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Synthesis and X-ray crystal structure of the chiral ligand (S, R)-*N*,*N*-diethyl-*N*′-(2-(*N*″,*N*″-dimethyl-1-aminoethyl))ferrocenoyl thiourea[1]

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Abstract

The chiral ligand for transition metal ions, (S, R)-*N*,*N*-diethyl-*N*′-(2-(*N*″,*N*″-dimethyl-1-aminoethyl))ferrocenoyl thiourea, has been prepared from (S)-*N*,*N*-dimethyl-1-ferrocenylethylamine. Its chirality is confirmed by X-ray structure analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocene; Transition metal; Thiourea; X-ray structure; Stereo chemistry

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1. Introduction

The use of chiral ligands and their complexes is undisputed. On the one hand, many transition metal ions show catalytic properties, on the other hand, chirality of the ligand often is transferred to the substrate in a definite manner.

In this context, ferrocene-containing ligands have been attracting special attention. Their unique geometry allows synthesis of planar chiral molecules that are widely used as chiral catalysts [1]. Enantioselective metallation, followed by electrophilic attack, is the normal approach to the optically pure compounds. Stereochemistry is controlled either by an external auxiliar [2] or by an inherent stereo center. The best known examples of the latter way are the easily accessible enantiomers of *N*,*N*-dimethyl-1-ferrocenylethylamine [3]. Although already synthesized in 1970, its diastereoselectively lithiated forms still nowadays are used as precursors for planar chiral compounds [4].

The coordination chemistry of *N*-substituted-*N*′-acylthioureas is well investigated [5]. These ligands with the combination of a hard and a soft donor atom are capable of binding a variety of transition metal ions. Considering possible catalytical or biologically important properties, coordination of the platinic group metals is especially interesting [6]. Recently, we and others synthesized *N*-substituted-*N*′-ferrocenoylthioureas and their chelates with transition metal ions [7].

2. Results and discussion

In this paper we report on the first chiral N,N-disubstituted-N′-ferrocenoylthiourea: (S, R)-*N*,*N*-diethyl-*N*′-(2-(*N*″,*N*″-dimethyl-1-aminoethyl)) ferrocenoyl thiourea. The synthetic route is outlined in Scheme 1.

Starting with (S)-*N*,*N*-dimethyl-1-ferrocenylethylamine, diastereoselective lithiation in ether at r.t. and subsequent electrophilic attack by solid carbon dioxide yields the (S, R)-2-(*N*,*N*-dimethyl-1-aminoethyl)ferrocene acid [8]. The respective acid chloride is available by treatment with stoichiometric amounts of oxalyl chloride in dry methylene chloride at r.t. After total

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[1] Dedicated to Professor Dr Hartmut Bärnighausen on occasion of his 65th birthday.

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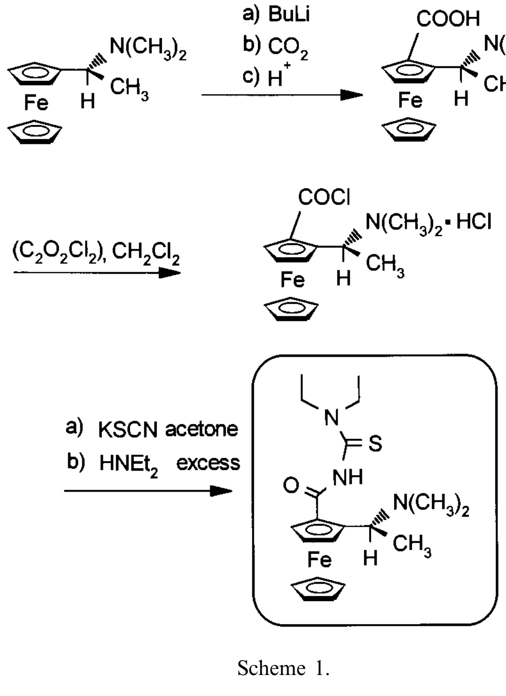
conversion, this liquid is added dropwise to a boiling solution of KSCN in acetone. Two hours of reflux are followed by addition of amine at 0°C. The title compound is purified by column chromatography at silica gel employing acetone as eluent giving a yield of 68% compared with (S, R)-2-(*N*,*N*-dimethyl-1-aminoethyl)-ferrocene acid.

Analytical data: m.p.: 167°C; $[\alpha]^{25} = +14.1$ ($c = 1$, ethanol); ^{1}H-NMR (ppm) (199.975 MHz, $CDCl_3$): 1.25 (s (br), 6H, CH_3), 1.36 (d, $J = 7$ Hz, 3H, CH_3), 2.23 (s, 6H, NCH_3), 3.6 and 3.8 (br, 4H, CH_2), 3.78 (s, 1H, Cp), 4.17 (s, 5H, Cp′), 4.25 (q, $J = 7$ Hz, 1H, CH), 4.35 (s, 1H, Cp), 4.99 (s, 1H, Cp), 13 (br, 1H, NH); ^{13}C-NMR (ppm) (100.577 MHz, $CDCl_3$): 7.90 (CH_3), 12.14 and 13.74 (CH_3), 38.78 (NCH_3), 47.48 and 48.09 (CH_2), 58.10 (CH), 69.40 (Cp), 69.95 (Cp), 70.87 (Cp′), 74.49 (Cp), 84.5 (Cp^{q}), 87.05 (Cp^{q}), 167.89 (CO), 182.1 (CS); FAB-MS: 416 ($M + H^{+}$ 20%), 370 (M^{+}-(N–$(CH_3)_2$)), 100%); IR [ν, cm^{-1}] (KBr): 3103 m, 2972 s, 1661 s, 1584 s, 1496 s, 1449 s, 1431 s, 1302 s, 1283 s, 1247 s, 528 m; elemental analysis [% calc./found] C: 57.83/57.75, H: 7.04/7.11, N: 10.11/10.18, O: 3.85/3.71, S: 7.70/7.74.

The respective antipode, (R, S)-*N*,*N*-diethyl-*N*′-(2-(*N*″,*N*″-dimethyl-1-aminoethyl))ferrocenoyl thiourea, is adequately obtainable when starting with (R)-*N*,*N*-dimethyl-1-ferrocenylethylamine. First experiments indicate a comparable coordination behavior of the chiral ligands compared with achiral ones.

The X-ray structure analysis [9] reveals the chirality of the title compound: the element of central chirality has (S) configuration and the element of planar chirality has (R) configuration (Fig. 1).



Scheme 1.

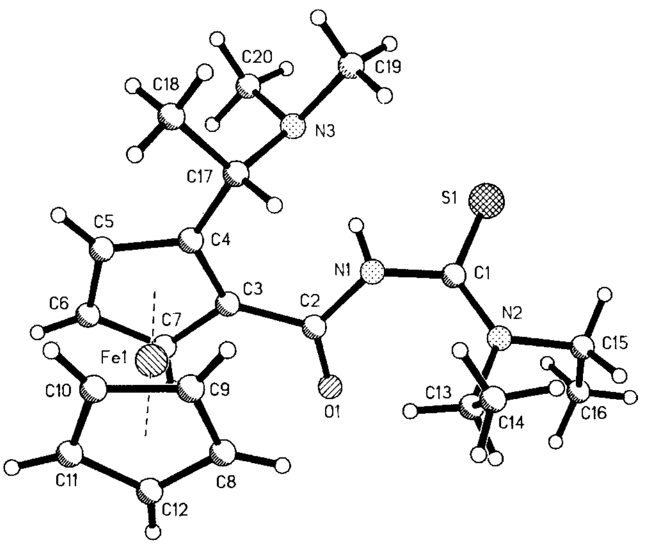


Fig. 1. Structure of the title compound.

The cyclopentadienyl rings are parallel (tilt angle 0.6(3)°). The conformation of these rings is nearly eclipsed (mean torsional angle 5.4°). The configuration of the substituents at the cyclopentadienyl ring C3–C7 is influenced by an intramolecular N–H···N hydrogen bridge (N1···N3 2.746(4) Å, H1···N3 1.98(3) Å, N1–H1···N3 161(2)°) between the substituents. Intermolecular hydrogen bridges do not exist.

The Fe–C bond lengths are between 2.023(3) and 2.049(3) Å. The *N*-acylthiourea fragment shows the keto form in which the expected bond lengths are found ([7]c).

The N–C bonds N1–C1 (1.402(4) Å) and N1–C2 (1.374(4) Å) differ significantly. The bond N2–C1 (1.318(4) Å) is clearly shortened in comparison with an N–C single bond. The bond S1–C1 (1.661(3) Å) is significantly longer than a C–S double bond, whereas the bond O1–C2 (1.218(4) Å) is a double bond. All bond lengths point to a partial electron delocalization in the structure fragment >N–C(S)–NH–C(O)–. As already observed for other *N*-acylthioureas and their chalcogeno analogous compounds, the configuration of this fragment is nearest to E,Z′ (ω(S1C1N1C2) = 118.1(3)°, ω(O1C2N1C1) = 8.6(5)°).

As usual, rotation around the Et_2N–CS bond is hindered also in solution. In the ^{1}H-NMR this is indicated by the broadening of the methyl signal and the two distinct resonances of the chemically equivalent CH_2-protons.

In summary, we have synthesized *N*′,*N*′-disubstituted *N*-ferrocenoylthioureas containing central as well as planar chirality at the ferrocene moiety. Considering the additional possibility of introducing optically active amines, these ligands represent interesting building blocks for chiral catalysts.

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[9] Crystal data for $C_{20}H_{29}FeN_3OS$: M = 415.37 g mol^{-1}, crystallizes from acetone as triangular plates, crystal dimensions 0.61 × 0.57 × 0.19 mm^3. Monoclinic, $a = 7.435(1)$, $b = 9.984(1)$, $c = 14.632(2)$ Å; $\beta = 101.95(1)°$, $V = 1062.6(2)$ Å^3, $Z = 2$, $D_{calc} =$ 1.298 g cm^{-3}, space group $P2_1$, Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å), μ(Mo–K$_\alpha$) = 0.821 mm^{-1}, $F(000) = 440$. Three-dimensional r.t. data were collected in the range $5 < 2\theta < 62°$ on a Stoe Stadi 4 diffractometer by the ω/θ scan method. Of the 6799 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by Ψ-scans, 3853 independent reflections exceeded the significance level $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares methods on F^2 (SHELXL-93). Hydrogen atoms were included in calculated positions and refined in riding mode with exception of H1, bonded to N1, which was located in a difference map and refined isotropically. Refinement converged at a final $R_1 = 0.041$ for 3853 observed reflections ($wR_2 = 0.117$ for all 6799 data, 244 parameters) with allowance for the thermal anisotropy of all non-hydrogen atoms, Flack parameter 0.01(2), minimum and maximum final electron density −0.437 and 0.367 eÅ^{-3}. Further information including atomic coordinates, bond lengths and angles, and thermal parameters has been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen and can be requested by giving the deposit number CSD-408407.