Five-coordinate Zinc(II) Complexes Containing Sterically Demanding Bio-mimetic N_3S_2 Ligands. Syntheses, Characterization and DFT Calculations

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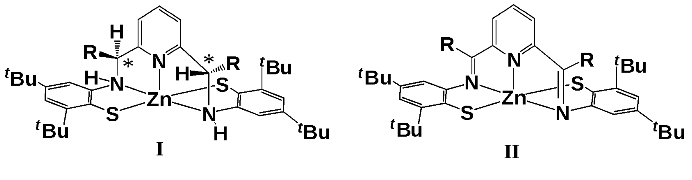
Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

In search of complexes having $[ZnN_3S_2]$ cores in the monomeric form with *trans*-thiolate donor atoms, new sterically demanding tri- and pentadentate ligands containing biomimetic N_3S_2 cores have been synthesized. The reaction of bis(2-mercapto-3,5-di-*tert*-butylaniline)zinc(II) with 2,6-diacetylpyridine leads to the formation of the zinc imine $[Zn(py^tBuN_2Me_2S_2)]$ (**3**) which is stable and can be isolated and characterized in the solid state. Complex **3** can be converted to the zinc amine function $[Zn(py^tBuN_2H_2Me_2S_2)]$ (**5**) without losing the metal center using $NaBH_4$ in methanol solution. On the other hand, complex **3** can be demetallated in an acidic medium to give the tridentate bis-benzothiazoline ligand **4**. Alternatively, ligand **4** can be obtained *via* condensation of 3,5-di-*tert*-butylmercaptoaniline with 2,6-diacetylpyridine in a 2:1 molar ratio. Opening the bis-benzothiazoline ligand **4** either by reduction with $NaBH_4$ in methanol or by zinc acetate leads to the formation of the pentadentate dithiole-amine ligand $py^tBuN_2H_2Me_2S_2\text{-}H_2$ (**6**), and the zinc imine complex **3**, respectively. Ligand **6** can also be obtained *via* demetallation of the zinc amine complex **5** in acidic medium. All compounds have been characterized using spectroscopic methods and elemental analysis, and also by using DFT (B3LYP/6-31G*) calculations in combination with experimental NMR data.

Key words: Zinc Complexes, Amine Sulfur Ligands, Template Synthesis, Steric Hindrance, NMR, DFT Calculations

Introduction

Investigations on the role of zinc thiolate complexes in biological chemistry have stimulated numerous studies on zinc coordination compounds with sulfur ligation [1]. In particular, zinc complexes with N_xS_y ligand cores are of increasing interest as structural and spectroscopic models for metal binding sites in a number of metallothioneins and metallo-regulatory proteins [2, 3]. The present study is a continuation of our work on the structures of zinc complexes derived from the biomimetic N_3S_2 moiety. In the past, we found a simple way for the synthesis of zinc complexes containing a sterically demanding pentadentate $py^tBuN_2H_2S_2\text{-}H_2$ ligand 2,6-bis(2-mercapto-3,5-di-*tert*-butylphenyl-aminomethyl)pyridine (Scheme 1) [3]. The complexes are assumed to be five-coordinate species. The formation of higher coordination numbers achieved through the bridging of sulfur donor atoms in the solid state could be prevented by the presence of



Scheme 1. Schematic structures of $[Zn(pyN_2RS_2)]$ complexes; R = H, Me.

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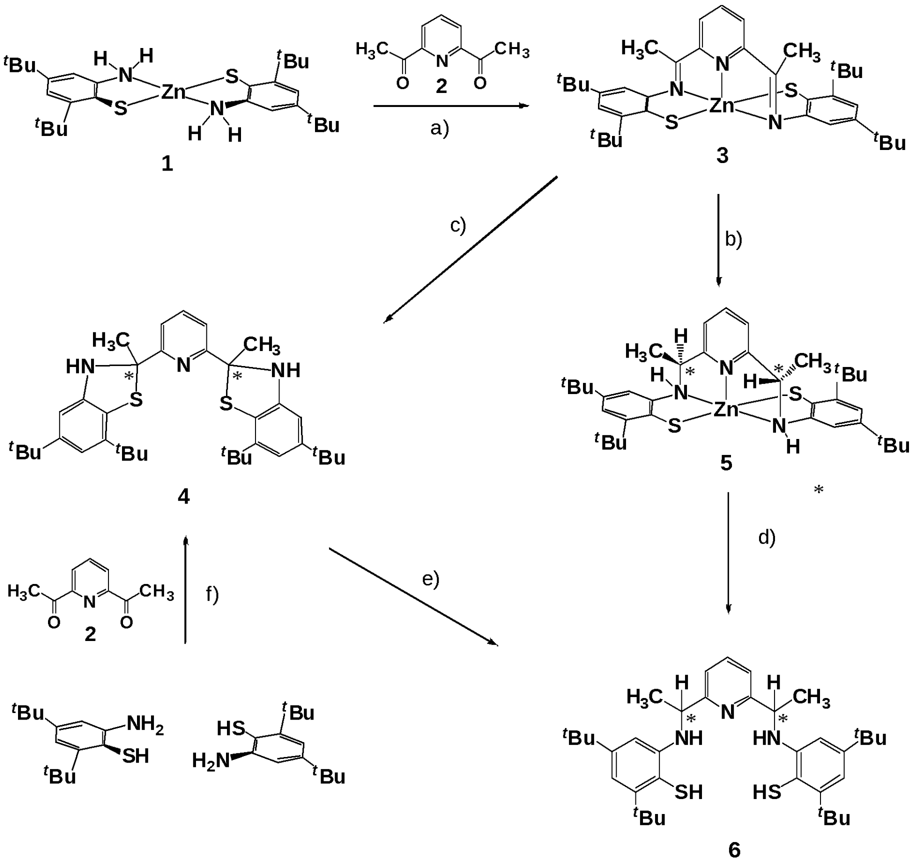


Scheme 2. Synthesis of the new bis-benzothiazoline py^{t}BuN$_2$H$_2$Me$_2$S$_2$ (**4**) and dithiolate-amine py^{t}Bu-N$_2$H$_2$Me$_2$S$_2$-H$_2$ (**6**) ligands as well as their zinc complexes. a) MeOH, 20 °C; b) NaBH$_4$, MeOH, 0 °C; c) HCl$_{aq}$, CH$_2$Cl$_2$, 20 °C; d) HCl$_{aq}$, CH$_2$Cl$_2$, 20 °C; e) NaBH$_4$, MeOH, 0 °C; f) MeOH, reflux, 10 h.

bulky *tert*-butyl groups in the *ortho* position to the thiolate sulfur atoms. The high solubility of the complexes supported the mononuclear behavior in solution. The zinc imine complex (Scheme 1, **II**, R = H) was found to be unstable. Soon after its formation it looses the metal center, and finally a stable thiazole moiety forms. A likely explanation for this lability can be related to the high sensitivity of the C-H unit, which is easily oxidized. In this study we therefore tried to overcome this problem by replacing these hydrogens by methyl groups, *i. e.* by using diacetylpyridine instead of diformylpyridine and to study the effect of methyl substituents on the stability as well as the structure of this system. In this context we describe the syntheses of new tri- and pentadentate N$_3$S$_2$ ligands, their zinc complexes and their DFT (B3LYP/6-31G*) calculated structures.

Results and Discussion

Template condensation of 2,6-diacetylpyridine (**2**) with the bis(3,5-di-*tert*-butyl-2-mercaptoaniline)-zinc(II) complex (**1**) [3] in a 1 : 1 molar ratio yields the five-coordinate zinc-imine complex **3** in a good yield (see Scheme 2).

The infrared spectrum of **3** shows no amine or carbonyl modes and instead displays a band at 1620 cm^{-1}, which is attributed to the vibrations of the imine function. The ^{1}H-NMR spectrum (CD$_2$Cl$_2$) exhibits a singlet at δ = 3.49 ppm assigned to both methyl hydrogens indicating C_2 symmetry. Further support for the C_2 symmetry comes from the ^{13}C-NMR spectrum which shows a characteristic singlet at δ = 17.5 ppm attributed to the methyl carbons at the bridges. The mass spectrum exhibits m/z = 664, which corresponds to the molecular ion peak of **3**. Complex **3** is soluble in all common organic solvents, thereby indicating its molecular and most likely mononuclear nature.

Complex **3** proved to be very stable and could be isolated and completely characterized in the solid state. This is in contrast to the observation for the analogous complex (Scheme 1, complex **II**, R = H) which is unstable and could not be isolated as a solid and

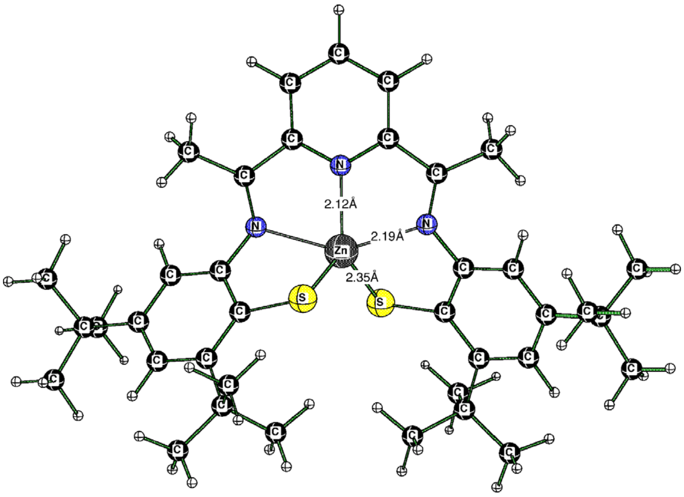
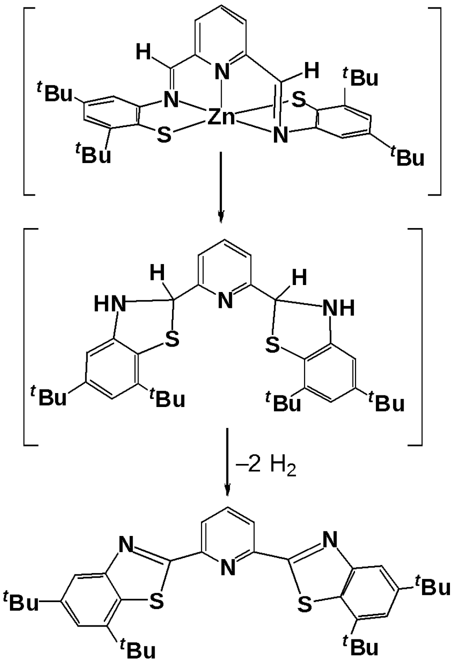


Fig. 1. DFT-calculated (B3LYP/6-31G*) structure for the zinc imine complex **3**.



Scheme 3. Demetallation of the analogous zinc imine complex followed by oxidation to give the stable five-membered ring [3].

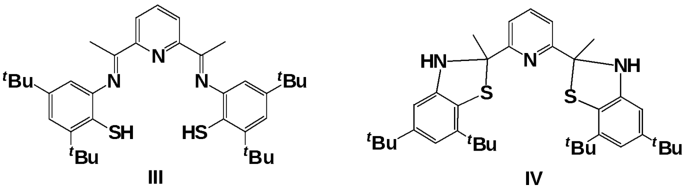
soon after formation lost the metal center followed by oxidation to give the very stable five-membered rings (Scheme 3) [3]. Apparently, the electron density as a result of the methyl group is responsible for such stabilization by increasing the donor capacity of the imine nitrogen atoms.

More information about the structure of **3** can also be obtained from the DFT (B3LYP/6-31G*) [7–11] calculation of the NMR data and comparison of the results with the experimental NMR data (Table 1). The experimental ^{1}H-NMR data fit with the DFT (B3LYP/6-31G*) calculated structure presented in Fig. 1 and show that the structural index τ [4], which represents the relative amount of trigonality (square-pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$; $\tau = (\beta - \alpha)/60$; where α and β are the two largest angles around the central atom) is 0.42. This reveals that the coordination geometry around zinc is best described as in between square-pyramidal and trigonal-bipyramidal. These results are in a good agreement with that reported by Goedken *et al.* for the closely related bis(2-thiobenzaldimino)-2,6-diacetylpyridine-zinc(II) complex, which is five-coordinate with the ligand donor atoms describing an approximate trigonal bipyramid [2d]. The C=N stretching frequency of the azomethine linkages is rather high, indicating localized double bonds which result from the steric interaction be-

Table 1. Experimental ^{1}H-NMR chemical shifts (δ)[a] and calculated (B3LYP/6-31G*) magnetic shielding of complexes **3** and **5** as well as ligands **4** and **6**.

Compound		^{t}Bu (C(C$\boldsymbol{H}_3$)$_3$)	C-C$\boldsymbol{H}_3$	C$\boldsymbol{H}$-CH$_3$	[aryl-$\boldsymbol{H}$]
3	Exp.	1.20, 1.22	3.49	–	6.80, 7.00, 7.19, 7.30, 7.80, 7.90, 8.14
	Calcd.	1.40, 1.71	2.59	–	6.83, 7.20, 7.82, 8.15
4	Exp.	1.16, 1.27	1.84	–	6.70, 6.78, 7.56, 7.85
	Calcd.	1.21, 1.39	2.01	–	6.91, 6.96, 7.42, 7.73
5	Exp.	1.24, 1.49	3.44	4.40	6.90, 7.24, 7.43, 7.93
	Calcd.	1.31, 1.70	2.82	5.06	7.05, 7.14, 7.34, 7.62
6	Exp.	1.20, 1.31	2.02	3.42	6.68, 6.78, 7.57, 7.60
	Calcd.	1.18, 1.62	1.60	4.27	6.54, 6.64, 7.21, 7.56

[a] δ in ppm relative to TMS in CDCl$_3$.



Scheme 4. Constitution of the Schiff base **III** and the bis-benzothiazoline **IV**.

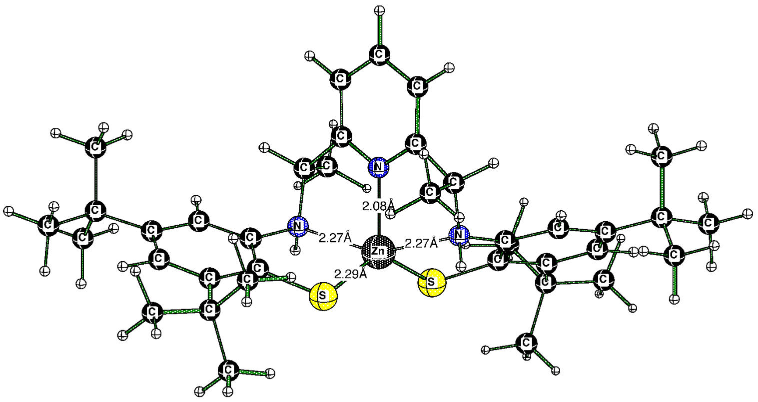


Fig. 2. DFT-calculated (B3LYP/6-31G*) structure for the zinc amine complex **5**.

tween the methyl groups and the neighboring protons of the aromatic rings.

Acidic hydrolysis of complex **3** in dichloromethane afforded a yellow product. Its mass spectrum shows a molecular ion peak at *m/z* = 602 which could represent the bis-benzothiazoline **III** or the tautomeric Schiff base **IV** (Scheme 4). The latter proposal could be discarded because the infrared spectrum shows no bands in the range of S–H absorptions, indicating that the S atoms are involved in a cyclic system. The absence of the C*H*=N proton signal in the ^{1}H-NMR spectrum of **4** also supports the bis-benzothiazoline form. DFT (B3LYP/6-31G*) calculations of the ^{1}H-NMR chemical shifts in combination with the experimental ^{1}H-NMR data also confirm the formation of the bis-benzothiazoline form **IV** (Table 1). Moreover, the bis-benzothiazoline form is more stable than the Schiff base form by about 20.5 kcal mol^{-1}. Alternatively, the bis-benzothiazoline **4** can be obtained *via* condensation of 3,5-di-*tert*-butylmercaptoaniline with 2,6-diacetylpyridine in a 2 : 1 molar ratio in methanol under reflux. Opening the bis-benzothiazoline ligand **4** is achieved either by reduction with $NaBH_4$ in methanol or by zinc acetate and leads to the formation of the dithiolate ligand **6** or the zinc imine complex **3**, respectively (Scheme 2).

On the other hand, reduction of complex **3** by using $NaBH_4$ in methanol leads to the formation of the zinc amine complex **5** in a good yield (see Scheme 2). Its mass spectrum exhibits the molecular ion peak at m/z = 668. The ^{1}H-NMR spectrum of **5** shows that both methyl protons appear as one doublet at δ = 3.44 ppm, and the two methylene protons as one multiplet at 4.40 ppm, which confirms the formation of only one diastereoisomer with C_2 symmetry. More information about the structure can also be obtained from the DFT (B3LYP/6-31G*) calculation of the ^{1}H-NMR spectra and comparison of these data with the experimental data (Table 1). The experimental ^{1}H-NMR data fit with the DFT (B3LYP/6-31G*) calculated structure shown in Fig. 2 with the structural index τ = 0.33, indicating that the structure could be best described as distorted trigonal-bipyramidal. As mentioned in the introduction, a review of the literature has shown that the structures of three other ZnN_3S_2 complexes, namely [Zn(terpy)(*i*PrO)$_2$PS$_2$]$_2$ [5], [Zn(BMIP)] [6], and [Zn(BMAP)] [2h], have been reported in which a similar disposition of the donor atoms in the ligands results in nearly the same type of complex geometry as observed here with a minor distortion due to the bulky groups.

Demetallation of the zinc complex **5** under acidic condition leads to the formation of the free dithiolate-amine py^{t}BuN$_2$H$_2$Me$_2$S$_2$-H$_2$ ligand 2,6-bis-{1-(2-mercapto-3,5-di-*tert*-butylphenylamino}ethyl)-pyridine (**6**) (see Scheme 2). Characteristic bands appear in the infrared (KBr) spectrum of **5** at 3373 and 2510 cm^{-1} which are attributed to the N-H and S-H stretching vibrations, respectively. The mass spectrum of **5** shows a molecular ion peak at *m/z* = 604. The ^{1}H-NMR spectrum exhibits a doublet at δ = 7.56 ppm which is assigned to the N-H protons. The methyl protons appear as a doublet at δ = 2.02 ppm, and the *tert*-butyl groups appear as two singlets at δ = 1.20 and 1.31 ppm.

In conclusion, we reported the synthesis of zinc imine complexes that contain new sterically demanding pentadentate N_3S_2 ligands *via* template condensation. This zinc imine complex is very stable and can be isolated and completely characterized in the solid state. This is in contrast to the observation for the analogous complex which contains hydrogen atoms instead of methyl groups, such that the stabilization can be traced to stronger N-donation. The zinc imine functions can be easily converted to the chiral zinc amine functions without losing the metal center but with a change of the coordination geometry around zinc, as deduced from the DFT (B3LYP/6-31G*) calculation in a combination with the experimental NMR data. Demetallation of both complexes leads to the formation of new tri- and pentadentate sulfur amine ligands. Future studies will focus on the use of these ligands for other transition metals such as iron. In particular, we will target structures containing amine-sulfur ligands at iron centers with a high electron density that mimic the molecular environment of the active site in enzymes that activate dinitrogen.

Experimental Section

Material and methods

Unless noted otherwise, all procedures were carried out under an atmosphere of N_2 using Schlenk techniques. Dry solvents were used. As far as possible, reactions were monitored by IR or NMR spectroscopy. Spectra were recorded on the following instruments: IR (KBr discs or CaF_2 cuvettes, solvent bands compensated): Perkin Elmer 983, 1620 FT IR, and 16PC FT-IR; NMR: Jeol-JNM-GX 270, EX 270, and Lambda LA 400 with the protio-solvent signal used as an internal reference. Elemental analyses: Carlo Erba EA 1106 or 1108 analyzer; mass spectra: Jeol MSTATION 700 spectrometers. The bis(3,5-di-*tert*-butyl-2-mercaptoaniline)zinc(II) complex (**1**) was synthesized as reported in the literature [3]. $NaBH_4$, LiOMe and 2,6-diacetylpyridine were purchased from Aldrich.

DFT calculations

Quantum-chemical methods: All structures were fully optimized at the B3LYP/6-31G(d) density functional theory (DFT) level [7] by using the GAUSSIAN 03 program [8]. Frequencies were computed at the same level to characterize stationary points and to obtain zero-point vibrational energies (ZPEs). DFT, in particular B3LYP, was shown to provide accurate geometries and good harmonic vibrational frequencies for a broad range of molecules and ions (see, *e. g.* [9]). As shown recently, the level of theory selected (B3LYP/6-31G(d)) is well suited for NMR [10] and NICS calculations [11]. Following the approach of van Eikema Hommes and Clark [10b], we converted the calculated magnetic shielding constants (σ) into δ(C) relative to $SiMe_4$ by applying Eq. 1 [10b].

$$\delta = 200.65 + (-1.0715\sigma)(R^2 = 0.9984) \qquad (1)$$

*[Zn(py^{t}BuN$_2$Me$_2$S$_2$)] (**3**)*

A mixture of 2,6-diacetylpyridine (128 mg, 0.95 mmol) and **1** (510 mg, 0.95 mmol) in MeOH (20 mL) was stirred for 1 h at r. t. and for 5 h at 60 °C. Upon cooling the reaction mixture to r. t. and reducing the volume to 5 mL, a red precipitate was formed which was filtered off, washed with cold methanol (5 mL) and dried *in vacuo* to give 141 mg of **3**·CH_2Cl_2·3H_2O (74 %). – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 1.20 (*s*, 18H, ^{t}Bu), 1.22 (*s*, 18H, ^{t}Bu), 3.49 (s, 6H, 2C*H*$_3$), 6.80 (*d*, 1H, Ar-*H*), 7.00 (d, 1H, Ar-*H*), 7.19 (*d*, 1H, Ar-*H*), 7.30 (*d*, 1H, Ar-*H*), 7.80 (*d*, 1H, Ar-*H*), 7.90 (*d*, 1H, Ar-*H*), 8.14 (*t*, 1H, H_β pyridine). – ^{13}C{^{1}H}NMR (100.4 MHz, CD_2Cl_2): δ = 30.36, 30.90, 32.65 (C(*C*H$_3$)$_3$), 35.66, 36.28, 36.67 (*C*(CH$_3$)$_3$), 17.5 (=C-*C*H$_3$), 165.5 (=*C*-CH$_3$), 117.6, 120.9, 124.1, 143.2, 144.2, 145.2, 151.0, 151.7, 159.3, (Ar). – IR (KBr, cm^{-1}): ν = 2961, 2905, 2868 (s, C–H), 1620 (vs, C=N). – MS (FD$^+$, CH_2Cl_2): *m/z* = 664 [M]$^+$. – $C_{38}H_{57}Cl_2N_3O_3S_2Zn$ (804.32): calcd. C 56.74, H 7.14, N 5.22, S 7.97; found C 57.08, H 7.15, N 5.08, S 6.75.

*[Zn(py^{t}BuN$_2$H$_2$Me$_2$S$_2$)] (**5**)*

$NaBH_4$ (0.37 mg, 10 mmol excess) was added slowly during 1 h under vigorous stirring to a solution of **3**·CH_2Cl_2·3H_2O (100 mg, 0.125 mmol) in MeOH (20 mL). The solvent was removed, and the solid residue was treated with H_2O (200 mL), neutralized with glacial acetic acid and extracted with CH_2Cl_2 (4 × 100 mL). The combined extracts were washed with H_2O (100 mL), dried over Na_2SO_4 and evaporated to dryness to give 70 mg of **5**·0.75 CH_2Cl_2 in 74 % yield. – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 1.24 (*s*, 18H, 2^{t}Bu), 1.49 (*s*, 18H, 2^{t}Bu), 3.44 (d, 6H, 2C*H*$_3$), 4.40 (*m*, 2H, C*H*), 6.90 (*d*, 2H, Ar-*H*), 7.24 (d, 2H, Ar-*H*), 7.43 (*d*, 2H, H_β pyridine), 7.93 (*t*, 1H, H_γ pyridine). – IR (KBr, cm^{-1}): ν = 3421 (w, N–H), 2963, 2905 (s, C–H). – MS (FD$^+$, CH_2Cl_2): *m/z* = 668 [M]$^+$. – $C_{37}H_{53}N_3S_2Zn$·0.75

CH_2Cl_2 (669.38): calcd. C 61.85, H 7.49, N 5.73, S 8.75; found C 61.48, H 8.10, N 5.87, S 8.78.

Bis-benzothiazoline ligand **4**

A solution of **3** (0.2 g, 0.3 mmol) in dichloromethane (20 mL) was combined with concentrated HCl (5 mL) and stirred for 3 h. The organic layer was separated from the aqueous phase, washed with water and dried over anhydrous Na_2SO_4. After filtration, the filtrate was evaporated to dryness *in vacuo* to give **4** in 40 % yield. – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 1.16 (s, 18H, 2C(CH_3)$_3$), 1.27 (2, 18H, 2C(CH_3)$_3$), 1.84 (d, 6H, 2CH$_3$), 6.66 (d, 2H, C$_6H_4$), 6.70 (d, 2H, C$_6H_4$), 6.78 (m, 2H, H_β pyridine), 7.56 (s, 2H, H_γ pyridine), 7.85 (d, 2H, N*H*). – ^{13}C{^{1}H} NMR (100.4 MHz, CD_2Cl_2): δ = 29.2, 31.5 (2C(*C*H$_3$)$_3$), 34.6, 35.5 (2*C*(CH$_3$)$_3$), 52.6 (CH$_3$), 77.91 (*C*CH$_3$), 106.6, 118.0, 120.7, 137.4, 143.4, 147.4, 148.4, 161.7 (Ar). – IR (KBr, cm^{-1}): ν = 3381 (w, N–H), 2960, 2962 (s, C–H). – MS (FD$^+$, CH_2Cl_2): *m/z* = 602 [M]$^+$. – $C_{37.5}H_{52}Cl_2N_3S_2$ (644.4): calcd. C 69.89, H 8.13, N 6.52, S 9.95; found C 69.45, H 8.83, N 6.60, S 9.12.

*py^{t}BuN$_2$H$_2$Me$_2$S$_2$-H$_2$ (**6**)*

*a) From [Zn(py^{t}BuN$_2$H$_2$Me$_2$S$_2$)] (**5**):* Aqueous HCl (37 %, 8 mL) was added to a solution of **5**·0.75 CH_2Cl_2 (300 mg, 0.41 mmol) in CH_2Cl_2 (40 mL), and the mixture was stirred for 2 h at 20 °C. The CH_2Cl_2 phase was separated from the aqueous phase, dried over anhydrous Na_2SO_4 and evaporated to dryness to afford a yellow solid of py^{t}BuN$_2$H$_2$Me$_2$S$_2$-H$_2$ (**6**). Yield 200 mg of **6**·2.5 CH_2Cl_2·1.5 CH_3OH (78 %).

*b) From **4**:* $NaBH_4$ (0.30 mg, 8 mmol excess) was added slowly under vigorous stirring to a solution of **4** (60 mg, 0.10 mmol) in MeOH (20 mL). The solvent was removed, and the solid residue was treated with H_2O (200 mL), neutralized with glacial acetic acid and extracted with CH_2Cl_2 (4 × 100 mL). The combined extracts were washed with H_2O (100 mL), dried over Na_2SO_4 and evaporated to dryness to give 35 mg of **6**·2.5 CH_2Cl_2·1.5 CH_3OH in 58 % yield. – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 1.20 (s, 18H, 2C(CH_3)$_3$), 1.31 (s, 18H, 2C(CH_3)$_3$), 2.02 (d, 6H, 2CH$_3$), 3.42 (m, 2H, C*H*-CH$_3$), 6.65 – 6.72 (2d, 2H, C$_6H_4$), 6.78 (m, 2H, C$_6H_4$), 7.54 – 7.60 (m, 3H, C$_6H_4$), 7.56 (d, 2H, N-H). – IR (KBr, cm^{-1}): ν = 3373 (w, N–H), 2959, 2900 (s, C–H), 2510 (w, S–H). – MS (FD$^+$, CH_2Cl_2): *m/z* = 606 [M]$^+$. – $C_{41.5}H_{68}Cl_5N_3O_2S_2$ (882.4): calcd. C 56.49, H 7.77, N 4.76, S 7.27; found C 56.20, H 8.65, N 4.67, S 6.51.

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