proofing the deprotonation of the thioamide ligands. The thioamide band for the free thioamide appears at 1505 cm^{-1}, whereas **1** exhibits this absorption at 1569 cm^{-1}. This is in agreement with the shorter bond length of the C-N bond in the complex compared to the free thioamide.

Surprisingly, the ^1H NMR spectrum of **1** in $CDCl_3$ at -20°C shows an extraordinarily downfield shifted doublet for two protons at 9.03 ppm. This signal was assigned by a NOESY experiment to the two protons in ortho position at the thiobenzamide phenyl ring (H8, H12). The two signals for the olefinic protons of the cod ligand appear at 3.67 and 3.49-3.43 ppm. Similar complexes of rhodium(I) show these signals between 4.3 and 4.0 ppm.[15-17]

When warming up to room temperature the ^1H NMR spectrum of the solution of **1** in $CDCl_3$ contains the additional signals of an isomer of complex **1**. The ^1H NMR spectrum of this isomer was obtained by a subtraction procedure. In contrast to complex **1** the aromatic protons of its isomer appear in the usual range (δ = 7.45-7.20 ppm). There are four separate signals for both the methylidene (δ = 5.21, 4.43, 4.28, 3.38 ppm) and the methylene protons (δ = 2.65-2.47, 2.36-2.10, 1.42-1.30, 1.68-1.45 ppm) of the cod ligands. The quartet for H14 of the (*R*)-1-phenylethyl moiety in **1** splits into a doublet of a quartet at 4.78 ppm with J = 6.4 and 2 Hz. Crystallisation of a solution of **1** in $CDCl_3$ containing 30% of **1** and 70% of its isomer (determined by ^1H NMR) gave 60% of complex **1**, indicating the reversibility of the isomerisation reaction.

The splitting of the methine proton of the (*R*)-1-phenylethyl group in the isomer of **1** indicates a coordination of the N atom of the thiobenzamide ligand to rhodium leading to a coupling with the ^{103}Rh nucleus ($^3J_{Rh-H}$ = 2Hz). However, the present spectroscopic results do not allow further conclusions concerning the structure of the isomer of **1**.

Experimental

The reactions involving air- and moisture sensitive compounds were performed in dry and degassed solvents under a nitrogen atmosphere using standard Schlenk techniques. ^{1}H NMR measurements were recorded on a Bruker AC 250 spectrometer (250 MHz) with TMS as external standard. IR data were obtained on a BioRad FTS 155 FTIR spectrophotometer, mass spectra on a Finnigan MAT 95.

N-[(*R*)-1-Phenylethyl]thiobenzamide[19]: preparation from N-[(*R*)-1-phenylethyl]benzamide with Lawesson's reagent in toluene according to ref. 20. Yield: 77%, m.p.: 66°C, $[\alpha]_D^{23}$ = +212 (1.1, $CHCl_3$).

Bis{(1,5-cyclooctadiene)[μ-N-((*R*)-1-phenylethyl)thiobenzamidato]rhodium} **1**: N-[(*R*)-1-Phenylethyl]thiobenzamide (240 mg, 1.0 mmol) and NaH (36 mg, 1.5 mmol) were dissolved in a mixture of 4 ml of CH_2Cl_2 and 2 ml of THF. After stirring for 15 min at room temperature the solution was filtered and added to a solution of $[Rh(cod)Cl]_2$[21] (240 mg, 0.5 mmol) in 10 ml of toluene. The mixture was stirred for 30 min at room temperature and the solvents were evaporated. The residue was taken up in 5 ml of toluene and filtered through Celite® (Merck). The solution was concentrated to a volume of 3 ml and 10 ml of n-pentane were added. Crystallisation at room temperature yielded 215 mg (0.53 mmol, 53%) orange crystals. M.p.: 165°C; $[\alpha]_D^{23}$ = −49.2 (0.29, $CHCl_3$); ^{1}H NMR (δ, ppm, T = 253K): 9.03 (d, J = 6.9 Hz, 2H), 7.64-7.50 (m, 5H), 7.37-7.20 (m, 3H), 5.70 (q, J = 6.4 Hz, 1H), 3.67 (s(br), 2H), 3.49-3.43 (m, 2H), 2.03-1.83 (m, 4H), 1.56 (d, J = 6.4 Hz, 3H), 1.50-1.46 (m, 4H); IR (KBr, cm^{-1}): 1569, 1487 and 1446 (C=C); MS (FD, toluene) m/z, %: 902.4 (30, M), 451.1 (100, M/2); calc. for $C_{46}H_{52}N_2Rh_2S_2$: C 61.27, H 5.82, N 3.11; found: C 61.23, H 5.94, N 3.18.

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12. *Data collection:* Syntex Nicolet R3 diffractometer (Mo-Kα radiation, 293 K, graphite crystal monochromator); 2θ range: 3.0-60°; total no. of unique reflections: 6123; no. of independent reflections ($I>2.5\sigma_I$): 4914; transmission factors: 0.66 (min.), 1.00 (max.). Structure solution by direct methods with SHELXTL PLUS-Release 4.2/800; the positions of the H atoms were calculated by the option HFIX. *Data refinement:* No. of reflections, 2θ range for empirical absorption correction: 7, 9.0-43.0°; no. of LS parameters: 469; largest shift/e.s.d.-max.: 0.056; goodness of fit: 2.08; final R indices: R = 0.046, R_w = 0.039; residual electron density: -0.72 (min.), 0.91 (max.) e⊕$^{-3}$. *Crystal parameters:* empirical formula: $C_{46}H_{52}N_2S_2Rh_2$; crystal colour/shape: orange-yellow/tables; crystal size: 0.1×0.8×1.0 mm^3; M = 902.86 gmol^{-1}; crystal system: monoclinic; space group: C2 (No. 5); cell constants: a = 10.564(4), b = 16.864(5), c = 23.584(7) ⊕, β = 95.05(3)°; volume: 4179(2) ⊕^{3}; density: 1.44 gcm^{-3}; Z = 2 × 2; F(000) = 1856; μ = 0.92 mm^{-1}. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-405791.
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