Inorganica Chimica Acta 423 (2014) 268-280

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Salicylaldehyde-(2-hydroxyethyl)imine – A flexible ligand for group 13 and 14 elements

Lydia E.H. Paul^a, Ines C. Foehn^a, Anke Schwarzer^a, Erica Brendler^b, Uwe Böhme^{a,*}

^a Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Straße 29, D-09599 Freiberg, Sachsen, Germany ^b Institut für Analytische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Straße 29, D-09599 Freiberg, Sachsen, Germany

ARTICLE INFO

Article history: Received 26 May 2014 Received in revised form 5 August 2014 Accepted 7 August 2014 Available online 1 September 2014

Keywords: Schiff base ligands X-ray diffraction Silicon Germanium Tin Indium

ABSTRACT

The reaction of salicylaldehyde-(2-hydroxyethyl)imine (H₂L), **1**, with organoelement halides from group 13 and 14 leads to a variety of coordination compounds. Depending on the size of the central atom and the organic substituents, tetra-, penta- or hexacoordinated complexes emerge. When the central atom of the complex has a small atom radius and small substituents, like methyl groups, coordination number four is preferred. Thereby macrocyclic compounds of the composition $L_2(SiMeR)_2$ (R = Me, cyclohexyl) are formed. With phenyl substituted element halides Ph₂ECl₂ pentacoordinated complexes LEPh₂ (E = Si, Ge, Sn) were isolated. Hexacoordinated complexes of the composition L_2E (E = Si, Sn) were obtained from ECl₄ and **1**. A surprising result was obtained from the reaction of **1** with InCl₃. The resulting complex is a monoanionic trimer, obeying the composition [HNEt₃][L₃In₃Cl₃(μ^3 -OH)]·(DME)₂(THF) in the solid state structure. The prepared compounds were characterised by NMR and IR spectroscopy, elemental and X-ray structure analysis. Furthermore solid state NMR measurements and chemical shift tensor analysis with the help of quantum chemical methods were used to analyse the electron density distribution around the central atoms of several products. The results of this study demonstrate the structural variety that can be created with a single O,N,O' chelating ligand.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Schiff bases in general are versatile ligands [1-3]. Salicylaldehyde-(2-hydroxyethyl)imine $(H_2L)^1$ has shown to be a good coordination partner for various elements or metals. Numerous complexes have been prepared and characterised, see for instance the zinc complexes published by Dey et al. [4]. Salicylaldehyde-(2-hydroxyethyl)imine is able to form stable complexes with transition metals [5] and with group 14 elements [6]. Within these complexes, the O donor atoms can act as bridge between metal centres yielding either polynuclear complexes [6] or complexes with different stoichiometry for the same metal [1].

Silicon and tin Schiff base complexes are a fast developing field of research [7] which is due to their various possible applications. These complexes can exhibit fungicidal [8,9], bactericidal [10], antimicrobial [11] or bacteriostatic [12] properties. In some cases

E-mail address: Uwe.Boehme@chemie.tu-freiberg.de (U. Böhme).

it was shown that they are potent antitumor reagents [9]. Therefore the large number of recently published reports regarding Si/ Sn complexes with tridentate O,N,O'-ligands is not surprising [13–20]. Most of known O,N,O'-ligands show a imine [19,21], amine [20] or aza [16] moiety. In comparison only few publications exist dealing with germanium [6,22], indium [23] and aluminium [24] Schiff base complexes.

The focus of the presented work lies on the synthesis and characterization of new complexes with group 13 and 14 elements as central atom and salicylaldehyde-(2-hydroxyethyl)imine as possible chelating ligand. Feasible similarities and/or differences in complex formation, coordination numbers and crystal structures are investigated. In addition, solid state NMR spectra are recorded from selected substances to determine the silicon and tin NMR chemical shift tensors.

2. Experimental

2.1. General considerations

All chemicals obtained from commercial suppliers were used as received. Since both the educts and the synthesized complexes are sensitive to moisture, preparation was performed in Schlenk tubes







^{*} Corresponding author. Tel.: +49 3731 392050; fax: +49 3731 394058.

¹ The chemical name "salicylaldehyde-(2-hydroxyethyl)imin" is used throughout this paper. It reflects the preparation and functionality of the ligand system in a proper way. Alternative names would be: 2-(salicylidenamino)ethanol or (E)-2-{[[(2-hydroxyethyl)imino]methyl}phenol.

under argon atmosphere using anhydrous and air-free solvents. Melting points were determined with a Polytherm A from Wagner & Munz using samples in sealed capillaries. Standard ¹H, ¹³C, ¹¹⁹Sn, and ²⁹Si NMR solution spectra were recorded on a Bruker DPX 400 spectrometer at 293 K [¹H (400.13 MHz), ¹³C (100.61 MHz), ²⁹Si (79.49 MHz), ¹¹⁹Sn (149.17 MHz)]. ¹H, ¹³C, ²⁹Si chemical shifts are reported relative to tetramethylsilane, ¹¹⁹Sn chemical shifts relative to tetramethyltin as external reference. Used solvents are specified below.

The solid-state NMR spectra were recorded with a Bruker Avance 400 WB spectrometer operating at 79.52 MHz (²⁹Si) and 149.24 MHz (¹¹⁹Sn), respectively. ²⁹Si spectra were recorded by CPMAS using a 7 mm probe, 5 ms contact time and a spinning frequency of 4 kHz, if not noted otherwise. The chemical shift scale was referenced with Q_8M_8 (strongest shielded Q⁴-group at -109 ppm relative to TMS). ¹¹⁹Sn solid state NMR spectra were obtained using a 4 mm probe and single pulse excitation applying 30° pulses and repetition times of 30 s. The chemical shift was referenced with SnO₂ (-603 ppm relative to tetramethyltin) [25]. Principal components of the chemical shift tensor were calculated from spinning side band spectra using DMFIT [26] and HBA [27].

IR spectra were recorded in the range $400-4000 \text{ cm}^{-1}$ at room temperature with a Nicolet 380 FT-IR spectrometer. The samples (KBr pellets) were prepared under N₂ atmosphere. Elemental analyses were performed with a Vario Micro CHNS.

2.2. Synthesis of the ligand salicylaldehyde-(2-hydroxyethyl)imine (1) [4]

2-Amino-1-ethanol (6.11 g, 0.1 mol) was solved in methanol (50 mL) and slowly added to a solution of salicylaldehyde (12.21 g, 0.1 mol) in methanol (100 mL). The resulting reaction mixture was refluxed for 1.5 h. After cooling to room temperature, the solvent was removed under reduced pressure. The raw product was purified by fractioned distillation yielding an oily, orange-yellow liquid. Yield: 12.3 g (74.5%); b.p. 156 °C at 0.6 kPa.

¹H NMR (CDCl₃): δ 3.65 (t, 2H, CH₂, ${}^{3}J_{HH}$ = 5.0 Hz); 3.83 (t, 2H, CH₂, ${}^{3}J_{HH}$ = 5.0 Hz); 6.81–7.29 (m, 4H, CH_{ar}); 8.27 (s, 1H, H–C=N). ¹³C NMR (CDCl₃): δ 61.3, 61.9 (CH₂); 117.3, 118.5, 118.6, 131.6, 132.7, 161.9 (CH_{ar}); 166.8 (C=N).

IR: v 3363 (OH-valence); 1279 (OH fingerprint); 1151, 1067 (C–O valence); 1633 (C=N valence); 1582, 1528 (C_{ar} valence); 758 (C–H deformation) cm⁻¹.

2.3. General procedure for the synthesis of the coordination compounds **2–11**

The appropriate dichlorodiorganylsilane, -germane or -stannane, SnCl₄ or InCl₃ was dissolved in tetrahydrofuran and cooled down with an ice bath to 273 K. Triethylamine was added slowly, afterwards a solution of **1** in tetrahydrofuran was added dropwise at this temperature. Warming up to room temperature and stirring for several days at r.t. forms a white precipitate. This triethylamine hydrochloride was collected via suction filtration, washed with tetrahydrofuran three times (à 10 mL). The solvent was removed completely under reduced pressure to give a yellow residue. The raw material was solved in dimethoxyethane (DME) and stored at 276 K for crystallisation process. Collection of the solid via suction filtration and drying in vacuum yield a bulk material for further analysis.

2: Dichlorodimethylstannane (4.00 g, 18.2 mmol) in THF (60 mL), triethylamine (3.68 g, 36.4 mmol) and **1** (3.0 g, 18.2 mmol) in THF (60 mL) yield intense yellow crystals (1.4 g, 24.7%), m.p. 432.9 K. *Anal.* Calc. for the complex (LSnMe₂)₂ with $C_{22}H_{30}N_2O_4Sn_2$ (623.872 g/mol): C, 42.36; H, 4.85; N, 4.49. Found: C, 41.34; H, 4.83; N, 4.40%. The sample was dried carefully in

vacuum before performing the elemental analysis. Thereby most of the containing dichlorodimethylstannane was removed. Otherwise the expected values for the complex found in the X-ray structure would be the following: *Anal.* Calc. for the complex (LSnMe₂)₄SnCl₂Me₂ with C₄₆H₆₆Cl₂N₄O₈Sn₅ (1467.49 g/mol): C, 37.65; H, 4.53; N, 3.82%.

¹¹⁹Sn NMR (CDCl₃): δ –155.5 ppm (weak, broad).

¹¹⁹Sn NMR (CPMAS): δ –301 ppm.

¹H NMR (CDCl₃): δ 0.67, 1.61 (Sn–CH₃); 3.70 (t, 2H, CH₂ ligand); 4.09 (t, 2H, CH₂ ligand); 6.67–7.35 (m, 4H, CH_{ar}); 8.42 (s, 1H, H–C=N) ppm.

¹³C NMR (CDCl₃): δ 8.9, 15.3 (CH₃); 60.0, 62.2 (CH₂ ligand); 116.2–167.0 (Ar); 171.6 (C=N) ppm.

IR: v 2915 (CH₂O valence); 2826 (CH₂N valence); 1629 (C=N valence); 1621, 1449 (C=C valence phenyl); 494 (Sn–N valence); 409, 403, 401 (Sn–O valence) cm⁻¹.

3: Dichlorodimethylsilane (2.35 g, 18.2 mmol) in THF (60 mL), triethylamine (3.68 g, 36.4 mmol) and **1** (3.0 g, 18.2 mmol) in THF (60 mL) yield yellow crystals (1.2 g, 30%), m.p. 371.6 K. *Anal.* Calc. for $C_{22}H_{30}N_2O_4Si_2$ (442.66 g/mol): C, 59.69; H, 6.83; N, 6.33. Found: C, 59.75; H, 6.62; N, 6.60%.

²⁹Si NMR (C₆D₆): δ –8.9 ppm.

¹H NMR (C_6D_6): δ 0.07 (s, 6H, Si–CH₃); 3.05 (m, 2H, CH₂ ligand); 3.94 (s, 2H, CH₂ ligand); 6.60–7.09 (m, 4H, CH_{ar}); 8.33 (s, 1H, H–C=N) ppm.

¹³C NMR (C_6D_6): δ -3.1 (Si-CH₃); 61.3, 61.5 (CH₂ ligand); 117.2-161.7 (Ar); 166.4 (C=N) ppm.

IR: ν 1634 (C=N valence); 1115, 1050 (C-O fingerprint); 1582, 1497 (C_{ar} valence); 1373 (CH₃ deformation); 947 (Si-O stretch) cm⁻¹.

4: Dichlorocyclohexylmethylsilane (3.59 g, 18.2 mmol) in THF (60 mL), triethylamine (3.68 g, 36.4 mmol) and **1** (3.0 g, 18.2 mmol) in THF (60 mL) yield pale yellow crystals (1.8 g, 34.2%), m.p. 428.5 K. *Anal.* Calc. for $C_{32}H_{46}N_2O_4Si_2$ (578.89 g/mol): C, 66.40; H, 8.01; N, 4.84. Found: C, 65.94; H, 7.41; N, 4.81%.

²⁹Si NMR (CDCl₃): δ –14.3 ppm.

¹H NMR (CDCl₃): δ 0.62 (t, 2H, CH₂ cyclohexyl), 1.14 (m, 4H, CH₂ cyclohexyl), 1.66 (m, 4H, CH₂ cyclohexyl); 0.17 (s, 3H, CH₃); 3.70 (m, 2H, CH₂ ligand); 3.91 (m, 2H, CH₂ ligand); 6.86–7.26 (m, 4H, CH_{ar}); 8.32 (s, 1H, H–C=N) ppm.

¹³C NMR (CDCl₃): δ –4.4 (Si–CH₃); 26.5–27.9 (CH₂ cyclohexyl); 61.7, 61.9 (CH₂ ligand); 117.3–161.6 (Ar); 166.8 (C=N) ppm.

IR: v 1644 (C=N valence); 1129, 1106 (C–O fingerprint); 1598, 1578 (C_{ar} valence); 1370 (CH₃ deformation); 921 (Si–O stretch) cm⁻¹.

5: Reaction of dichlorosilacyclobutane (2.57 g, 18.2 mmol) in THF (40 mL), triethylamine (4.05 g, 40.0 mmol) and **1** (3.0 g, 18.2 mmol) in THF (80 mL) was carried out as described above. The raw material was solved in a DME-*n*-hexane mixture (1:1) and filtered through SiO₂. Addition of diethylether and DME gives a solid which was separated via suction filtration. After seven days storing at 253.2 K intense yellow crystals (1.1 g, 25.9%) were collected. The compound seems to be relatively unstable outside the mother liquid even under argon atmosphere. M.p. 410–412 K. *Anal.* Calc. for C₁₂H₁₅NO₂Si (233.34 g/mol): C, 61.77; H, 6.48; N, 6.00. Found: C, 60.76; H, 6.38; N, 5.83%.

²⁹Si NMR (CDCl₃): δ –81.5 ppm.

²⁹Si NMR (CPMAS): δ –84.8 ppm.

¹H NMR (CDCl₃): δ 1.29–1.61 (m, 6H, CH₂ silacyclobutane); 3.70–4.03 (m, 4H, CH₂ ligand); 6.97–7.08 (m, 2H, CH_{ar}); 7.33– 7.46 (m, 2H, CH_{ar}); 8.22 (s, 1H, H–C=N) ppm.

¹³C NMR (CDCl₃): δ 13.3 (CH₂–Si, silacyclobutane); 27.4 (CH₂ silacyclobutane); 53.4 (CH₂ ligand); 60.1 (CH₂ ligand); 119.4, 120.3, 121.6, 130.9, 134.9, 159.0 (Ar); 159.5 (C=N) ppm.

IR: v 2934, 2874 (C–H valence); 1640 (C=N valence); 1134, 1067 (C–O fingerprint); 1614, 1578 (C_{ar} valence); 1339 (CH₃ deformation); 914 (Si–O stretch) cm⁻¹.

6: Dichlorodiphenylsilane (4.61 g, 18.2 mmol) in THF (60 mL), 3.68 g triethylamine (36.4 mmol) and **1** (3.0 g, 18.2 mmol) in THF (60 mL) yield yellow crystals (1.27 g, 20.2%), m.p. 475.5 K. *Anal.* Calc. for $C_{21}H_{19}NO_2Si$ (345.46 g/mol): C, 73.01; H, 5.54; N, 4.05. Found: C, 72.73; H, 5.49; N, 4.16%.

²⁹Si NMR (CDCl₃): δ –94.4 ppm.

¹H NMR (CDCl₃): δ 3.39 (t, 2H, CH₂ ligand); 4.22 (t, 2H, CH₂ ligand); 6.69–8.30 (m, 14H, CH_{ar}); 8.85 (s, 1H, H–C=N) ppm.

 ^{13}C NMR (CDCl₃): δ 53.3, 59.9 (CH₂ ligand); 117.1–161.3 (Ar); 166.7 (C=N) ppm.

IR: v 1666 (C=N valence); 1071 (C–O fingerprint); 1605, 1566 (C_{ar} valence); 915 (Si–O stretch) cm⁻¹.

7: Dichlorodiphenylgermane (5.42 g, 18.2 mmol) in THF (60 mL), triethylamine (3.68 g, 36.4 mmol) and **1** (3.0 g, 18.2 mmol) in THF (60 mL) yield intense yellow crystals (1.5 g, 21.1%), m.p. 357.6 K. *Anal.* Calc. $C_{21}H_{19}GeNO_2$ (389.96 g/mol): C, 64.68; H, 4.91; N, 3.59. Found: C, 64.01; H, 5.74; N, 3.83%.

¹H NMR (CDCl₃): δ 3.77 (t, 2H, CH₂ ligand); 3.93 (t, 2H, CH₂ ligand); 6.87–7.59 (m, 14H, CH_ar); 8.41 (s, 1H, H–C=N) ppm.

¹³C NMR (CDCl₃): δ 62.1, 62.5 (CH₂ ligand); 117.3–161.3 (Ar); 167.3 (C=N) ppm.

IR: v 1649 (C=N valence); 1100 (C–O fingerprint); 1584, 1529 (C_{ar} valence) cm⁻¹.

8: Dichlorodiphenylstannane (6.26 g, 18.2 mmol) in THF (60 mL), triethylamine (3.68 g, 36.4 mmol) and **1** (3.0 g, 18.2 mmol) in THF (60 mL) yield intense yellow crystals (2.8 g, 35.2%), m.p. 482.5 K. *Anal.* Calc. for $C_{21}H_{19}NO_2Sn$ (436.06 g/mol): C, 57.84; H, 4.39; N, 3.21. Found: C, 57.66; H, 4.16; N, 3.24%.

¹¹⁹Sn NMR (CDCl₃): δ –329.8 ppm.

¹H NMR (CDCl₃): δ 3.76 (t, 2H, CH₂ ligand); 4.27 (t, 2H, CH₂ ligand); 6.68–8.43 (m, 14H, CH_{ar}); 8.49 (s, 1H, H–C=N) ppm.

¹³C NMR (CDCl₃): δ 59.8 (CH₂ ligand), 62.5 (CH₂ ligand); 116.4–140.6 (Ar); 171.9 (C=N) ppm.

IR: v 1630 (C=N valence); 1055 (C–O fingerprint); 1599, 1543 (C_{ar} valence); 447 (Sn–O valence) cm⁻¹.

9: Reaction of silicon tetrachloride (1.55 g, 9.1 mmol) in THF (30 mL), triethylamine (4.0 g, 39.3 mmol) and **1** (3.0 g, 18.2 mmol) in THF (70 mL) was carried out as described above. In addition to stirring at room temperature, the reaction mixture was stirred overnight at this temperature, refluxed for 7 h and afterwards at r.t. for four days. The raw material was solved in a DME-*n*-hexane mixture (1:1), filtered and washed with diethylether to give a yellow crystalline solid (0.99 g, 30.7%), m.p. 498–501 K (decomposition starting at 473 K). *Anal.* Calc. for $C_{18}H_{18}N_2O_4Si$ (354.44 g/mol): C, 61.00; H, 5.12; N, 7.90. Found: C, 60.87; H, 5.09; N, 7.97%.

²⁹Si NMR (CDCl₃) δ –172.46 ppm.

 ^{29}Si NMR (CPMAS): δ -172.22, -172.58 ppm.

¹H NMR (CDCl₃): δ 3.84–4.08 (m, 8H, CH₂ ligand); 6.70–6.74 (m, 4H, CH_{ar}); 7.21–7.32 (m, 4H, CH_{ar}); 8.28 (s, 2H, H–C=N) ppm.

¹³C NMR (CDCl₃): δ 56.1 (CH₂ ligand); 58.6 (CH₂ ligand); 117.1, 117.5, 121.1, 132.6, 136.1, 162.7 (Ar); 164.6 (C=N) ppm.

IR: v 2937. 2866 (C–H valence); 1631 (C=N valence); 1088 (C-O fingerprint); 1609, 1533 (C_{ar} valence), 755 (Si–O valence) cm⁻¹.

10: Tintetrachloride (1.18 g, 4.5 mmol) in THF (60 mL), triethylamine (3.68 g, 36.4 mmol) and **1** (1.5 g, 9.1 mmol) in THF (30 mL) yield intense yellow crystals (0.9 g, 44.9%), m.p. 526.0 K. *Anal.* Calc. for $C_{18}H_{18}N_2O_4Sn$ (445.04 g/mol): C, 48.58; H, 4.08; N, 6.29. Found: C, 49.83; H, 4.47; N, 6.22%.

¹¹⁹Sn NMR (CDCl₃): δ –573.27 ppm.

¹H NMR (CDCl₃): δ 3.83 (m, 4H, CH₂); 4.10 (t, 4H, CH₂); 6.72– 7.32 (m, 8H, CH_{ar}); 8.48 (s, 2H, HC=N); impurities: 1.43, 3.39 (triethylamine hydrochloride); 1.66, 3.68 (THF); 3.54, 3.64 (DME) ppm.

¹³C NMR (CDCl₃): δ 57.4, 60.7 (CH₂ ligand); 117.3–167.8 (Ar); 171.8 (C=N); solvents: 58.9, 69.1 (DME); 25.3, 71.8 (THF) ppm. IR: v 2880 (CH₂O valence); 2814 (CH₂N valence); 1637 (C=N valence); 1632, 1447 (C=C valence phenyl); 460 (Sn–N valence); 436, 439 (Sn–O valence) cm⁻¹.

11: Indiumtrichloride (1.95 g, 8.8 mmol) in THF (30 mL), triethylamine (1.78 g, 17.6 mmol) and **1** (1.46 g, 8.8 mmol) in THF (30 mL) yield intense yellow crystals (0.8 g, 25.7%), m.p. 516.0 K. *Anal.* Calc. for $C_{33}H_{44}$ Cl₃In₃N₄O₇ (without THF and DME; 1059.54 g/mol): C, 37.40; H, 4.19; N, 5.29. Found: C, 37.51; H, 3.98; N, 4.97%.

¹H NMR (CDCl₃): δ 1.30 (t, 9H, CH₃ triethylammonium); 3.04 (q, 6H, CH₂ triethylammonium); 4.25 (t, 6H, CH₂ ligand); 4.51 (t, 6H, CH₂ ligand); 6.62–7.09 (m, 12H, CH_{ar}); 8.32 (s, 3H, H–C=N); 10.34 (s, 1H, triethylammonium); 3.39 (m, 12H, CH₃ DME); 3.54 (m, 8H, CH₂ DME) ppm.

¹³C NMR (CDCl₃): no resonances due to insufficient solubility.

IR: v 3315 (OH valence); 2990 (CH₂O valence); 2871 (CH₂N valence); 1641 (C=N valence); 1629, 1477 (C=C valence phenyl); 419 (In-N valence); 406 (In-O valence) cm⁻¹.

2.4. Crystal Structure analyses of the synthesized complexes

Single crystals of the complexes suitable for X-ray structure analysis were grown from DME solution at 276 K and mounted on a glass fiber and transferred to the nitrogen gas stream of the diffractometer (BRUKER Kappa CCD X8 Apex II; Mo K α radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97) [28]. The hydrogen atoms were refined with a riding model. Crystallographic data of compounds **2–11** are summarised in Table 1.

2.4.1. Quantum chemical calculations

The DFT calculations were carried out using GAUSSIAN 09 [29]. NMR shielding tensors were calculated with the Gauge-Independent Atomic Orbital method (GIAO) [30]. ²⁹Si NMR data were calculated using the B3PW91 [31,32] density functionals, in combination with the 6-311+G(2d,p) [33–35] basis set for all atoms, with the geometries from X-ray structure analyses. Calculated absolute shielding values were converted to relative shifts δ with the calculated shielding for tetramethylsilane at the same level of theory.

¹¹⁹Sn NMR data were calculated using the B3PW91 density functionals, in combination with the DGDZVP [36] basis set for tin and the 6-311+G(2d,p) basis set for all other atoms, with the geometry from X-ray structure analysis. The calculated absolute shielding value for compound **8** was converted to relative shift δ by setting the calculated isotropic shift equal to the measured value. This leads to smaller differences than using the calculated shift of tetramethyltin.

3. Results and discussion

The reaction of dichlorodiorganosilanes, -germanes and stannanes with ligand **1** should lead to the formation of mononuclear pentacoordinated complexes with one ligand molecule per central atom Si, Ge, and Sn. In contrast, ECl_4 as starting material is expected to give mononuclear hexacoordinated complexes of the EL_2 type bearing two ligand molecules. The isolated products were characterised with NMR and IR spectroscopic methods. Single crystal X-ray structure determination was used to elucidate the molecular structures and the coordination geometries of the central atoms.

	G
	of
	Data
	ographic
-	Ĕ
able	rvsta
-	<u> </u>

Crystallographic Data of Compounds 2–1	11.									
Compound	2	3	4	5	9	7	8	6	10	11
Chemical formula Formula mass	C ₄₆ H ₆₆ Cl ₂ N ₄ O ₈ Sn ₅ 1467.38	C ₂₂ H ₃₀ N ₂ O ₄ Si ₂ 442.66	C ₃₂ H ₄₆ N ₂ O ₄ Si ₂ 578.89	C ₁₂ H ₁₅ NO ₂ Si 233.34	C ₂₁ H ₁₉ NO ₂ Si 345.46	C ₂₁ H ₁₉ GeNO ₂ 389.96	C ₂₁ H ₁₉ NO ₂ Sn 436.06	C ₂₀ H ₂₀ Cl ₆ N ₂ O ₄ Si 593.17	C ₁₈ H ₁₈ N ₂ O ₄ Sn 445.03	C ₄₃ H ₆₄ Cl ₃ ln ₃ N ₄ O ₁₂ 1279.79
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic	orthorhombic	triclinic
a (Å)	9.6118(3)	10.1780(5)	8.4691(5)	18.1162(7)	21.9839(13)	9.1958(2)	9.0664(2)	10.270(5)	11.0814(6)	13.5477(8)
p (Å)	11.5881(3)	11.4263(6)	8.6938(7)	6.5485(2)	7.2204(4)	9.2694(2)	9.4356(2)	11.858(5)	18.7834(12)	13.9844(8)
c (Å)	12.7644(4)	11.4576(5)	11.6706(7)	19.3526(7)	22.5402(14)	10.9880(3)	11.2327(3)	12.414(5)	8.3429(4)	14.7506(9)
ر») ه	105.877(2)	106.147(2)	103.812(4)	00.00	00.00	87.839(2)	86.924(2)	63.474(10)	90.00	104.129(4)
β (°)	102.770(1)	106.254(2)	101.745(3)	90.524(2)	103.465(2)	75.906(1)	77.866(1)	66.621(10)	90.00	95.072(3)
γ (°)	93.660(1)	104.529(3)	102.894(3)	90.00	00.00	72.663(1)	71.325(1)	83.085(12)	90.00	95.952(3)
Unit cell volume ($Å^3$)	1321.91(7)	1148.04(10)	782.89(9)	2295.78(14)	3479.5(4)	866.53(4)	889.90(4)	1238.6(10)	1736.54(17)	2676.6(3)
T (K)	153(2)	93(2)	153(2)	93(2)	153(2)	153(2)	153(2)	93(2)	250(2)	153(2)
Space group	$P\bar{1}$	$P\overline{1}$	$P\bar{1}$	C2/c	$P2_1/n$	$P\bar{1}$	$P\overline{1}$	$P\bar{1}$	$Pca2_1$	$P\bar{1}$
No. of formula units per unit cell, Z	1	2	1	8	8	2	2	2	4	2
Absorption coefficient, μ (mm ⁻¹)	2.482	0.185	0.151	0.189	0.149	1.781	1.449	0.773	1.497	1.489
No. of reflections measured	16616	27995	8325	20306	16724	20295	24906	29145	11890	44266
No. of independent reflections	6916	6700	3750	2775	8370	3961	4728	5995	3412	11587
Rint	0.0179	0.0302	0.0275	0.0207	0.0283	0.0259	0.0249	0.0312	0.0349	0.0359
Final R_1 values $(I > 2\sigma(I))$	0.0175	0.0352	0.0421	0.0413	0.0648	0.0245	0.0174	0.0260	0.0280	0.0364
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.0414	0.0968	0.1008	0.1050	0.1883	0.0608	0.0434	0.0776	0.0543	0.0875
Final R_1 values (all data)	0.0201	0.0443	0.0590	0.0425	0.0872	0.0296	0.0196	0.0295	0.0393	0.0579
Final $wR(F^2)$ values (all data)	0.0422	0.1012	0.1074	0.1053	0.1984	0.0623	0.0442	0.0794	0.0589	0.0975
Goodness of fit (GOF) on F^2	1.067	1.074	1.076	1.283	1.135	1.088	1.056	1.104	1.025	1.133
Maximum/minimum (e $ m \AA^{-3})$	0.364/-0.560	0.490/-0.284	0.332/-0.273	0.387/-0.294	0.424/-0.377	0.487/-0.181	0.344/-0.296	0.413/-0.314	0.397/-0.295	1.734/-1.235

3.1. Reaction of ligand **1** with compounds R_2ECl_2

3.1.1. Synthesis and structure description of alkylated group 14 derivatives

Alkyl and aryl disubstituted dichlorostannanes, -silanes, and germanes were used to form mononuclear pentacoordinated complexes (Fig. 1).

The solution of the reaction mixture of **2** shows a weak broad resonance at -155.5 ppm. This is in between the chemical shift range of 4- and 5-fold coordination for this class of substances and may indicate a fast change of the coordination geometry within the solution. The ¹¹⁹Sn solid state NMR spectrum of the amorphous product 2 showed the expected fivefold coordinated complex having a δ (¹⁹⁹Sn) = -301 ppm. Attempts were undertaken to grow crystals suitable for X-ray diffraction, but did not succed from CHCl₃ as solvent. At least single crystals of 2 were isolated from DME solution. Surprisingly, the X-ray structure shows a different coordination mode of the Sn atoms than the solution and solid state NMR data. Indeed, Sn atoms appear as penta- and hexacoordinated complex with a ratio of the tin atoms of 2:2:1 (for Sn1:Sn2:Sn3). Sn2 shows a pentacoordinated environment while Sn1 and Sn3 are hexacoordinated. It is assumed that these associates found in the crystal structure dissociate in solution (see Fig. 1).

Complex 2 was found to crystallise in the triclinic space group $P\bar{1}$ with two independent half molecules in the asymmetric unit. 2-I represents a dimer created by an inversion centre in the centre of the four-membered ring, Sn1–O1–Sn1^[i]–O1^[i] (Symmetry code: [i] 1 - x, -y, 1 - z). Sn1 is surrounded by three oxygen atoms, one nitrogen and two carbon atoms resulting in a hexacoordinated environment. The bond angles at Sn1 indicate a distorted octahedral coordination sphere. The Sn-O-bond lengths show a slightly longer phenolic O-Sn (Sn1-O2: 2.2178 Å) bond than an alcoholic O–Sn bond (Sn1–O1: 2.1141 Å). This is caused by the conjugation of the shorter C5–O2 (1.305 Å) with the aromatic moiety leading to a longer O2-Sn1 bond. The longer aliphatic C1-O1 bond (1.406 Å) results in a shorter O1–Sn1 bond.

The second molecule, 2-II, of the obtained crystal structure possesses two different tin atoms with Sn3 situated on an inversion centre. This Sn3 atom comes from the starting material, Me₂SnCl₂, to which two molecules of the expected pentacoordinated complex are bound via the oxygen atom O3 (Fig. 1).

As observed with 2-I, the Sn-O bonds are of different length depending on the adjacent C-O bond. The longest and therefore weakest bond in the molecule is the bridging Sn3-O3 bond with 2.244 Å. The octahedral coordination environment of Sn3 is represented in the angles at Sn3. This is in contrast to the NMR data. But dissociation of the molecule in solution leads to the formation of two equivalents of pentacoordinated complex and one equivalent of the tetracoordinated educt molecule, Me₂SnCl₂, which is in agreement with the spectral data. The last tin atom, Sn2, shows a pentacoordinated environment. The coordination geometry in pentacoordinate complexes can best be described with the parameter τ which is defined as $\tau = (\beta - \alpha)/60^{\circ}$ with β as largest and α as the second largest angle at the central atom. If $\tau = 0$ a perfect square pyramid is described, while τ = 1 indicates a perfect trigonal bipyramid [37]. In the case of Sn2 in 2-II, the geometry parameter τ = 0.36 indicates a distorted square pyramidal geometry.

Though different C–H···O [38], C–H··· π [39] interactions (see Supplementary material, Table S1) of moderate strength are present in the crystal structure, these intermolecular contacts show no significant influence on the molecular geometry. The phenyl moieties are involved in C-H \cdots π contacts in the range of 3.5 Å, while $\pi - \pi$ stacking interactions are absent.

Using Me₂SiCl₂ instead of Me₂SnCl₂ leads to the formation of yellow crystals of **3**. The vibrational spectrum proves the absence



Fig. 1. Reaction of ligand **1** with Me₂SnCl₂ and the identified products in solution and the solid state including the molecular structure of compound **2** and the used atomic numbering scheme. The thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms and the disorder at C10 in two positions are omitted for clarity.

of a hydroxyl group. The signals at 947 cm⁻¹ indicate the presence of a Si–O bond. In contrast, the ¹H and ¹³C NMR data show no significant changes in comparison to the isolated ligand **1**. The ²⁹Si chemical shift in solution reveals the existence of a tetracoordinated Si species with a signal at -8.9 ppm. Therefore, the formation of a mononuclear pentacoordinated complex is doubtful.

Similar results were found for the reaction with dichloro(cyclohexyl)(methyl)silane forming **4**: (1) a disappearing hydroxyl group, (2) a Si–O stretch vibration at 921 cm⁻¹ in the IR spectrum, and (3) a ²⁹Si chemical shift at -14.3 ppm indicating a tetracoordinated Si compound.

Single crystals of both compounds **3** and **4** were grown from DME solutions. Fig. 2 shows the molecular structures of **3** and **4**. Both complexes crystallise in the triclinic space group $P\bar{1}$, **3** with two half molecules, and **4** with half a molecule in the asymmetric part of the unit cell connected via an inversion centre. Both, **3** and **4**, are 18-membered macrocyclic compounds (Scheme 1, Fig. 2). The formation of a macrocycle consisting of two diorganosilicon moieties and two ligand molecules leads to the preferred tetracoordinated environment of the silicon atoms as indicated in the spectroscopic analyses.

The two independent molecules of **3** differ significantly in the Si–O bond lengths and C/O–Si–C/O angles to one another and within one molecule. The geometric parameters of the central Si atoms indicate a slightly distorted tetrahedral coordination sphere. The C/O–Si–O angles lie between 106.1 and 113.1° (average: 109.5°) in **3**-I and between 105.5° and 114.6° (average: 109.5°) in **3**-II. The plane generated by the macrocycle is not planar due to the sp² and sp³ hybridisation of the atoms involved. In both molecules, the phenyl rings are orientated outside the macrocycles.

A similar geometric situation is found in the crystal structure of **4** possessing a slightly distorted tetrahedral coordination environment as well. The C/O–Si–C/O bond angles range from 105.3° to 113.5° (average: 109.5°). Once again, the Si–O bond lengths differ significantly but are still in the range of the expected value of a Si–O single bond. As specified by the torsion angles and the hybridisation of the involved atoms, the macrocycle is not planar. Again, the phenyl rings are orientated outside the macrocycle.

Though the molecular structures of 3 and 4 are very similar, their crystal packing are not. Hence, 4 is only subjected to closed-packing and maximum symmetry effects and shows no

relevant C–H··· π [39] or C–H···O/N interactions [38]. In contrast, the packing of **3** reveals several different intermolecular interactions. First, C–H···O/N contacts in the range from 2.49 to 2.61 Å for the hydrogen-acceptor distance and 3.20–3.53 Å for the donor–acceptor distance (θ = 126–170°) appear. In addition, C–H··· π contacts are in the range of 2.70–2.85 Å (144–172°) as a part of the network of significant intermolecular interactions generating the molecular packing.

While neither Me_2SiCl_2 nor $Me(C_6H_{11})SiCl_2$ react with **1** to give mononuclear pentacoordinated complexes we decided to test dichlorosilacyclobutane as starting material (Fig. 3).

The intense yellow compound **5** gives a 29 Si NMR signal at -81.5 ppm in chloroform solution and -84.8 ppm in the solid state. This indicates the same geometric environment at the silicon atom in solution and the solid state as well as a pentacoordinated central atom. Single crystals were obtained from DME solution and the expected coordination at the silicon atom was proven with X-ray structure analysis.

In detail, **5** was found to crystallise with one independent molecule in the asymmetric part of the unit cell in the monoclinic space group *C*2/*c*. Selected geometric parameters are given in Table 2 and reveal a distorted trigonal bipyramidal coordination of the silicon atom. The equatorial positions in this coordination polyhedron are occupied by the atoms O1, O2, and C12. N1 and C10 are at the apical positions with an bond angle N1–Si1–C10 173.10(8)°. All bond lengths and angles including those involving silicon are in the range of the expected values for such coordination geometry. Moreover, the conjugated plane of the ligand, $C_6H_4(O)C=N$, is planar with a r.m.s. deviation of 0.0244 Å. The silicon atom is not situated in this plane but shows a distance to the plane of 0.4946 Å.

Intra- or intermolecular interactions of **5** does not influence the molecular structure but the molecular packing within the crystal structure. The aryl ring interacts in a π - π stacking contact with a centre-to-centre distance of 3.9846(11) Å and a slippage of 1.957 Å. Additionally, the silabutane moiety interacts with the aryl ring in a C-H··· π type of interaction (2.89 Å, θ = 139°). As expected, the oxygen atoms are able to take part in C-H···O interactions forming several intermolecular contacts (see Supplementary material, Table S2).



Fig. 2. Molecular structure of the crystallographic independent molecules I and II of 3 and 4 showing the atomic numbering scheme. The thermal ellipsoids of the nonhydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



Scheme 1. Reaction of ligand 1 with Me₂SiCl₂ and Me(C₆H₁₁)SiCl₂.

Hence, the overall results of the reaction between ligand **1** and alkylated group 14 derivatives are as follows. The cyclic derivative **5** shows the expected pentacoordinated Si complex. Me_2ECl_2 (E = Si, Sn) give either the macrocylic tetracoordinated silicon compound (**3**) or a mixture of penta- and hexacoordinated tin complexes (**2**) in the solid state. Compound **2** shows different coordinated in chloroform solution. Penta- and hexacoordinated species were proved to exist in the solid state structure. These species dissociate in solution.



Fig. 3. Reaction of ligand **1** with dichlorosilacyclobutane, (CH₂)₃SiCl₂. The molecular structure of **5** shows the atomic numbering scheme. The thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

Selected geometric paramete	rs (Å, deg) in compound 5 .
	5
Si1-01	1.6868(14)
Si1-02	1.7096(14)

Si1-01	1.6868(14)
Si1-02	1.7096(14)
Si1-C12	1.892(2)
Si1-C10	1.910(2)
Si1-N1	1.9871(17)
τ	0.79
Si · · ·A in Å ^a	0.4946

^a A is defined as the least-square plane of the following atoms C3–C9, O2, N1.

3.1.2. Synthesis and comparative reflections on the crystal structures of the monomeric arylated group 14 derivatives

Only the inflexible silacyclobutane derivative was able to give mononuclear pentacoordinated complexes of the type L_2ER_2 . Therefore, phenyl substituted derivatives were applied to check the influence of the aromatic character of the substituents on the molecular geometry of the complex formation (Scheme 2).

First, the vibrational IR spectra of all three compounds **6–8** give no hint of the existence of a hydroxyl group present in the isolated product. Stretch vibrations at 915 cm⁻¹ (**6**) and 447 cm⁻¹ (**8**) indicate the Si–O and Sn–O bond formation. Solution ¹³C NMR data of complexes **6–8** show a slight change in the chemical shift of both the imine and the CH₂ moiety of ligand **1** giving a second hint for successful coordination at the central atom. The chemical shifts in the ²⁹Si NMR spectrum of **6** at δ –94.4 ppm and in the ¹¹⁹Sn NMR spectrum of **8** at δ –329.8 ppm imply the formation of higher coordinated species in both cases.

Though the crystal structure of **8** has been described previously [40], we decided to remeasure the obtained crystal to ensure the results of the presented synthetic pathway. Indeed, the pentacoordinated environment of the central Sn atom was confirmed. In the following our data set is used for reflective comparisons of the crystal structure of **6–8**. Single crystals of **6–8** suitable for X-ray structure analysis were yielded by slow crystallisation from DME solution under inert conditions. While Fig. 4 illustrates the molecular structure of the products, Table 3 presents relevant geometric parameters.

The complexes of Ge and Sn, **7** and **8**, crystallise in the same triclinic space group, $P\bar{1}$ with one molecule in the asymmetric part of the unit cell with similar unit cell dimensions and atom positions.



Scheme 2. Reaction of ligand 1 with dichlorodiphenyl derivatives, Ph₂ECl₂.

Therefore, **7** and **8** are said to be isomorphous. The molecular overlay is depicted in Fig. 5(d) and will be discussed later on. In contrast, **6** is not isomorphic to **7** and **8** since it crystallises in the monoclinic space group $P2_1/n$ with two independent molecules in the asymmetric unit.

The molecular structures of **6–8** represent each a pentacoordinated compound with one ligand molecule coordinated at central group 14 elements Si, Sn or Ge, respectively. The ratio of atom radii of silicon (1.173 Å), germanium (1.223 Å) and tin (1.399 Å) [41] is given with: 1:1.04:1.20. The bond ratios derived from the X-ray structures are shown in Table 4. For the Ge–O bond, the ratio is slightly higher than calculated indicating a weaker Ge–O bond compared to the Si–O bond. In contrast, the Sn–O appears as

expected. The ratios of the element-nitrogen bonds feature other deviations. While the Ge–N is slightly shorter than expected, the Sn–N bond is substantial shorter indicating a stronger coordinative bond between Sn and N than between Si/Ge and N. Nevertheless, the differences are rather small. Moreover, all bond lengths and angles apart from the central atom are in the range of the expected values.

Comparison of the geometric parameters leads to no general trend regarding the pentacoordinated environment of the central atom. In case of **6** τ_1 = 0.59 and τ_2 = 0.59, for complex **7** τ = 0.68, and complex **8** features a value of τ = 0.55. All values indicate strong distortion at the central atom with a slight tendency towards trigonal bipyramidal coordination.

As mentioned above, **7** and **8** are isomorphous crystal structures. Hence, as indicated in Fig. 5(d), the molecular geometries are very similar. Apart from the central atom, the ligand itself has an influence on the molecular structure of the whole complex. The conjugated part of the ligand, $C_6H_4(O)C=N$, is planar in all three structures, **6–8**, with r.m.s. deviations of 0.03–0.05 Å. Besides, the aliphatic moiety, $-CH_2-CH_2O-$, is more flexible and adjusts to the requirements of the central atom. This is illustrated by the angles at the central atom and the distance of the central atom to the least-squares plane of the conjugated moiety of the ligand (C3–C9, O2, N1, Table 3). Indeed, the latter shows no real trend for the group 14 elements.



Fig. 4. Molecular structure of the crystallographic independent molecules 6-I, 6-II, 7, and 8 showing the atomic numbering scheme. The thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

Table 3
Selected geometric parameters (Å, deg) in compounds 6-8, standard deviations are omitted for clarity.

	E1-01	E1-02	E1-C10	E1-C16	E1-N1	τ	$E{\cdots}A \text{ in } \mathbb{A}^d$
6 -I	1.672	1.707	1.917	1.880	2.046	0.59	0.460
6 -II ^a	1.673	1.713	1.916	1.878	2.042	0.59	0.324
7	1.871	1.970	1.957	1.959	2.015	0.68	0.687
8	2.046	2.108	2.131	2.119	2.187	0.55	0.447
Bond ratio ^{b,c}	1:1.12:1.22	1:1.14:1.23	1:1.00:1.11	1:1.04:1.13	1:0.99:1.07		

^a N1 = N2; C10 = C31; C16 = C37; O2 = O4; O1 = O3.

^b Atom radii of Si (1.173 Å), Ge (1.223 Å), Sn (1.399 Å) [41]; resulting ratios: Si:Ge:Sn:1:1.04:1.20.

^c Due to the similarity of **6**-I and **6**-II, only **6**-I is used representing the Si derivative.

^d A is defined as the least-squares plane of the following atoms C3-C9, O2, N1; C24-C30, O4, N2.



Fig. 5. Least-squares overlays of (a) 6-I and 6-II, b) 6-I and 7, c) 6-I and 8, and d) 7 and 8. The r.m.s. deviations are (a) 0.0304 Å, (b) 0.0404 Å, (c) 0.050 Å, and (d) 0.0353 Å for an overlay of the following atoms: 02/04, N1/N3, C3-C9/C24-C30. All hydrogen atoms are omitted for clarity.

To sum up, the differences in the molecular structure cannot only be explained by the size of the central atom and its fit in the "bite" of the ligand. Moreover, the flexibility of the 2-oxyethyl moiety of the ligand has a significant influence on the geometry of the whole complex. Other influences are packing effects, inter-, and intramolecular interactions. Especially the intramolecular C-H···O contacts of the phenyl ring (see Supplementary material, Table S3) reveal a significant effect.

In silicon complex **6** only one out of two phenyl rings present in the structure participates in intramolecular C–H···O interactions using the *ortho* substituted hydrogen atoms. As a result this phenyl ring (C16–C21) is not co-planar to the plane of the ligand as the other one (C11–C15) is. Similar contacts are found in the structures of **7** (Ge) and **8** (Sn). But there, both phenyl rings are involved. Therefore, both phenyl rings leave the plane of the ligand. Apart from the intramolecular interactions mentioned above, several other contacts of the type C-H···O and C-H··· π occur in the crystal packing. Stacking interactions of the aromatic units are not present.

The superimposed molecular structures depicted in Fig. 5 illustrate the differences of the molecular geometry depending on the central atom. The deviation between both crystallographic independent molecules of **6** should be caused by packing effects and illustrate the flexibility of the ligand system (Fig. 5a). The superimposed structures of the silicon complex **6-I** with the germanium and tin complexes (Fig. 5b and c) reveal large differences in the bond angles N–E–C and C–E–C. This leads to different orientations of the phenyl groups. The best fit between two structures in this series was found in the overlay of the germanium and the tin complexes (Fig. 5d). This was expected, since both X-ray structures are isomorphous. 3.2. Synthesis and comparative reflections on the crystal structures of group 14 derivatives with composition EL_2

As mentioned above, the reaction of a diorganodichlorosilane, germane or -stannane with **1** leads to the formation of monomeric pentacoordinated compounds **5–8** or to dimer or macrocyclic complexes **2–4**. Moreover, the reaction of ECl_4 with **1** results in monomeric hexacoordinated compounds with two ligands in the coordination sphere of E (Scheme 3).

As expected for **10**, the ¹¹⁹Sn NMR spectrum shows one peak at δ –573.3 ppm, which implies that a hexacoordinated tin atom is present at least in solution. The ¹H and ¹³C NMR spectra support the conclusion that a complex was formed since the resonances for both the CH₂ groups and the imine group of the ligand are shifted in comparison to the isolated ligand **1**. The IR data of the obtained product show the appearance of Sn–N (460 cm⁻¹) and Sn–O (439 cm⁻¹) bonds while any hydroxy group is absent.

The growth of single crystals of **9** and **10** was successful from DME solution. Similar to the monomeric derivatives **6** and **8**, the silicon and tin complexes **9** and **10** crystallise in different, not isomorphous space groups. Compound **9** was found to crystallise in the monoclinic space group $P\bar{1}$, **10** in the orthorhombic space group $Pca2_1$, each with one molecule in the asymmetric unit (Fig. 6).

Both complexes show octahedral coordination geometry and represent the meridional isomers. This leads to a situation where all four oxygen atoms are situated in one plane while the nitrogen atoms represent the tops of the octahedron. As indicated in Table 4, the averaged Si–N bond length in **9** is in the range of the expected values for a Si–N single bond (Si–N: 1.91 Å, [41]), while the Si–O bond length is shortened (Si–O: 1.91 Å, [41]). A similar situation is found in **10**. While the averaged Sn–O bond length is shortened (Sn–O: 2.14 Å, [41]), the Sn–N bond length is as expected (Sn–N: 2.14 Å, [41]).



Scheme 3. Reaction of ligand 1 with ECl₄.

Table 4

Selected geometric parameters (Å, deg) in compounds ${\bf 9}$ and ${\bf 10}$, standard deviations are omitted for clarity.

	E-O ^{a,b}	E-N ^{a,b}	E···A1 in Å ^c	$E{\cdots}A2 \text{ in } \mathbb{A}^c$	A1/A2 in deg
9 10	1.756 2.024	1.893 2.154	0.2154(9) 0.3391(41)	0.3225(9) 0.7580(36)	84.83(3) 67.80(8)

^a Average values are given for the reason of clarity.

^b Single bond lengths: Si–O (1.91 Å), Si–N (1.91 Å), Sn–O (2.14 Å), Sn–N (2.14 Å) [41];

^c A is defined as the least-squares plane of the following atoms: A1 (C3–C9, O2; N1), A2 (C12–C18, O4, N2).

The comparison of the E–N and E–O bond lengths of the pentacoordinated complexes **6** and **8** to the hexacoordinated compounds **9** and **10** reveals remarkable effects. The bond lengths involving tin become shorter by the change from penta- to hexacoordination (Sn–N: 2.19 \rightarrow 2.15 Å; Sn–O: 2.08 \rightarrow 2.02 Å). The Si–O bond gets slightly longer (1.69 \rightarrow 1.76 Å), while the Si–N bond shortens significantly (2.04 \rightarrow 1.89 Å).

The planar structure of the conjugated moiety of the ligand, C_6 - $H_4(O)C=N$, was calculated as described above for compounds **6–8**. The calculated r.m.s. deviations in **9** and **10** are 0.01–0.04 Å. The distances of the central atom to this plane are similar in **9**, but **10** shows an offset of about 0.4 Å indicating a non-central position of the Sn atom (Table 4).

Intramolecular interactions influencing the molecular geometry significantly are not present in both crystal structures of **9** and **10**. On the other hand, the molecular packing differs significantly from the Si to Sn compound. While **9** is dominated by several π – π stacking (3.9 Å, slippage: 2.432 Å) and C–H··· π interactions in the range of 2.68 Å (angle around H: 147°), **10** does not show any π involved contacts. Both crystal structures reveal C–H···O interactions of moderate strength (see Supplementary material, Table S4). The synthesis of **9** and **10** demonstrates the ability of ligand **1** to form hexacoordinated complexes.

3.3. Synthesis and structure description of a group 13 derivative

Salicylaldehyde-(2-hydroxyethyl)imine (1) was reacted with $InCl_3$ in order to test the suitability of 1 as ligand towards group 13 elements. The ¹H NMR spectrum of complex **11** indicates a complex formation but due to the poor solubility of this complex no further information could be gained from any NMR spectra determined in solution. However, the infrared spectrum of **11** shows the OH valence vibration band is still present at 3315 cm⁻¹. In addition, In-N and In-O valence vibration bands appear at 419 and



Fig. 6. Molecular structure of 9 and 10 showing the atomic numbering scheme. The thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. Solvent molecules are omitted for clarity in the case of compound 9.

406 cm⁻¹. These results suggest either an incomplete reaction to a complex mixed with free ligand **1** or a different coordination mode of the ligand **1** with at least one hydroxyl group. Due to the shift of the OH valence vibration from 3363 to 3315 cm⁻¹ the last possibility is more appropriate.

While the spectroscopic data does not reveal a definite structure of the achieved coordination compound, the X-ray diffraction experiment with suitable single crystals grown from DME solutions gives a surprising result. Complex **11** (Scheme 4) was found to crystallise in the triclinic space group $P\bar{1}$ with one indium containing molecule in the asymmetric part of the unit cell. The analysed complex is neither neutral nor positive charged but monoanionic with three indium atoms in the asymmetric unit (Fig. 7). A triethylammonium cation acts as counterion and is solvatized by one DME molecule. A second DME molecule is disordered in two positions. Additionally, most likely a THF molecule is part of the unit cell. It is not possible to localise or refine all atom positions of the latter one. The overall composition of **11** in the solid state is therefore [HNEt₃][L₃In₃Cl₃(μ^3 -OH)]⁻(DME)₂(THF) with L = 2-[(2oxidobenzylidene)amino]ethanolat.

The anion of **11** consists of an alternating In-O six-membered ring (In1-O1-In2-O3-In3-O5) adopting the typical chair conforma-



Scheme 4. Obtained product from the reaction of InCl₃ and ligand 1.

tion. To describe the conformation of a six-membered ring the Cremer & Pople puckering parameters are applied [42,43]: $q_2 = 0.020(2)$ Å, $q_3 = 1.149(2)$ Å, $\varphi_2 = 128(6)^\circ$, $\vartheta = 0.00(10)^\circ$ and a puckering amplitude of Q = 1.149(2) Å indicate the chair conformation. The average bond length within the ring is 2.157 Å. In contrast, the angles differ depending on the affected atom. While the average angle around the oxygen atom is 107.3°, the In atoms show an average angle of 97.5°. Additionally, the three In atoms of the six-membered ring are bridged with a μ^3 -OH group forming a tetracyclic moiety. To the best of our knowledge, this conformation was not observed so far for indium complexes. The reported structure of a polycyclic In-O-complex represents a distorted cube [44]. The structural motif featuring an [M–O]₃ six-membered ring which is bridged by a μ^3 -OH group was found in several copper complexes with pentacoordinated central atoms [45].

In **11**, the geometry at each In atom is best described as a distorted octahedron with a coordination number of six. In addition to the μ^3 -OH group, three chlorine and three ligand molecules are involved in the complex formation. Each of the alcoholic O atoms (O1, O3, O5) of the ligand is shared by two In atoms. The phenolic O atom, the N atom, and the Cl atoms are coordinated to only one In atom each (Fig. 7).

The bond lengths of the indium to the oxygen atoms differ depending on the origin of the oxygen atom revealing the nonequivalency for the In-O bonds. Interestingly, the bond to the neighbouring ligand is shorter than the bond to the directly bonded one indicating a higher coordinative character. As mentioned above, each of the indium atoms possess a distorted octahedral coordination geometry. In an ideal octahedron adjoining atoms are perpendicular positioned to one another. In complex **11**, the angles vary between 75.2° and 99.3° for In1, between 75.°1 and 102.4° for In2 and 75.6° and 99.8° for In3. Therefore, the distortion at all three atoms is very distinct and can be explained by the fact that covalent and coordinative bonds contribute to the complexation and varying bond strengths influence the coordination geometry. Moreover, the resulting three octahedrons



Fig. 7. Molecular structure of the anion of 11 showing the atomic numbering scheme. The thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted for clarity except for H7A located at 07.

are connected along the edges forming a triade. This structural motif could be considered as a subunit of the Keggin structure [46].

As mentioned above, solvents and guest molecules were found to crystallise with the indium complex. These molecules are involved in different intermolecular interactions in the crystal packing of **11** (see Supplementary material, Table S5). The bridging hydroxyl group, O7–H7A, interacts with the not fully localised solvent molecule THF while the chlorine atoms form intermolecular contacts of the C–H···Cl type. These interactions form intermolecular strands of the complex along the crystallographic *a* axis. Finally, the [HNEt₃]⁺ ion interacts in a strong bifurcated hydrogen bond with one adjacent DME molecule [H4···O8 = 2.18(5) Å, N4···O8 = 2.913(5) Å, $\theta = 144(4)^{\circ}$ and H4···O9 = 2.43(5) Å, N4···O9 = 3.156(5) Å, $\theta = 144(4)^{\circ}$. The second DME molecule is coordinated weakly to the [HNEt₃]⁺ ion via a C–H···O contact (H32A···O10 = 2.58 Å, C32···O10 = 3.368(6) Å, $\theta = 136.2^{\circ}$). The non-interacting part of the second DME molecule is disordered in two positions.

The synthesis of **11** shows the ability of the ligand system generated from **1** to stabilize the large indium atom in a rather unusual complex geometry.

3.4. Solid state NMR measurements and chemical shift tensor analyses

Solid state NMR experiments were carried out in order to gain insight into the electronic structure at the central atoms in **3**, **5**, **6**, **8**, and **9**. Quantum chemical calculations were performed to find out the orientation of the principal tensor components of silicon or tin atoms in these molecules. The experimental and calculated values are given in Table 5 and 6, the orientation of the principal tensor components is shown in Fig. 8-11.

Compound **3** crystallises with two crystallographic independent half molecules in the asymmetric unit. Therefore two signals in the ²⁹Si CP/MAS NMR are found. The calculated values show some differences to the measured data. Nevertheless an unambiguous assignment of the tensor components is possible. Fig. 8 shows the spatial orientation of the tensor components for one molecule of **3**. The orientation in the other molecule is essentially the same, therefore the discussion is limited to one of the crystallographic independent molecules. The shielding tensor shows a more prolate form with the principal components δ_{11} and δ_{22} of Si1 being oriented nearly in plane with the two oxygen atoms in the coordination sphere of the silicon atom. With δ_{33} the highest shielding of the tetracoordinated silicon atom is observed perpendicular to the oxygen atoms.

There is a good agreement between calculated and experimental principal tensor components for the pentacoordinated and for the hexacoordinated silicon compounds in Table 5. Compounds **5** and **6** should be considered as distorted trigonal bipyramids for

Table 5

 ^{29}Si MAS NMR data and results of GIAO calculations (B3PW91/6-311+G(2d,p)) of ^{29}Si NMR shifts of compounds **3**, **5**, **6**, and **9**.

Molecule		δ_{iso}^{a}	δ_{11}	δ_{22}	δ_{33}	Ω^{b}	κ^{b}
3 -I	exp.	0	34.5	13.0	-47.5	82	0.47
	calc.	8.9	42.7	24.5	-40.6	83.2	0.6
3 -II	exp.	-2.38	33.0	9.3	-49.4	82.4	0.42
	calc.	7.1	42.3	21.8	-42.8	85.2	0.5
5	exp.	-84.8	2.1	-121.8	-134.8	136.9	-0.81
	calc.	-86.9	7.4	-120.2	-147.8	155.2	-0.6
6 -I	exp.	-101.1	-27.2	-127.4	-148.7	121.5	-0.65
	calc.	-101.1	-24.1	-125.6	-153.5	129.3	-0.6
6 -II	exp.	-98.5	-24.5	-119.3	-151.6	127.1	-0.49
	calc.	-97.5	-17.9	-115.9	-158.8	141.0	-0.4
9	exp.	-172.4	-147.9	-177.4	-191.8	43.9	-0.34
	calc.	-176.5	-148.7	-183.9	-196.7	48.0	-0.5

^a Chemical shift in solid state.

^b Herzfeld-Berger convention [47,48], $\Omega = \delta_{11} - \delta_{33}$, $\kappa = 3 (\delta_{22} - \delta_{iso})/\Omega$.

Table 6

 119 Sn MAS NMR data and results of GIAO calculations (B3PW91/ DGDZVP and 6–311+G(2d,p)) of 119 Sn NMR shifts of **8**.

Molecule		δ_{iso}^{a}	δ_{11}	δ_{22}	δ_{33}	$arOmega^{b}$	κ^{b}
8	exp.	-331.4	-135.7	-225.7	-632.8	497.1	0.64
	calc.	-331.4	-137.4	-223.8	-633.1	495.7	0.65

^a Chemical shift in solid state.

^b Herzfeld-Berger convention [47,48], $\Omega = \delta_{11} - \delta_{33}$, $\kappa = 3 (\delta_{22} - \delta_{iso})/\Omega$.



Fig. 8. Orientation of the ²⁹Si CSA tensor principal components of 3-I.

the following discussion. Adequate to this geometry a rather oblate shielding tensor can be observed indicated by κ -values of -0.81 (**5**), -0.65 and -0.49 (**6**-I and **6**-II, respectively). The principal tensor component δ_{11} is orientated in both compounds along the axis of the trigonal bipyramid, i.e. the lowest shielding of the pentacoordinated silicon atom is in this direction. The higher shielded tensor components δ_{22} and δ_{33} are situated in the trigonal plane of the coordination polyhedra. The shielding in this coordination geometry might be explained with simple geometric arguments. There are three equatorial substituents (O1, O2, C), which cause much larger shielding than the two axial substituents. Furthermore the axial substituents have longer bond distances to silicon than the equatorial substituents.

The orientation of the tensor components in the crystallographic independent molecule **6**-II is essentially the same as in molecule **6**-I and is therefore not discussed further.

The hexacoordinated silicon compound 9 features a substantially smaller anisotropy of the silicon NMR signal than the pentacoordinated compounds. This is due to the more evenly distributed ligand environment in the distorted coordination octahedra in 9. This octahedron is formed by four oxygen atoms in one plane which are supplemented by two perpendicular nitrogen atoms. The investigation of similar hexacoordinated silicon complexes in the literature showed that substituents with free electron pairs influence the shielding in orthogonal direction [49]. This is also observed at the hexacoordinated silicon atom in 9. where the nitrogen atoms lead to the highest shielding in perpendicular direction. The oxygen atoms have a smaller shielding effect in perpendicular direction since they withdraw electron density due to their higher electronegativity. The shielding of the silicon atom shows a small span of only 43.9 ppm. Together with the octahedral coordination polyhedron the electron density distribution present around this silicon atom is more spherical compared to the other complexes.



Fig. 9. Orientation of the ²⁹Si CSA tensor principal components of 5 and 6-I.



Fig. 10. Orientation of the ²⁹Si CSA tensor principal components of 9.

For complex **8** a ¹¹⁹Sn solid state NMR spectrum was measured. The values determined for the chemical shift tensors are listed in Table 6. The lower shielding tensor components δ_{11} and δ_{22} lie in the same plane as the tridentate ligand 1 (Fig. 11). The highest shielding δ_{33} is perpendicular to that plane. δ_{11} points along the O–Sn–O axis and δ_{22} towards the Sn–N bond. In contrast, shielding δ_{33} runs parallel to the free electron pairs located at the oxygen atoms O1 and O2 and the π -electrons of the nitrogen atom. In contrast to the pentacoordinated silicon complexes 5 and 6, the shielding tensor shows a more prolate form and the orientation of the principal components found here is different to orientation pattern in **5** and **6** (see above). This fact is explained with the different coordination geometry found in this complex. The angle C10-Sn1-C16 is 125.85(5)° and the angle O1–Sn1–O2 159.13(5)°. These are larger angles than in the comparable silicon compound 6. Therein the following angles were observed for the two crystallographic



Fig. 11. Orientation of the tensor components in 8.

independent molecules: C10–Si1–C16 101.4(1)°, O1–Si1–O2 133.8(1)°, C31–Si2–C37 103.3(1)° and O3–Si2–O4 132.6(1)°. The orientation of the tensor components in **6** was explained with a trigonal bipyramidal coordination geometry of the silicon atoms with the parameter τ = 0.59.

The larger bond angles in **8** lead to a distorted coordination geometry with $\tau = 0.55$. If one considers this as a strong distorted trigonal bipyramid, then the atoms O1–Sn1–O2 form the axis of the bipyramid. The lowest shielding (δ_{11}) is in this direction. The highest shielding tensor components δ_{33} is again in the trigonal plane of the bipyramid, which is in line with the discussion of the tensor components in **5** and **6**, but together with a δ_{22} showing a significantly smaller shielding contribution for the Sn complex indicating the stronger deviation from the trigonal bipyramid in **8**.

4. Conclusion

The reaction of salicylaldehyde-(2-hydroxyethyl)imine (1) with assorted organoelement compounds from group 13 and 14 leads to a great variety of coordination compounds. Depending on the size of the central atom and the organic substituents, tetra-, penta- or hexacoordinated complexes emerge. When the central atom of the complex has a small atom radius and small substituents like methyl groups, coordination number four is preferred as it was shown with compounds 3 and 4. Especially in the presence of phenyl substituents group 14 elements can achieve a pentacoordinated environment. When the substituents at the silicon atom in the starting material are rather labile or reactive, coordination number six is easily reached. In complex 10 all four chloride atoms are replaced by the ligand system. A surprising result was obtained with indium as example for group 13 elements. The complex resulting from the reaction of **1** with InCl₃ is monoanionic and not neutrally charged. Recently, anionic In-complexes with salen ligands were described [50]. The coordination number of the indium atoms is six and this preference can again be attributed to the larger atom radius compared to the other elements investigated. Solid state NMR measurements and chemical shift tensor analysis from selected derivatives were used to investigate the electron density distribution around the central atom. Thereby distinct features of the pentacoordinated compounds became visible. If the coordination geometry at the central atom is considered as distorted trigonal bipyramid, then the lowest shielding of the central atom is in direction of the axis of the coordination polyhedron. The higher shielding tensor components are always in the trigonal plane of the bipyramid. This statement is valid for silicon and tin compounds.

The results of this study demonstrate the structural variety that can be created with a single O,N,O' chelating ligand.

Acknowledgement

A.S. thanks the TU Bergakademie Freiberg for the Postdoctoral Research Fellowship "Mary Hegeler".

Appendix A. Supplementary material

CCDC 1004180–1004183 and 1004266–1004271 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.08.026.

References

- M. Calligaris, L. Randaccio, in: G. Wilkinson, R. D. Gillard, J. A. McCleverty (eds.), Schiff Bases as Acyclic Polydentate Ligands, in Comprehensive Coordination Chemistry, vol. 2, Pergamon Press, Oxford, 1987, p. 715.
- [2] R. Hernández-Molina, A. Mederos, in: J.A. McCleverty, T.J. Meyer (eds.), Acyclic and Macrocyclic Schiff Base Ligands, in Comprehensive Coordination Chemistry II, vol. 1, Elsevier Pergamon, Amsterdam, 2004, p. 411.
- [3] P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 252 (2008) 1871.
- [4] M. Dey, C.P. Rao, P. Saarenketo, K. Rissanen, E. Kolehmainen, Eur. J. Inorg. Chem. (2002) 2207.
- [5] (a) S. Celen, E. Gungor, H. Kara, A.D. Azaz, J. Coord. Chem. 66 (2013) 3170;
 (b) J. Szklarzewicz, M. Skaisgirski, P. Paciorek, K. Kurpiewska, P. Zabierowski, M. Radon, Polyhedron 68 (2014) 112;
 - (c) E. Hecht, T. Rüffer, H. Lang, Z. Anorg. Allg. Chem. 630 (2004) 1326;
 - (d) D.L. Peng, Russ. J. Coord. Chem. 39 (2013) 603;
 - (e) S.R. Petrusenko, O.M. Stetsyuk, I.V. Omelchenko, Acta Crystallogr., Sect. E 69 (2013) m326.
- [6] N.B. Sharma, A. Singh, R.C. Mehrotra, Main Group Met. Chem. 27 (2004) 191.
- [7] J.P. Tandon, S.R. Gupta, R.N. Prasad, Monatsh. Chem. 107 (1976) 1379.
- [8] M. Jain, S. Gaur, S.C. Diwedi, S.C. Joshi, R.V. Singh, A. Bansal, Sulfur Silicon Relat. Elem. 179 (2004) 1517.

- [9] M. Nath, R. Yadav, J. Therm. Anal. Calorim. 55 (1999) 135.
- [10] L. Tian, Z. Shang, X. Zheng, Y. Sun, Y. Yu, B. Qian, X. Liu, Appl. Organomet. Chem. 20 (2006) 74.
- [11] M. Nath, S. Goyal, Sulfur Silicon Relat. Elem. 177 (2002) 447.
- [12] T.M. Aminabhavi, N.S. Biradar, S.B. Patil, V.L. Roddabasanagoudar, W.E. Rudzinski, Inorg. Chim. Acta 107 (1985) 231.
- [13] U. Böhme, S. Fels, Acta Crystallogr., Sect. C 66 (2010) o202.
- [14] U. Böhme, B. Günther, Inorg. Chem. Commun. 10 (2007) 482.
- [15] U. Böhme, J. Haushälter, Inorg. Chem. Commun. 12 (2009) 35.
- [16] U. Böhme, S. Jähnigen, Acta Crystallogr., Sect. C 64 (2008) 0364.
- [17] G. Warncke, U. Böhme, B. Günther, M. Kronstein, Polyhedron 47 (2012) 46.
- [18] U. Böhme, S. Fels, Inorg. Chim. Acta 406 (2013) 251.
- [19] S. Schlecht, W. Frank, M. Braun, Sulfur Silicon Relat. Elem. 186 (2011) 1585.
- [20] S. Schlecht, M. Finze, R. Bertermann, W. Frank, A. Domann, M. Braun, Eur. J. Inorg. Chem. (2013) 1488.
- [21] U. Böhme, S. Wiesner, B. Günther, Inorg. Chem. Commun. 9 (2006) 806.
- [22] S. Bhambhani, S. Saxena, A.K. Rai, Main Group Met. Chem. 21 (1998) 747.
- [23] S. Bansal, Y. Singh, A. Singh, Heteroat. Chem. 15 (2004) 21.
- [24] (a) M. Bouyhayi, Y. Sarazin, O.L. Casagrande Jr, J.-F. Carpentier, Appl. Organometal. Chem. 26 (2012) 681;
- (b) J.P. Tandon, G.N. Prasad, Monatsh. Chem. 104 (1973) 1064.
 [25] C. Cossement, J. Darville, J.-M. Gilles, J.B. Nagy, C. Fernandez, J.-P. Amoureux, Magn. Reson. Chem. 30 (1992) 263.
- [26] DM2011: release 5.12.2011; D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.O. Durand, B. Bujoli, Z. Gan, G. Hoatson, Magn. Reson. Chem. 40 (2002) 70.
- [27] HBA Graphical Herzfeld-Berger Analysis, 1995, 2012 K. Eichele, Version 1.7.3, 23.8.2012.
- [28] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [29] Gaussian 09, Revision B.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian Inc, Wallingford CT, 2010.
- [30] K. Wolinski, J.F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251.
- [31] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [32] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
- [33] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, J. Wiley & Sons, Chichester, 1986.
- [34] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
- [35] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, J. Chem. Phys. 77 (1982) 3654.
- [36] N. Godbout, D.R. Salahub, J. Andzelm, E. Wimmer, Can. J. Chem. 70 (1992) 560.
 [37] A.W. Addison, T.N. Rao, J. Reedijk, J. Van Rijn, G.C. Verschoor, J. Chem. Soc.,
- Dalton Trans. (1984) 1349. [38] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond, Oxford University Press, 1999
- [39] M. Nishio, CrystEngComm 6 (2004) 130.
- [40] L.S. Zamudio-Rivera, R. George-Tellez, G. Lopez-Mendoza, A. Morales-Pacheco, E. Flores, H. Höpfl, V. Barba, F.J. Fernandez, N. Cabirol, H.I. Beltran, Inorg. Chem. 44 (2005) 5370.
- [41] L. Pauling, J. Am. Chem. Soc. 69 (1947) 542.
- [42] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
- [43] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.
- [44] A.M. Arif, A.R. Barron, Polyhedron 7 (1988) 2091.
- [45] (a) B. Le Guennic, S. Petit, G. Chastanet, G. Pilet, D. Luneau, N.B. Amor, V. Robert, Inorg. Chem. 47 (2008) 572;
 (b) J.-P. Costes, F. Dahan, J.-P. Laurent, Inorg. Chem. 25 (1986) 413;
 (c) C. Biswas, M.G.B. Drew, A. Figuerola, S. Gómez-Coca, E. Ruiz, V. Tangoulis, A. Ghosha, Inorg. Chim. Acta 363 (2010) 846;
 (d) F.Z.C. Fellah, J.-P. Costes, L. Vendier, C. Duhayon, S. Ladeira, J.-P. Tuchagues, Eur. J. Inorg. Chem. (2012) 5729.
- [46] A.F. Holleman, E. Wiberg, N. Wiberg, Lehrbuch der Anorganischen Chemie, Walter De Gruyter, Berlin, New York, 102nd ed., 2007, 1597.
- [47] J. Herzfeld, A.E. Berger, J. Chem. Phys. 73 (1980) 6021.
- [48] J. Mason, Solid State Nucl. Magn. Reson. 2 (1993) 285.
- [49] (a) D. Gerlach, E. Brendler, T. Heine, J. Wagler, Organometallics 26 (2007) 234;
 (b) E. Brendler, T. Heine, A.F. Hill, J. Wagler, Z. Anorg. Allg. Chem. 635 (2009) 1300;

(c) G.W. Fester, J. Eckstein, D. Gerlach, J. Wagler, E. Brendler, E. Kroke, Inorg. Chem. 49 (2010) 2667;

(d) L.A. Truflandier, E. Brendler, J. Wagler, J. Autschbach, Angew. Chem. 123 (2011) 269 (Angew. Chem., Int. Ed. 50 (2011) 255);

(e) F. Bitto, K. Kraushaar, U. Böhme, E. Brendler, J. Wagler, E. Kroke, Eur. J. Inorg. Chem. (2013) 2954.

[50] N. Maudoux, J. Fang, T. Roisnel, V. Dorcet, L. Maron, J.-F. Carpentier, Y. Sarazin, Chem. Eur. J. 20 (2014) 7706.