## Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 7415



# Synthesis and characterization of novel S,N and Se,N homodimetallic Ag(I)-complexes<sup>†</sup>

Ján Cvengroš,\* Elisabeth Maennel and Nico Santschi\*

*Received 2nd March 2012, Accepted 23rd April 2012* DOI: 10.1039/c2dt30509g

Novel C2-symmetric doubly bidentate Se,N and S,N-ligands based on a readily available Tröger's base backbone were synthesized and fully characterized. Their coordination properties were studied in dinuclear Ag(1)-complexes employing <sup>1</sup>H, <sup>77</sup>Se and <sup>1</sup>H–<sup>15</sup>N HETCOR NMR spectroscopy as well as X-ray diffraction crystallography. In solution, a single ligand can accommodate two silver atoms by coordination to nitrogen and sulfur or selenium. The investigations in the solid state revealed the presence of a pentacoordinated silver atom (NSO<sub>3</sub> and N<sub>3</sub>Se<sub>2</sub> donor sets are influenced by the solvent employed during the crystallization). In the solid state, the Ag(1)-complex with the S,N-ligand **2b** forms dimeric structures bridged by the two perchlorate counterions. The analogous Se,N-ligand **2c** coordinates to Ag(1) and forms polymeric enantiomerically pure helices, although the crystal is racemic.

#### Introduction

Recent tremendous development in the field of catalysis heavily relies on the application of various established ligands.<sup>1</sup> It is a common practice that one or several representatives of various ligand classes are screened upon designing a novel transformation - be it in an asymmetric or non-stereoselective manner. Regarding the immense arsenal of powerful sophisticated ligands accessible to researchers, this strategy usually proves successful and the new reactions can be performed with high efficiencies and selectivities. The development of new, potent and cheap ligands remains, however, a challenging task. The ever-increasing pressure of environmental and economic factors calls for the delivery of efficient ligands in a minimum number of steps starting from cheap materials. There are several strategies for the development of efficient ligands. Implementation of new backbone motifs and application of new elements as coordination sites certainly belong to the riskier approaches. Despite the fact that designing ligands from scratch might be a very laborious and lengthy task, it may also result in new systems with unprecedented reactivity. The application of bidentate ligands containing chalcogens is undoubtedly much less documented compared to the P,P; P,N or N,N alternatives.<sup>2</sup> Several examples of sulfur- and selenium-based ligands point out that the coordination properties of these atoms should not be ignored.<sup>3</sup>

nitrogen atoms.<sup>5</sup> Numerous Tröger's base analogues were successfully applied in various fields such as molecular recognition, bioorganic chemistry or supramolecular chemistry.<sup>6</sup> The reports on their use in catalysis are, however, scarce.<sup>7</sup> We have contemplated using the Tröger's base scaffold as a skeletal unit for a new class of ligands.<sup>8</sup> Herein we would like to report on our first efforts in the synthesis, characterization and coordination properties of novel S,N and Se,N ligands based on Tröger's base. **Results and discussion** 

Tröger's base<sup>4</sup> and its derivatives are typically mentioned in

the context of chiral molecules containing stable stereogenic

### Synthesis and characterization of the ligands

The synthesis starts with the formation of the 4,10-dibromo-Tröger's base 1 by the condensation of 2-bromo-4-methylaniline with paraformaldehyde in trifluoroacetic acid affording 1 in 98% yield.9 The subsequent lithium-bromine exchange followed by quenching with a suitable electrophile led directly to the S,Nand Se,N-ligands 2a-c (Table 1). The stability of the lithiated species seems to be rather low resulting in low efficiency of the nucleophilic substitution on the chalcogen center. The use of sulfur thus only led to a 19% yield of the S-butylated ligand 2a whereas butyl bromide originating from the lithium-bromine exchange acted as an alkylating agent.<sup>10</sup> The other by-products detected in the reaction mixture were the corresponding species bearing different substituents (BuS and H or BuS and Bu) arising from the incomplete reaction of the lithiated Tröger's base with sulfur. The yield of 2a could only be slightly increased when butyl iodide was added to the reaction mixture. However, upon applying more reactive electrophiles such as (PhS)<sub>2</sub> and PhSeCl, the anticipated ligands 2b and 2c were obtained in good vields.

Department of Chemistry and Applied Biosciences, HCI H230 Swiss Federal Institute of Technology, ETH Zürich, CH-8093 Zürich, Switzerland. E-mail: cvengros@inorg.chem.ethz.ch; Fax: +41 44 632 13 10; Tel: +41 44 633 43 31

<sup>†</sup>Electronic Supplementary Information (ESI) available. CCDC 865870 (S,N-ligand **2a**), 865869 (Se,N-ligand **2c**), 865871 (Ag-complex **3b**) and 865872 (Ag-complex **3c**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30509g

Table 1Synthesis of S,N and Se,N-ligands







Fig. 1 ORTEP representation of ligands 2a and 2c. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å): 2a: S1–C1 1.7652(19), S2–C13 1.7678(18), N1–C6 1.440(2), N1–C9 1.464(2), N2–C9 1.466(2). 2c: Se1–C2 1.9249(18), Se2–C18 1.9263(19), N1–C17 1.440(2), N2–C1 1.435(2), N1–C15 1.472(2), N2–C15 1.463(2).

The crystallization of **2a** by slow diffusion of hexane into dichloromethane and of **2c** by slow evaporation of its solution in dichloromethane yielded single crystals suitable for X-ray diffraction. The ORTEP views of the ligand molecules are shown in Fig. 1. The single crystal analysis did not reveal any abnormal features and the bond lengths and angles are in the range of other Tröger's base-analogues. The most characteristic structural feature of Tröger's base, the dihedral angle between the two aromatic planes, was found to be 96.3(5)° for **2a** and 99.1(6)° for **2c**.<sup>11,12</sup>

#### Synthesis and characterization of the silver(1) complexes

With the ligands in our hands, we studied their coordination properties in Ag(1)-complexes. Considering that selenium has an NMR-active isotope with spin  $\frac{1}{2}$ , it appeared promising to focus

on the Se,N-ligand 2c and its corresponding silver complex 3c. The latter was prepared by adding the solution of 2c in d<sub>8</sub>-THF to the solution of 2 equivalents of AgClO<sub>4</sub> in the same solvent. The <sup>1</sup>H, <sup>77</sup>Se and <sup>1</sup>H–<sup>15</sup>N HETCOR spectra recorded at 298 K indicated the formation of a single species, the disilver complex 3c. The comparison with the corresponding spectra of the free ligand revealed that the singlet of <sup>77</sup>Se shifted upfield from 377 ppm to 267 ppm, hence strongly suggesting the coordination of the selenium atom to silver (Fig. 2). Unfortunately, we did not observe the  ${}^{1}J$  coupling between silver and selenium probably due to a kinetically labile bond.<sup>13</sup> The variable temperature <sup>77</sup>Se NMR studies support this explanation as broadening of the signal was observed at lower temperatures, however, no coalescence occurred at temperatures as low as 195 K. Furthermore, the shift of the cross-peaks on the <sup>15</sup>N-axis in <sup>1</sup>H-<sup>15</sup>N HETCOR from 42.4 ppm to 49 ppm suggests the coordination of silver to the nitrogen atom. Additionally, significant changes in the chemical shifts of protons in the vicinity of selenium and nitrogen simultaneously corroborate the formation of these coordination bonds to silver.

Upon concentration, the NMR sample yielded a white solid which wasn't soluble in THF anymore. In general, the solubility of the compound obtained was limited. After significant efforts, we managed to obtain single crystals suitable for X-ray diffraction by vapor diffusion of pentane into a 1:1 THF–acetonitrile mixture. The corresponding ORTEP plot is shown in Fig. 3. The complex crystallizes in enantiomerically pure helices, whereas the whole crystal is racemic. The polymer consists of repeating  $[Ag_2(2c)_2(ClO_4)_2]$  units which ran along the *a* axis. The dihedral angle between the aromatic planes is  $102.88(14)^\circ$ .

The oxygen atoms of one of the perchlorate anions (Cl2) are disordered over two sites with site occupancy factors of 0.87 and 0.13. Each silver atom is pentacoordinated possessing either a distorted tetragonal pyramidal (Ag1,  $\tau = 0.10$ ) or a distorted trigonal-bipyramidal geometry (Ag2,  $\tau = 0.62$ ).<sup>14</sup> Silver(1) typically prefers a tetrahedral or linear arrangement<sup>15</sup> and, although known, the five coordinate geometry is less common.<sup>16</sup> For Ag1 the basal plane is formed by two *trans*-arranged nitrogen and selenium atoms from two different molecules of ligand **2c**. The apical site is occupied by a nitrogen donor atom of acetonitrile. The central silver atom lies 0.935 Å out of the N<sub>2</sub>Se<sub>2</sub> plane towards N5. Ag2 lies in the equatorial plane formed by two selenium atoms from two molecules of **2c** and the nitrogen atom of



Fig. 2 Comparison of <sup>1</sup>H, <sup>77</sup>Se and <sup>1</sup>H–<sup>15</sup>N HETCOR spectra of free ligand 2c and its Ag(1)-complex 3c.

acetonitrile. The axial sites are then occupied by nitrogen atoms N4 and N2 from two molecules of ligand 2c. To the best of our knowledge, there are no reports on crystal structures of analogous Ag(1) complexes with a  $N_3Se_2$  donor set. The most similar structures containing a pentacoordinated Ag(1)-atom describe the coordination of silver to two nitrogen and two selenium atoms with a fifth coordination site being occupied by another silver atom.<sup>17</sup> Comparison of the corresponding Ag–Se bond lengths from the Cambridge Structural Database (5 structures, selenium bearing phenyl or cyclopentadienyl rings) revealed that all Ag-Se bonds lie in the range of the reported structures (Fig. 3). The reported Ag-N distances for silver-tertiary dialkylarylamine complexes (4 hits in CSD) correspond to the bond lengths between silver and nitrogen atoms belonging to the ligand 2c, except for the bond Ag2-N4 (2.735(3) Å) which indicates a rather labile bond. Finally, the distances between silver and the nitrogen atom of acetonitrile (2.312(4) Å and 2.237(6) Å) fall in the middle of the range (from 2.066 Å<sup>18</sup> to 3.208 Å<sup>19</sup>) of 323 reported structures (with a mean value of 2.329 Å) containing acetonitrile coordinated to a silver atom.

In analogy to the previous complex synthesis, we have carried out experiments with the sulfur-containing ligand **2b**. However, considering the low sensitivity and usually very broad signals of <sup>33</sup>S NMR, we have limited our NMR investigations to <sup>1</sup>H and <sup>13</sup>C spectra. As expected, chemical shifts were affected upon coordination and the changes correspond well to the

observations made previously for 2c. The *exo*-benzylic protons thus shifted from 4.51 ppm to 5.14 ppm, *endo*-protons from 4.42 ppm to 3.97 ppm and the signal for the methylene bridge moved from 4.25 ppm to 5.07 ppm upon complexation to silver. Variations for the carbon signals were also registered, although to a lesser extent. For example, the methylene carbon shifted from 67.8 ppm to 68.6 ppm and the benzylic carbons from 55.5 ppm to 57.5 ppm.

To our delight, we were also able to grow a suitable crystal of **3b** for X-ray analysis by vapor diffusion of pentane into a mixture of acetonitrile, tetrahydrofuran and acetone. An ORTEP plot is shown in Fig. 4. Unfortunately, the necessity of adding acetone to the crystallization mixture, due to solubility issues, led also to the incorporation of this solvent into the crystal structure. The differences in the coordination geometries of the two Ag(I) complexes 3b and 3c could thus not be easily concluded as results of the two different donor atoms (Se vs. S). Instead of polymers, as observed for the complex 3c, dimeric species of composition  $[Ag_4(2b)_2(THF)_4(Me_2CO)_2(ClO_4)_4]$  are formed here. The dihedral angle between the aromatic planes is  $109.2(13)^{\circ}$ , a value that approaches the largest dihedral angles reported for Tröger's base analogues.<sup>12</sup> THF and both of the perchlorate anions are also coordinating, whereas one of the latter is bridging two Tröger's bases and the other is terminally coordinated. Furthermore, the entire terminal perchlorate anion is disordered over two sites with site occupancy factors of 0.73 and 0.27,





**Fig. 3** ORTEP representation of complex **3c**. Above is the asymmetric unit. Hydrogen atoms and the disordered solvent molecules (THF, CH<sub>3</sub>CN) are omitted for clarity. Below is the view of the polymeric structure. Hydrogen atoms, the disordered solvent molecules (THF, CH<sub>3</sub>CN) and perchlorate anions are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and bond angles (°): Ag1–N1 2.514(3), Ag1–N3 2.649(3), Ag1–N5 2.312(4), Ag1–Se1 2.7539(5), Ag1–Se2 2.6984(6), Ag2–N4 2.735(3), Ag2–N6 2.237(6), Ag2–Se4 2.6165(6), N5–Ag1–N1 131.75(13), N5–Ag1–N3 86.59(13), N1–Ag1–N3 141.63(11), N5–Ag1–Se2 118.81(11), N1–Ag1–Se2 72.08(8), N3–Ag1–Se2 91.92(7), N5–Ag1–Se1 100.01(11), N1–Ag1–Se1 98.83(8), N3–Ag1–Se1 68.07(7), Se2–Ag1–Se1 135.45(2), N6–Ag2–Se4 113.44(15), N6–Ag2–N4 91.31(18),

respectively. In the case of the bridging perchlorate anion, only the oxygen atoms are disordered over two sites (0.54 and 0.46). Finally, also the C56 and C57 of the tetrahydrofuran coordinated to silver are doubly disordered (0.60 and 0.40).

Se4-Ag2-N4 68.63(7), Se3-Ag2-N4 118.64(7), Se3-Ag2-Se4 138.59(2), N6-Ag2-Se3 107.26(15).

Within one dimer, two distinct silver atoms with different coordination environments are observed. The terminal ones coordinate to sulfur and nitrogen atoms of the ligand **2b** and the coordination sphere is completed with one molecule of each of acetone, tetrahydrofuran and perchlorate resulting in a severely distorted trigonal bipyramidal geometry around silver ( $\tau = 0.40$ ). Silver lies in the equatorial plane formed by the O1, O13 and S1 atoms. The axial positions are occupied by the N1 and O14 atoms. The axis is slightly bent as the N1–Ag1–O14 angle is 160.38(14)°.

The coordination environment around the central silver atoms differs only slightly from that of the terminal ones by the coordination of an additional perchlorate anion instead of acetone. The  $\tau$  value of 0.55 suggests that the geometry around these silver atoms should have more trigonal-bipyramidal character than in the previous case. Ag2(1), however, lies 0.648 Å out of the plane formed by the equatorial ligands O11, O12 and S2 towards O20. The comparison with 12 similar silver(I) complexes bridged by two perchlorate anions from CSD shows that the distances between silver and oxygen of the perchlorate anions (2.543(5) Å and 2.440(10) Å) in **3b** belong to the lower half of the reported values (from 2.353  ${\rm \AA}^{20}$  to 2.904  ${\rm \AA}^{21}$  with a mean value of 2.581 Å). Only one of these 12 structures contains a five coordinate Ag(I) atom.<sup>22</sup> Compared to the situation around the terminal silver atoms, the Ag2-S2 bond length is slightly shorter than the Ag1-S1 one (2.5702(13) Å vs. 2.6514(14) Å). On the other hand, Ag2-N2 is longer than Ag1-N1 (2.597(4) Å vs. 2.488(4) Å). The direct comparison of the bond lengths





**Fig. 4** ORTEP representation of complex **3b**. Above is the monomeric structure of **3b** containing all solvent molecules coordinated to the silver atom. Hydrogen atoms, the disordered THF molecules and perchlorate anions are omitted for clarity. Below is the dimeric structure of **3b** showing the bridging *via* two disordered perchlorate anions. Solvent molecules are partially omitted. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and bond angles (°): Ag1–S1 2.6514(14), Ag1–N1 2.488(4), Ag1–O14 2.495(4), Ag1–O1b 2.361(19), Ag1–O13 2.339(5), Ag2–S2 2.5702(13), Ag2–N2 2.597(4), Ag2–O12 2.543(5), Ag2–O11 2.425(5), Ag2–O20a 2.440(10), O13–Ag1–O1b 114.5(5), O13–Ag1–N1 100.62(17), O1b–Ag1–N1 103.7(5), O13–Ag1–O14 90.43(17), O1b–Ag1–O14 86.0(5), N1–Ag1–O14 160.38(14), O13–Ag1–S1 136.37(14), O1b–Ag1–S1 109.0(5), N1–Ag1–S1 71.13(9), O14–Ag1–S1 89.67(11), O11–Ag2–O20a 75.4(3), O11–Ag2–O12 103.25(17), O11–Ag2–S2 115.78(12), O20a–Ag2–S2 127.8(2), O12–Ag2–S2 121.46(12), O11–Ag2–N2 79.79(14), O20a–Ag2–N2 154.6(2), O12–Ag2–N2 77.59(13), S2–Ag2–N2 69.06(8).

between silver and the nitrogen of the synthesized ligands in 3c and 3b shows similar values in the range from 2.488(4) Å to 2.735(3) Å.

The mass spectrometric investigations corroborated the above mentioned observations. Uncalibrated matrix-assisted laser desorption/ionization (MALDI) mass spectrometry of material obtained through concentration of an NMR sample of **2b** (1.0 equiv.) and AgClO<sub>4</sub> (2.0 equiv.) in d<sub>8</sub>-THF indicated the presence of free ligand **2b**, Ag(**2b**)<sup>+</sup> (m/z 573.0588, found: 573.0666) and Ag(**2b**)<sup>+</sup> (m/z 1039.2126, found: 1039.2258). These findings hint towards a dimeric or polymeric structure in solution and in the absence of additional donors such as aceto-nitrile or acetone.<sup>23</sup> Application of the same method to **3c** crystallized from a THF–MeCN solution showed the same species:

**2c**,  $Ag(2c)^+$  (*m*/*z* 668.9477, found: 668.9571) and  $Ag(2c)_2^+$  (*m*/*z* 1228.9912, found: 1229.0072), hence further substantiating the polymeric nature found by X-ray diffractometry.

#### Conclusions

We have designed and readily synthesized a new class of Tröger's base inspired Se,N- and S,N-ligands. The complexation studies revealed that these structures can coordinate silver(i) atoms in a doubly bidentate fashion. In the solid state, polymeric one-dimensional structures are formed in the case of **3c**, whereas **3b** crystallizes as dimeric perchlorate-bridged species. This, however, is proposed to stem from the method of crystallization and not from the donor atom (S *vs.* Se) employed. In both cases, a rather uncommon, five coordinate geometry around the silver atom is observed. Although the incorporation of acetone into the crystal structure of **3b** hampered the direct comparison with **3c**, it suggests that this type of complex could be applied as Lewis acids for the activation of carbonyl compounds. Furthermore, since both sulfenyl and selenenyl groups usually act as good  $\pi$ -acceptors, their combination with a nitrogen atom (being a good donor) bodes well for an interesting catalytic performance of such structures. Applications of these systems in supramolecular architectures as well as their catalytic activity are currently being studied in our laboratory.

#### Experimental

The reactions were carried out in dried glassware under argon using Schlenk techniques. All solvents were freshly distilled under argon from an appropriate drying agent before use. Flash chromatography was performed with Fluka silica gel 60. NMR spectra were measured on Bruker Avance 300, 400 and 500 spectrometers. The chemical shifts are referenced to TMS (<sup>1</sup>H and <sup>13</sup>C) and Me<sub>2</sub>Se (<sup>77</sup>Se) as external standards. High-resolution mass spectra were measured by the MS-Service of the "Laboratorium für Organische Chemie der ETH". Elemental analyses were carried out by the Laboratory of Microelemental Analysis (ETH Zürich). X-ray structures were measured on a Bruker APEX2 CCD area detector diffractometer with Mo-K<sub> $\alpha$ </sub> radiation. Single crystals were coated at room temperature with perfluoroalkylether oil and mounted on a 0.1 mm glass capillary. The structures were solved by direct methods in SHELXTL and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against  $F^2$ ). Crystal data and details of data collection and structure refinement for **3b** and **3c** are given in Table 2. CCDC 865870 (S,Nligand **2a**), CCDC 865869 (Se,N-ligand **2c**), CCDC 865871 (Ag-complex **3b**) and CCDC 865872 (Ag-complex **3c**) contain the supplementary crystallographic data for this paper and are also available in the ESI† for this article.

#### 4,10-Bis(butylthio)-2,8-dimethyl-6,12-dihydro-5,11methanodibenzo[*b*,*f*][1,5]diazocine (2a)

4,10-Dibromo-TB 1 (0.52 g, 1.27 mmol) was placed in a Schlenk flask under argon and dry THF (15 mL) was added. Then it was cooled down to -78 °C and *n*-BuLi (1.6 M in hexane, 1.7 mL, 2.67 mmol, 2.1 equiv.) was added dropwise to form a pale-yellow suspension. After 5 min, sulfur (0.11 g, 3.43 mmol, 2.7 equiv.) was added in one portion and the resulting yellow thick mixture was stirred overnight at ambient temperature. A clear orange solution had formed. Butyl iodide (0.39 mL, 3.43 mmol, 2.7 equiv.) was added and stirring was continued for 4 h at RT. The reaction was guenched with a saturated aqueous solution of NH<sub>4</sub>Cl (10 mL) and the mixture was extracted with EtOAc ( $3 \times 10$  mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The crude mixture was purified by flash chromatography (SiO<sub>2</sub> (100 g), Hex–EA = 30:1) to give a white solid. Yield: 176 mg (0.41 mmol, 33%). M.p. = 104-107 °C. C<sub>25</sub>H<sub>34</sub>N<sub>2</sub>S<sub>2</sub> requires 70.37% C; 8.03% H; 6.57% N. Found:

 Table 2
 Details of crystal data and structure refinement for complexes 3b and 3c

Compound	3b	3c
Empirical formula	C <sub>80</sub> H <sub>96</sub> Ag <sub>4</sub> Cl <sub>4</sub> N <sub>4</sub> O <sub>22</sub> S <sub>4</sub>	C <sub>62</sub> H <sub>58</sub> Ag <sub>2</sub> N <sub>6</sub> Se <sub>4</sub> ,2(ClO <sub>4</sub> ),0.38(C <sub>4</sub> H <sub>8</sub> O), 0.62(CH <sub>3</sub> CN)
Formula weight	2167.13	1670.45
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P2_1/c$
Unit cell dimensions: $a$ (Å)	10.6111(3)	13.9683(3)
<i>b</i> (Å)	11.8157(3)	21.6538(4)
c(Å)	18.9074(5)	21.3918(4)
$\alpha$ (°)	86.053(2)	90
$\beta(\circ)$	89.515(2)	94.7900(10)
$\gamma$ (°)	64.611(2)	90
Volume (Å <sup>3</sup> )	2135.95(10)	6447.7(2)
Z	1	4
Density (Mg $m^{-3}$ )	1.685	1.721
Absorption coefficient $(mm^{-1})$	1.201	3.016
F(000)	1100	3524
Crystal size (mm)	$0.20 \times 0.19 \times 0.10$	$0.24 \times 0.16 \times 0.10$
Crystal habit	Prism	Prism
$\Theta$ range for data collection	1.08 to 27.10°	1.34 to 28.70°
Limiting indices	$-13 \le h \le 13, -15 \le k \le 15, -24 \le l \le 24$	$-17 \le h \le 18, -29 \le k \le 29, -28 \le l \le 28$
Reflections collected	23 087	77 242
Independent reflections	9403 [ $R(int) = 0.0500$ ]	16635[R(int)=0.0436]
Completeness to $\theta = 27.10$	99.7%	99.9%
Max. and min. transmission	0.8883 and 0.7934	0.7504 and 0.5326
Data/restraints/parameters	9403/0/538	16 635/24/947
Goodness-of-fit on $F^2$	1.021	1.017
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0497, wR_2 = 0.1080$	$R_1 = 0.0452, wR_2 = 0.0988$
R indices (all data)	$R_1 = 0.0831, wR_2 = 0.1261$	$R_1 = 0.0803, WR_2 = 0.1165$
Largest diff. peak and hole (e $Å^{-3}$ )	1.207 and -0.851	2.881 and -2.155

69.51% C; 8.13% H; 6.11% N. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ [ppm] 1.00 (t,  ${}^{3}J$  = 7.3 Hz, 6H, CH<sub>3</sub>), 1.56 (m, 4H, CH<sub>2</sub>), 1.77 (m, 4H, CH<sub>2</sub>), 2.25 (s, 6H, CH<sub>3</sub>), 2.97 (m, 4H, CH<sub>2</sub>), 4.30 (d,  ${}^{2}J$  = 17.1 Hz, 2H, ArCH<sub>endo</sub>N), 4.36 (s, 2H, NCH<sub>2</sub>N), 4.51 (d,  ${}^{2}J$  = 17.1 Hz, 2H, ArCH<sub>endo</sub>N), 6.56 (s, 2H, Ar-H), 6.83 (s, 2H, Ar-H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ [ppm] 14.1, 21.5, 22.7, 31.1, 31.3, 54.8 (CH<sub>2</sub>N), 68.1 (NCH<sub>2</sub>N), 124.0, 124.4, 128.8, 133.5, 134.4, 141.8. HRMS (ESI): calcd *m*/*z* for C<sub>25</sub>H<sub>35</sub>N<sub>2</sub>S<sub>2</sub>: 427.2236 ([MH]<sup>+</sup>), found: 427.2237 ([MH]<sup>+</sup>).

#### 2,8-Dimethyl-4,10-bis(phenylthio)-6,12-dihydro-5,11methanodibenzo[*b*,*f*][1,5]diazocine (2b)

4,10-Dibromo-TB 1 (0.50 g, 1.23 mmol) was placed in a Schlenk flask under argon and dry THF (20 mL) was added. The solution was then cooled to -78 °C and n-BuLi (1.6 M in hexane, 1.95 mL, 3.12 mmol, 2.54 equiv.) was added dropwise to form a pale-yellow suspension. After 5 min, diphenyl disulfide (0.80 g, 3.66 mmol, 2.98 equiv.) was added under an argon counterflow and the resulting mixture was allowed to slowly warm to RT over 20 h. The reaction mixture was poured onto 50% NH<sub>4</sub>Cl solution (100 mL). The organic layer was separated and the aqueous one was extracted once with additional EtOAc (50 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and finally concentrated under reduced pressure to give a yellow oil. The product (350 mg, 0.75 mmol, 61%) was precipitated as a white solid upon treatment with hexane (100 mL). M.p. = 174-176 °C.  $C_{29}H_{26}N_2S_2$  requires 74.64% C; 5.62% H; 6.00% N. Found: 74.58% C; 5.77% H; 5.98% N. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] 2.09 (s, 6H, CH<sub>3</sub>), 4.38 (d, <sup>2</sup>J = 16.9 Hz, 2H, ArCH<sub>endo</sub>N), 4.39 (s, 2H, NCH<sub>2</sub>N), 4.58 (d,  $^{2}J =$ 17.4 Hz, 2H, ArCH<sub>exo</sub>N), 6.56 (s, 2H, Ar-H), 6.61 (s, 2H, Ar-H), 7.32–7.41 (m, 6H, Ar-H), 7.47–7.49 (m, 4H, Ar-H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ [ppm] 21.1, 55.2 (CH<sub>2</sub>N), 67.9 (NCH<sub>2</sub>N), 125.4, 127.7, 128.1, 128.8, 129.6, 132.9, 133.5, 133.7, 134.6, 142.2. HRMS (ESI): calcd m/z for  $C_{29}H_{27}N_2S_2$ : 467.1610 ([MH]<sup>+</sup>), found: 467.1619 ([MH]<sup>+</sup>).

#### 2,8-Dimethyl-4,10-bis(phenylselanyl)-6,12-dihydro-5,11methanodibenzo[*b*,*f*][1,5]diazocine (2c)

The title compound was synthesized in analogy to 2b. Phenylselenyl chloride (0.70 g, 3.66 mmol, 2.98 equiv.) was used instead of diphenyl disulfide. The crude product was treated repeatedly with hexane until the washings were colorless. The title compound was obtained as an off-white microcrystalline solid (550 mg, 0.98 mmol, 80%). M.p. = 228-230 °C. C<sub>29</sub>H<sub>27</sub>N<sub>2</sub>Se<sub>2</sub> requires C 62.15%; H 4.68%; N 5.00%. Found: C 61.98%; H 4.77%; N 5.00%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ [ppm] 2.07 (s, 6H, CH<sub>3</sub>), 4.37 (d,  ${}^{2}J$  = 17.7 Hz, 2H, ArCH<sub>en-</sub>  $_{do}$ N), 4.39 (s, 2H, NC $H_2$ N), 4.56 (d,  $^2J = 17.1$  Hz, 2H, ArC $H_{e-1}$ <sub>ro</sub>N), 6.56 (s, 2H, Ar-H), 6.61 (s, 2H, Ar-H), 7.35–7.43 (m, 6H, Ar-H), 7.62–7.67 (m, 4H, Ar-H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ [ppm] 21.1, 55.3 (CH<sub>2</sub>N), 67.8 (NCH<sub>2</sub>N), 125.4, 128.4, 128.6, 128.8, 129.7, 130.7, 135.1, 136.3, 142.5 (one aromatic carbon was not found). HRMS (ESI): calcd m/z for C<sub>29</sub>H<sub>27</sub>N<sub>2</sub>Se<sub>2</sub>: 563.0504 ([MH]<sup>+</sup>), found: 563.0498 ([MH]<sup>+</sup>).

#### Ag<sub>2</sub>(2b)(ClO<sub>4</sub>)<sub>2</sub> (3b)

Ligand **2b** (20.7 mg, 44 µmol) and AgClO<sub>4</sub> (18.2 mg, 88 µmol, 2 equiv.) were weighed into a NMR tube, then dissolved in  $d_8$ -THF (0.8 mL) to yield a colorless solution. It was shaken for 10 min. After recording the NMR-spectra, the solvent was removed affording a white solid (38 mg, 43 µmol, 97%). <sup>1</sup>H-NMR (400 MHz,  $d_8$ -THF):  $\delta$  [ppm] = 2.05 (s, 6H, *CH*<sub>3</sub>), 3.93 (d, <sup>2</sup>J = 17.1 Hz, 2H, ArC*H*<sub>endo</sub>N), 5.02 (s, 2H, NC*H*<sub>2</sub>N), 5.10 (d, <sup>2</sup>J = 17.1 Hz, 2H, ArC*H*<sub>exo</sub>N), 6.69 (s, 2H, Ar-*H*), 6.70 (s, 2H, Ar-*H*), 7.37–7.46 (m, 6H, Ar-*H*), 7.60–7.62 (m, 4H, Ar-*H*). <sup>13</sup>C-NMR (100 MHz,  $d_8$ -THF):  $\delta$  [ppm] = 20.8 (*C*H<sub>3</sub>), 58.5 (*C*H<sub>2</sub>N), 69.6 (N*C*H<sub>2</sub>N), 127.8, 129.2, 129.5, 130.4, 130.5, 130.8, 131.9, 134.8, 136.6, 141.3. HRMS (ESI): calcd *m*/*z* for C<sub>29</sub>H<sub>26</sub>AgN<sub>2</sub>S<sub>2</sub>: 573.0588 ([Ag(**2b**)]<sup>+</sup>), found: 573.0666 ([Ag(**2b**)]<sup>+</sup>).

#### Ag<sub>2</sub>(2c)(ClO<sub>4</sub>)<sub>2</sub> (3c)

Ligand **2c** (25 mg, 45 µmol) and silver perchlorate (20.1 mg, 97 µmol, 2 equiv.) were weighed into a NMR-tube and  $d_8$ -THF (0.8 mL) was added. It was shaken for 10 min. After recording the NMR-spectra, the solvent was removed affording a white solid (43 mg, 44 µmol, 98%). <sup>1</sup>H-NMR (400 MHz,  $d_8$ -THF):  $\delta$  [ppm] 2.06 (s, 6H, *CH*<sub>3</sub>), 3.76 (d, <sup>2</sup>*J* = 17.0 Hz, 2H, ArCH<sub>endo</sub>N), 4.97 (s, 2H, NCHN), 5.09 (d, <sup>2</sup>*J* = 17.0 Hz, 2H, ArCH<sub>exo</sub>N), 6.72 (s, 2H, Ar-H), 6.91 (s, 2H, Ar-H), 7.37 (t, <sup>3</sup>*J* = 7.3 Hz, 4H, Ar-H), 7.44 (t, <sup>3</sup>*J* = 7.3 Hz, 2H, Ar-H), 7.72 (d, <sup>3</sup>*J* = 7.1 Hz, 2H, Ar-H). <sup>13</sup>C-NMR (100 MHz,  $d_8$ -THF):  $\delta$  [ppm] = 20.5 (CH<sub>3</sub>), 59.0 (CH<sub>2</sub>N), 69.1 (NCH<sub>2</sub>N), 128.3, 128.5, 129.0, 129.3, 130.0, 130.6, 131.8, 135.6, 136.6, 142.8. HRMS (ESI): calcd *m*/*z* for C<sub>29</sub>H<sub>26</sub>AgN<sub>2</sub>Se<sub>2</sub>: 668.9477 ([Ag(**2c**)]<sup>+</sup>), found: 668.9571 ([Ag(**2c**)]<sup>+</sup>).

#### Notes and references

- (a) T. P. Yoon and E. N. Jacobsen, *Science*, 2003, **299**, 1691–1693;
   (b) *Privileged Chiral Ligands and Catalysts*, ed. Q.-L. Zhou, Wiley-VCH, Weinheim, 2011.
- 2 (a) Phosphorus Ligands in Asymmetric Catalysis, ed. A. Börner, Wiley-VCH, Weinheim, 2008, vol. I–III; (b) F. Fache, E. Schulz, M. L. Tommasino and M. Lemaire, Chem. Rev., 2000, 100, 2159–2232; (c) C. A. Caputo and N. D. Jones, Dalton Trans., 2007, 4627–4640; (d) A. A. Mohamed, Coord. Chem. Rev., 2010, 254, 1918–1947.
- 3 (a) K. Hiroi and T. Sone, Curr. Org. Synth., 2008, 5, 305–320; (b) K. Hiroi, in Handbook of Organopalladium Chemistry for Organic Synthesis, ed. E.-i. Negishi, John Wiley & Sons, Inc., 2002, vol. 1, pp. 67–79.
- 4 J. Tröger, J. Prakt. Chem., 1887, 36, 225-245.
- 5 (a) B. G. Bag, Curr. Sci., 1995, 68, 279–288; (b) M. Demeunynck and A. Tatibouet, in Progress in Heterocyclic Chemistry, ed. G. W. Gribble and T. L. Gilchrist, Elsevier Science Ltd., Oxford, 1999, vol. 11, p. 1; (c) M. Valík, R. M. Strongin and V. Král, Supramol. Chem., 2005, 17, 347–367; (d) B. Dolenský, J. Elguero, V. Král, C. Pardo and M. Valík, Adv. Heterocycl. Chem., 2007, 93, 1–56; (e) S. Sergeyev, Helv. Chim. Acta, 2009, 92, 415–444.
- 6 Additional examples of recent applications not covered by the reviews in 5: (a) S. Sergeyev, D. Didier, V. Boitsov, A. Teshome, I. Asselberghs, K. Clays, C. M. L. V. Velde, A. Plaquet and B. Champagne, *Chem.-Eur. J.*, 2010, **16**, 8181–8190; (b) Y.-M. Jeon, G. S. Armatas, D. Kim, M. G. Kanatzidis and C. A. Mirkin, *Small*, 2009, **5**, 46–50; (c) P. R. Brotherhood, I. J. Luck and M. J. Crossley, *Magn. Reson. Chem.*, 2009, **47**, 257–262; (d) C. Michon, M.-H. Goncalves-Farbos and J. Lacour, *Chirality*, 2009, **21**, 809–817; (e) E. B. Veale, D. O. Frimannsson, M. Lawler and T. Gunnlaugsson, *Org. Lett.*, 2009, **11**,

View Online

4040–4043; (*f*) Z. Wu, M. Tang, T. Tian, J. Wu, Y. Deng, X. Dong, Z. Tan, X. Weng, Z. Liu, C. Wang and X. Zhou, *Talanta*, 2011, **87**, 216–221; (*g*) E. B. Veale and T. Gunnlaugsson, *J. Org. Chem.*, 2010, **75**, 5513–5525; (*h*) S. Satishkumar and M. Periasamy, *Tetrahedron: Asymmetry*, 2009, **20**, 2257–2262.

- 7 (a) H. Wu, X. M. Chen, Y. Wan, L. Ye, H. Q. Xin, H. H. Xu, C. H. Yue, L. L. Pang, R. Ma and D. Q. Shi, *Tetrahedron Lett.*, 2009, **50**, 1062–1065; (b) Y. Goldberg and H. Alper, *Tetrahedron Lett.*, 1995, **36**, 369–372; (c) H. U. Blaser, H. P. Jalett, W. Lottenbach and M. Studer, *J. Am. Chem. Soc.*, 2000, **122**, 12675–12682; (d) D. R. Jensen, J. S. Pugsley and M. S. Sigman, *J. Am. Chem. Soc.*, 2001, **123**, 7475–7476; (e) M. Harmata and M. Kahraman, *Tetrahedron: Asymmetry*, 2000, **11**, 2875–2879; (f) B. Minder, M. Schurch, T. Mallat and A. Baiker, *Catal. Lett.*, 1995, **31**, 143–151; (g) Y-M. Shen, M.-X. Zhao, J. Xu and Y. Shi, *Angew. Chem., Int. Ed.*, 2006, **45**, 8005–8008; (h) D. Didier and S. Sergeyev, *ARKIVOC*, 2009, 124–134; (i) E. Poli, E. b. Merino, U. Díaz, D. Brunel and A. Corma, *J. Phys. Chem.*, C, 2011, **115**, 7573–7585; (j) X. Du, Y. L. Sun, B. E. Tan, Q. F. Teng, X. J. Yao, C. Y. Su and W. Wang, *Chem. Commun.*, 2010, **46**, 970–972.
- 8 For reports on ligands based on Tröger's base see e.g.: (a) U. Kiehne, T. Weilandt and A. Luetzen, Eur. J. Org. Chem., 2008, 2056–2064; (b) T. Weilandt, U. Kiehne, J. Bunzen, G. Schnakenburg and A. Luetzen, Chem.–Eur. J., 2010, 16, 2418–2426; (c) M. S. Khoshbin, M. V. Ovchinnikov, C. A. Mirkin, J. A. Golen and A. L. Rheingold, Inorg. Chem., 2006, 45, 2603–2609.
- 9 S. Sergeyev and F. Diederich, Chirality, 2006, 18, 707-712.
- 10 For examples of similar reactivity see e.g.: B. J. Al-Hourani, J. P. Bravo-Vasquez, L. R. H. High and H. Fenniri, *Tetrahedron Lett.*, 2007, 48, 9144–9147.
- 11 For the report on the smallest dihedral angle (84.06°) in benzoid Tröger's base systems, see: Q. Xin, X.-T. Tao, F.-Z. Wang, J.-L. Sun, D.-C. Zou, F.-J. Wang, H.-J. Liu, Z. Liu, Y. Ren and M.-H. Jiang, *Org. Electron.*, 2008, 9, 1076–1086.
- 12 For the report on the largest dihedral angle (113.15°) in benzoid Tröger's base systems, see: F. Hof, D. M. Scofield, W. B. Schweizer and F. Diederich, Angew. Chem., Int. Ed., 2004, 43, 5056–5059.

- 13 J. R. Black, N. R. Champness, W. Levason and G. Reid, J. Chem. Soc. Dalton Trans., 1995, 3439–3445.
- 14 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, J. Chem. Soc., Dalton Trans., 1984, 1349–1956.
- 15 (a) T. C. W. Mak and X.-L. Zhao, in *Encyclopedia of Inorganic and Bio-inorganic Chemistry*, John Wiley & Sons, Ltd., 2011; (b) D. Venkataraman, Y. H. Du, S. R. Wilson, K. A. Hirsch, P. Zhang and J. S. Moore, *J. Chem. Educ.*, 1997, **74**, 915–918.
- 16 For examples of five coordinate Ag(1)-complexes, see: (a) A. J. Blake, N. R. Champness, P. A. Cooke, J. E. B. Nicolson and C. Wilson, J. Chem. Soc., Dalton Trans., 2000, 3811–3819; (b) K. A. Hirsch, S. R. Wilson and J. S. Moore, Inorg. Chem., 1997, 36, 2960–2968; (c) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, Angew. Chem., Int. Ed. Engl., 1995, 34, 1895–1898; (d) G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, J. A. Ripmester and D. D. M. Rayner, Angew. Chem., Int. Ed. Engl., 1998, 37, 1407–1409; (e) P. L. Caradoc-Davies, L. R. Hanton and W. Henderson, J. Chem. Soc., Dalton Trans., 2001, 2749–2755; (f) L. P. Wu, J. Dai, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and Y. Ohno, J. Chem. Soc. Dalton Trans., 1998, 3255–3261.
- 17 Crystal structures CCDC 767271, CCDC 767278, CCDC 768223, CCDC 768224 deposited with the Cambridge Crystallographic Data Centre by C. Thone, N. Narro and P. G. Jones.
- 18 Y. Zhang, A. M. Santos, E. Herdtweck, J. Mink and F. E. Kuhn, New J. Chem., 2005, 29, 366–370.
- 19 A. Cingolani, Effendy, D. Martini, C. Pettinari, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2006, **359**, 2183–2193.
- 20 S. Y. Lee, J. H. Jung, J. J. Vittal and S. S. Lee, Cryst. Growth Des., 2010, 10, 1033–1036.
- 21 A. Bayler, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1998, **37**, 4353– 4359.
- 22 C.-C. Wang, C.-H. Yang, S.-M. Tseng, S.-Y. Lin, T.-Y. Wu, M.-R. Fuh, G.-H. Lee, K.-T. Wong, R.-T. Chen, Y.-M. Cheng and P.-T. Chou, *Inorg. Chem.*, 2004, 43, 4781–4783.
- 23 An alternative explanation for the observed MS-spectrum is that the Ag (2b)<sup>+</sup> species are in equilibrium with Ag(2b)<sub>2</sub><sup>+</sup>, free ligand 2b and solvated cations Ag<sup>+</sup>.