Synthesis and Site-selective Metalation of a Benzene-*o*-dithiol/ Pyridylimine Ligand

Johannes Dömer, Tania Pape, and F. Ekkehardt Hahn

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster,
Corrensstraße 30, 48149 Münster, Germany

Reprint requests to Prof. Dr. F. Ekkehardt Hahn. Fax: +49-25183-33013.
E-mail: fehahn@uni-muenster.de

Z. Naturforsch. **2010**, *65b,* 470 – 474; received January 7, 2010

The benzene-*o*-dithiol/pyridylimine (S-S)/(N-N) ligand H_2-**7**, representing the first example of a new type of bis(bidentate) heterodonor ligands with a mixed donor set, has been synthesized by Schiff base condensation of pyridine-2-carbaldehyde with an amine-substituted benzene-*o*-dithiol moiety. Bis(cyclopentadienyl)titanium dichloride reacts selectively at the S-S donor group of H_2-**7** to yield complex [Cp_2Ti(**7**)].

Key words: Heterodonor Ligands, S-S Ligands, N-N Ligands, Titanium, Schiff Bases

Introduction

Metallosupramolecular chemistry is directed towards the generation of molecular structures based on non-covalent metal-ligand interactions. Reactions proceeding under self-organization to metallosupramolecular structures have initially been studied for simple molecular architectures. Among the most important metallosupramolecular structures are synthetic helicates which can be considered to be models of the natural DNA helices [1]. A large number of polynuclear double- or triple-stranded helicates derived from polydentate ligands with oligopyridine- [2], catecholato- [3], imine- [4], and most recently benzene-*o*-dithiolato donor groups [5] have been described. Studies on heterometallic helicates are less common [6]. The main reason for this situation is the normally complicated synthesis of suitable polydentate ligands containing different donor groups for the selective binding of different metal ions. We have recently described the preparation of unsymmetrical benzene-*o*-dithiol/catechol ligands [7] which allowed the synthesis of triple-stranded heterodinuclear helicates [8]. Based on these results we have prepared unsymmetric ligands containing benzene-*o*-dithiol/salicylimine donor groups and used these for the generation of dinuclear nickel complexes [9]. Here we present the synthesis of a novel benzene-*o*-dithiol/pyridylimine (S-S)/(N-N) ligand H_2-**7** and its reaction with titanocene dichloride leading to complex [Cp_2Ti(**7**)] containing a metalated benzene-*o*-dithiolato donor group.

Results and Discussion

The synthesis of ligand H_2-**7** was achieved using a methodology developed for the preparation of unsymmetrical benzene-*o*-dithiol/salicylimine ligands (Scheme 1) [9]. Amine **1** bearing an additional *tert*-butoxycarbonyl (Boc) protected amine function was obtained by reaction of 4,4′-diaminodiphenylmethane with one equivalent of Boc-ON. Reaction of **1** with the acid chloride **2**, which was obtained from 2,3-di(isopropylmercapto)benzoic acid [10] and oxalyl chloride, gave compound **3**. Compound **3** reacts after removal of the Boc protection group in a Schiff base condensation with pyridine-2-carbaldehyde in methanol to give ligand **5** containing a bidentate pyridylimine donor group linked by a spacer to the *S*,*S*-diisopropyl-protected S-S donor group. All attempts to cleave the S-*i*Pr bonds in **5** with sodium/naphthalene [10] led to decomposition or to reduction of the imine function. Crystals of **5** suitable for an X-ray diffraction analysis have been obtained by evaporation of the solvents from a saturated solution of **5** in dichloromethane/*n*-hexane (1:1, v:v). The molecular structure of **5** is depicted in Fig. 1. All metric parameters in **5** are unspectacular and resemble the values for equivalent parameters in related compounds [10b, 11].

From the results described above it becomes obvious that the S-*i*Pr bonds of the dimercaptobenzene group have to be cleaved before the imine group is generated by Schiff base condensation. To this end compound **4** was reacted with sodium/naphthalene

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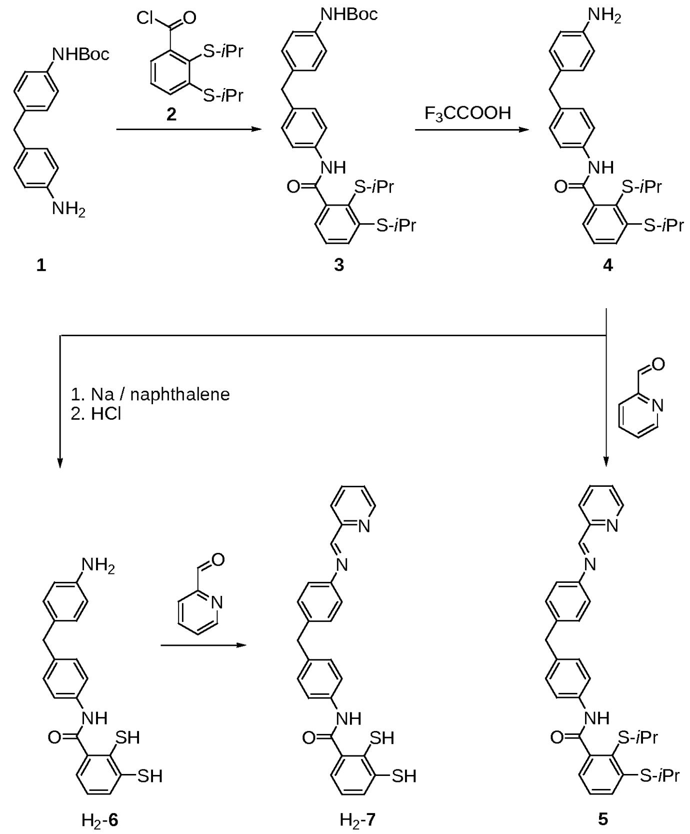


Scheme 1. Synthesis of ligands **5** and H_2-**7**.

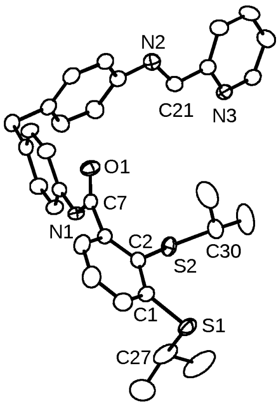
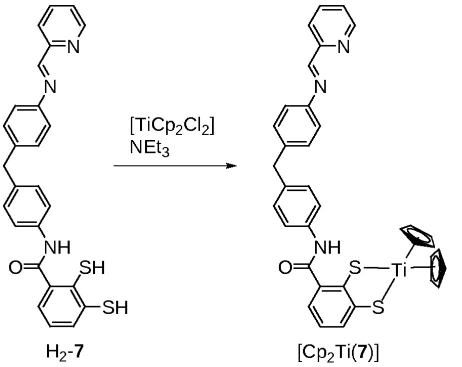


Fig. 1. Molecular structure of **5** (hydrogen atoms omitted for clarity, displacement ellipsoids at the 50 % probability level). Selected bond lengths (Å) and angles (deg): S1–C1 1.781(2), S2–C2 1.774(2), S1–C27 1.831(3), S2–C30 1.835(2), O1–C7 1.216(2), N1–C7 1.351(3), N2–C21 1.269(3); C1–S1–C27 100.37(11), C2–S2–C30 101.51(10).

in THF as we have described previously for related compounds [10]. Protonation of the initial reaction product with HCl gave the benzene-*o*-dithiol derivative H_2-**6** containing an amine substituted spacer. This amine function can be used to generate the pyridylimine function by reaction with pyridine-2-carbaldehyde in a Schiff base condensation. Compound H_2-**6** does indeed react with pyridine-2-carbaldehyde to give the unsymmetrical (S-S)/(N-N) ligand H_2-**7** in good (81 %) yield (Scheme 1). The free thiol donors in the precursor H_2-**6** did not interfere in this reaction.

Ligand H_2-**7** was reacted with one equivalent of titanocene dichloride in the presence of NEt_3 [12] to give the titanocene complex [Cp_2Ti(**7**)] in good (86 %) yield (Scheme 2). The dark-green complex [Cp_2Ti(**7**)] is stable in air and can be purified by column chromatography (SiO_2, dichloromethane/methanol 20 : 1, v : v).

Complex [Cp_2Ti(**7**)] was crystallized by vapor diffusion of *n*-hexane into a benzene/dichloromethane (1 : 1, v : v) solution of the complex. The X-ray diffraction analysis confirmed that only one of the bidentate donor groups has been metalated by a titanocene moiety (Fig. 2). Bond lengths and angles in [Cp_2Ti(**7**)] fall in the range previously reported for [Cp_2Ti(bdt)]



Scheme 2. Synthesis of the titanocene complex [$Cp_2Ti(\mathbf{7})$].

complexes (bdt^{2-} = benzene-*o*-dithiolato anion) [13]. The five-membered C_2S_2Ti ring is significantly bent along the S···S vector, a property regularly seen for titanium complexes with bdt^{2-} ligands [5a, 13, 14], but uncommon for bdt^{2-} complexes of other transition metals [10a, 13a, 15]. The selective metalation of the benzene-*o*-dithiolato donor group and the presence of an uncoordinated pyridylimine group was initially surprising as the hard titanium center was not expected to bind preferably to the soft sulfur donors but instead to the harder nitrogen donors. The reason for the selective metalation of the thiolato donors is most likely the neutralization of the charges both at titanium and sulfur while coordination of the nitrogen donors would lead to a dicationic $\{Cp_2Ti(N\text{-}N)\}^{2+}$ moiety. The selective metalation of the benzene-*o*-dithiolato donor observed in the reaction of H_2-**7** with titanocene dichloride constitutes a desirable und useful property which will be important for our ongoing studies concerning the preparation of heterobimetallic complexes with benzene-*o*-dithiolato/pyridylimine ligands.

Conclusion

With the benzene-*o*-dithiol/pyridylimine H_2-**7** we present a new directional heterodonor ligand. First studies of its coordination chemistry with titanocene derivatives revealed a selective metalation of the benzene-*o*-dithiolato donor group most likely due to charge minimization. Ongoing studies are directed towards using this property for the generation of heterobimetallic helical complexes with (S-S)/(N-N) benzene-*o*-dithiolato/pyridylimine ligands.

Experimental Section

Chemicals and solvents were purchased from Aldrich. NMR spectra were recorded on Bruker AC 200 and AMX 6400 spectrometers. MALDI mass spectra were obtained with a Varian MAT 212 spectrometer. Elemental analyses were performed with a Vario EL III CHNS Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster. If not noted otherwise, all preparations were carried out in Schlenk flasks under an argon atmosphere. Compounds **2** [10], **1**–**4** and H_2-**6** [9] were prepared according to published procedures.

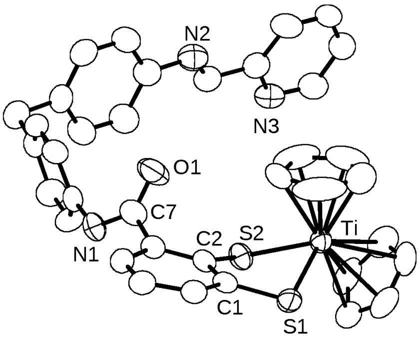


Fig. 2. Molecular structure of [$Cp_2Ti(\mathbf{7})$] (hydrogen atoms omitted for clarity, displacement ellipsoids at the 50 % probability level). Selected bond lengths (Å) and angles (deg): Ti–S1 2.405(2), Ti–S2 2.394(2), S1–C1 1.754(5), S2–C2 1.758(5); S1–Ti–S2 82.83(5), C1–S1–Ti 97.8(2), C2–S2–Ti 96.9(2).

*4-[2,3-Di(isopropylmercapto)benzamido]-4′-[2-pyridylmethyleneamino]diphenyl-methane (**5**)*

Samples of compound **4** (2.00 g, 4.4 mmol) und pyridine-2-carbaldehyde (566 mg, 5.3 mmol) were suspended in methanol (20 mL). The reaction mixture was stirred at ambient temperature for 12 h with formation of an off-white solid. The solid was isolated by filtration and dried *in vacuo*. Yield: 2.0 g (84 %). – ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.94 (s, 1 H, NH), 8.65 (m, 1 H, Ar-H), 8.58 (s, 1 H, N=CH), 8.16–7.10 (m, 14 H, Ar-H), 3.97 (s, 2 H, CH_2), 3.46 (sept, ^3J = 6.8 Hz, 1 H, $C\mathit{H}(CH_3)_2$), 3.41 (sept, ^3J = 6.5 Hz, 1 H, $C\mathit{H}(CH_3)_2$), 1.37 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.20 (d, ^3J = 6.5 Hz, 6 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 166.1 (C=O), 159.8 (C=N), 154.5, 149.5, 148.8, 145.7, 142.3, 139.8, 137.0, 136.6, 136.1, 129.6, 129.4, 129.0, 128.8, 128.1, 125.9, 124.9, 121.7, 121.2, 120.2 (Ar-C), 41.1 ($\mathit{C}(CH_3)_3$), 40.9 (CH_2), 36.1 ($\mathit{C}(CH_3)_3$), 23.0 (CH_3), 22.6 (CH_3). – $C_{32}H_{33}N_3OS_2$ (539.8): calcd. C 71.21, H 6.16, N 7.79, S 11.88; found C 71.25, H 6.37, N 7.67, S 11.68.

*4-[2,3-Dimercaptobenzamido]-4′-[2-pyridylmethyleneamino]diphenyl-methane (H_2-**7**)*

Compound H_2-**6** (400 mg, 1.1 mmol) and pyridine-2-carbaldehyde (120 mg, 1.1 mmol) were suspended in methanol (15 mL). The reaction mixture was stirred at ambient temperature for 3 d with formation of a yellow solid, which was isolated by filtration, washed with methanol and dried *in vacuo*. Yield: 404 mg (81 %). – ^{1}H NMR (200 MHz, [D$_7$]DMF, ppm): δ = 10.45 (s, 1 H, NH), 8.64 (s, 1 H, N=CH), 7.88 – 6.66 (m, 15 H, Ar-H), 4.81 (s br, 2H, SH), 3.93 (s, 2 H, CH$_2$). – ^{13}C NMR (50 MHz, [D$_7$]DMF, ppm): δ = 163.3 (C=O), 162.7 (HC=N), 150.0, 149.9, 138.7, 137.5, 137.4, 137.1, 130.6, 130.5, 130.3, 130.1, 129.7, 129.4, 124.2, 122.2, 121.2, 120.5, 115.9, 115.7, 115.6 (Ar-C), 40.8 (CH$_2$). – $C_{26}H_{21}N_3OS_2$ (455.6): calcd. C 68.54, H 4.65, N 9.22, S 14.08; found C 68.63, H 4.78, N 9.11, S 13.72.

*[Cp$_2$Ti(**7**)]*

Ligand H$_2$-**7** (230 mg, 0.64 mmol) und bis(cyclopentadienyl)titanium dichloride (164 mg, 0.64 mmol) were suspended in THF (20 mL). Triethylamine (0.9 mL) was added to the reaction mixture which was then stirred at ambient temperature for 12 h. Subsequently, all solvents were removed *in vacuo*. A green solid was obtained, composed of [Cp$_2$Ti(**7**)], triethylammonium chloride, and excess titanocene dichloride, and out of this mixture [Cp$_2$Ti(**7**)] was separated by column chromatography (SiO$_2$, dichloromethane/methanol, 20 : 1, v : v). Dark-green single crystals of [Cp$_2$Ti(**7**)] were obtained by diffusion of *n*-hexane into a solution of the complex in benzene/dichloromethane (1 : 1, v : v). Yield: 350 mg (86 %). – ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 9.13 (s, 1 H, NH), 8.70 (m, 1 H, Ar-H) 8.61 (s, 1 H, HC=N), 8.21 – 7.18 (m, 14 H, Ar-H), 6.08 (s br, 10H, C$_5$H$_5$), 3.99 (s, 2 H, CH$_2$). – ^{13}C NMR (50 MHz, CDCl$_3$): δ = 164.3 (C=O), 159.9 (HC=N), 159.1, 146.6, 140.1, 137.6, 136.8, 136.7, 132.7, 132.1, 129.6, 129.4, 128.8, 126.4, 125.0, 124.7, 123.5, 122.8, 121.9, 121.3, 120.3 (Ar-C), 113.2 (C$_5$H$_5$), 40.9 (CH$_2$). – $C_{36}H_{29}N_3OS_2Ti$ (631.6): calcd. C 68.46, H 4.63, N 6.65, S 10.15; found C 68.26, H 4.57, N 6.83, S 10.24.

*X-Ray structure determinations for compounds **5** and [Cp$_2$Ti(**7**)]*

Diffraction data for **5** and [Cp$_2$Ti(**7**)] were measured at 153(2) K using MoK_α (λ = 0.71073 Å, for **5**) or CuK_α (λ = 1.54178 Å, for [Cp$_2$Ti(**7**)]) radiation. Data were collected over the full sphere in the range $3.3 \le 2\theta \le 53°$ for **5** and $36.9 \le 2\theta \le 130.0°$ for [Cp$_2$Ti(**7**)]. Structure solution [16] and refinement [17] were achieved with standard Patterson and Fourier techniques, respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure models in calculated positions.

Selected crystallographic data for 5: Formula $C_{32}H_{33}N_3OS_2$, M = 539.73, colorless crystal, 0.32 × 0.24 × 0.05 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 8.8274(15), b = 24.239(4), c = 13.418(2) Å, β = 90.083(4)°, V = 2881.7(8) Å^3, $\rho_{\text{calcd.}}$ = 1.24 g cm^{-3}, μ = 0.2 mm^{-1}, empirical absorption correction ($0.9346 \le T \le 0.9894$), 25894 intensities collected ($\pm h$, $\pm k$, $\pm l$), 5972 independent (R_{int} = 0.0426) and 4698 observed intensities [$I \ge 2\sigma(I)$], 347 refined parameters refined against F^2, residuals for all data: R = 0.0673, $wR2$ = 0.1220; largest peak / hole in last Difference Fourier map 0.46 / −0.27 e Å^{-3}.

Selected crystallographic data for [Cp$_2$Ti(7)]: Formula $C_{36}H_{29}N_3OS_2Ti$, M = 631.64, green crystal, 0.16 × 0.06 × 0.04 mm^3, triclinic, space group $P\bar{1}$, Z = 2, a = 10.6495(6), b = 11.1328(6), c = 14.4977(7) Å, α = 112.052(3), β = 102.214(4), γ = 100.002(4)°, V = 1495.01(14) Å^3, $\rho_{\text{calcd.}}$ = 1.40 g cm^{-3}, μ = 4.0 mm^{-1}, empirical absorption correction ($0.5668 \le T \le 0.8563$), 7748 intensities collected ($\pm h$, $\pm k$, $\pm l$), 4526 independent (R_{int} = 0.0345) and 2874 observed intensities [$I \ge 2\sigma(I)$], 388 refined parameters against F^2, residuals for all data: R = 0.1007, $wR2$ = 0.1773; largest peak / hole in last Difference Fourier map: 0.58 / −0.26 e Å^{-3}.

CCDC 755366 (**5**) and CCDC 691378 ([Cp$_2$Ti(**7**)]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

Financial support by the Deutsche Forschungsgemeinschaft (SFB 424 and IRTG 1444) is gratefully acknowledged.

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