UNIVERSITATEA
BABEȘ-BOLYAI

Faculty of Chemistry and Chemical Engineering

Contributions to the chemistry of group 15 and 16 hypervalent compounds

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PhD Thesis Abstract

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Cluj-Napoca
2017

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Keywords: hypervalent compounds, organochalcogen compounds, organobismuth compounds, transannular bond, diphenyl ether, Bi···π interactions.

Introduction

The concept of hypervalency was proposed in 1969 by J. I. Musher and it is still, the universal accepted definition. It states that in order for a molecule containing elements of group V-VIII to be described as hypervalent, the elements must find themselves having other valences as their lowest stable valence.[1]

The *N-X-L* nomenclature was introduced in 1980 and it is still used to classify hypervalent molecules. Here, N is the number of valence electrons, X, the chemical symbol of the main atom and L the number of ligands (donor atoms) at the central atom.[2]

The importance of hypervalency in the stability of such compounds afforded the synthesis and characterization of some interesting species having different coordination numbers, as expected, for the central atoms. Hypervalent molecules have found applications in the area of material science, catalysis, CO_2 trapping and even in the biological field, thus explaining the growing interest in this field, alongside with the genuine preoccupation of scientists for the fundamental knowledge in the field of metal-carbon bonds and unusual organometallic species.[3,4]

Group 16 compounds

Introduction

Group 16 of the periodic table is called the chalcogen group and it contains the elements oxygen, sulfur, selenium, tellurium and the radioactive element polonium. All of them have a s2p4 electronic configuration on the valence shell. While for oxygen the characteristic oxidation state is 2−, for S, Se and Te, the oxidation states 1+, 2+, 4+ or 6+ are also common.

The properties of the organic combinations of these elements are strongly influenced by the electronegativity of the chalcogen in the compound. This decreases towards the lower periods and it is in an inversely proportional relation with the metallic character. Therefore, tellurium is a metalloid whereas sulfur and selenium are nonmetals. Oxygen is generally treated

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[1] J. I. Musher, *Angew. Chem., Int. Ed.*, **1969**, *8*, 54.

[2] K. K.-y. Akiba (Ed.), *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, **1999**.

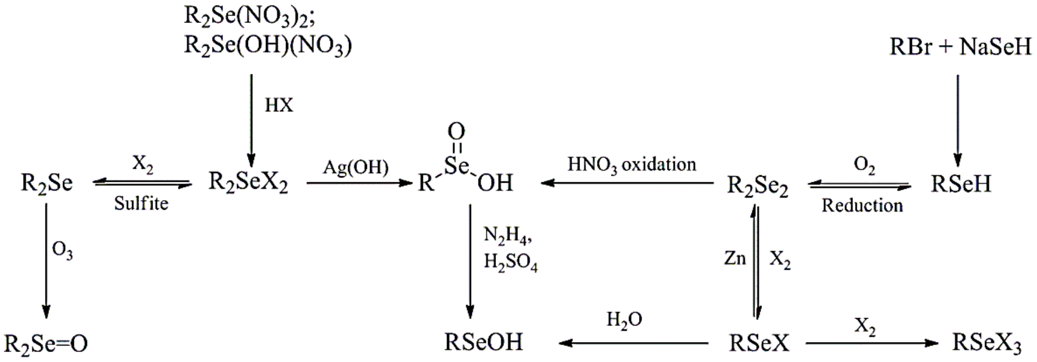
[3] A. J. Mukherjee, S. S. Zade, H. B. Singh, R. B. Sunoj, *Chem. Rev.,* **2010**, *110*, 4357 [and the references therein].

[4] C. I. Raţ, C. Silvestru, H. J. Breunig, *Coord. Chem. Rev.,* **2013**, *257*, 818 [and the references therein].

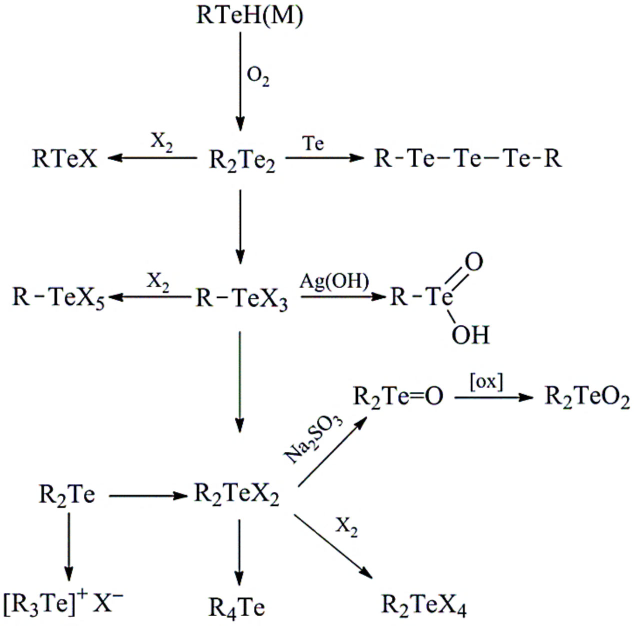
separately from the other elements due to the lack of accessible d-orbitals and of the difference in the bonding fashion of it with carbon.

Literature data

Most common oxidation states for sulfur, selenium and tellurium range from 2− to 6+ and the transition from one oxidation state to the other takes place relatively easily. As this reduction/oxidation behavior is relevant for the results presented in this work, Scheme 1.1 and 1.2, with a focus on organoselenium and organotellurium compounds, will give an overview regarding the possible transformations of such species.[5]



Scheme 1.1. Reactivity of organoselenium compounds, including redox processes.



Scheme 1.2. Reactivity of organotellurium compounds, including redox processes.

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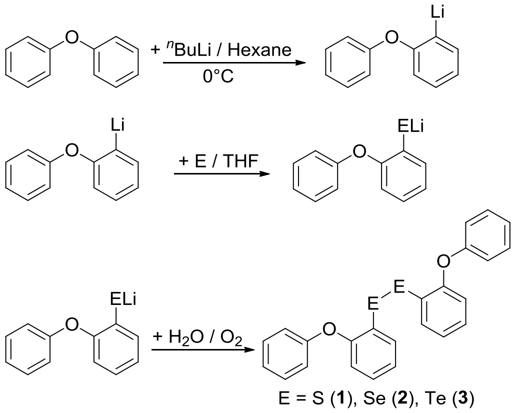
[5] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, **1985**, Pergamon Press, *Second Edition.*

Original contributions

This chapter presents the synthesis, characterisation and electrochemical properties of new diorganodichalcogenides based on the diphenyl ether moiety, their redox behaviour in reactions with an appropriate reducing or oxidizing reagent, as well as the proposed reaction mechanism for the formation of cyclic derivatives.

Diorganodichalcogenides. Preparation and structural characterization.

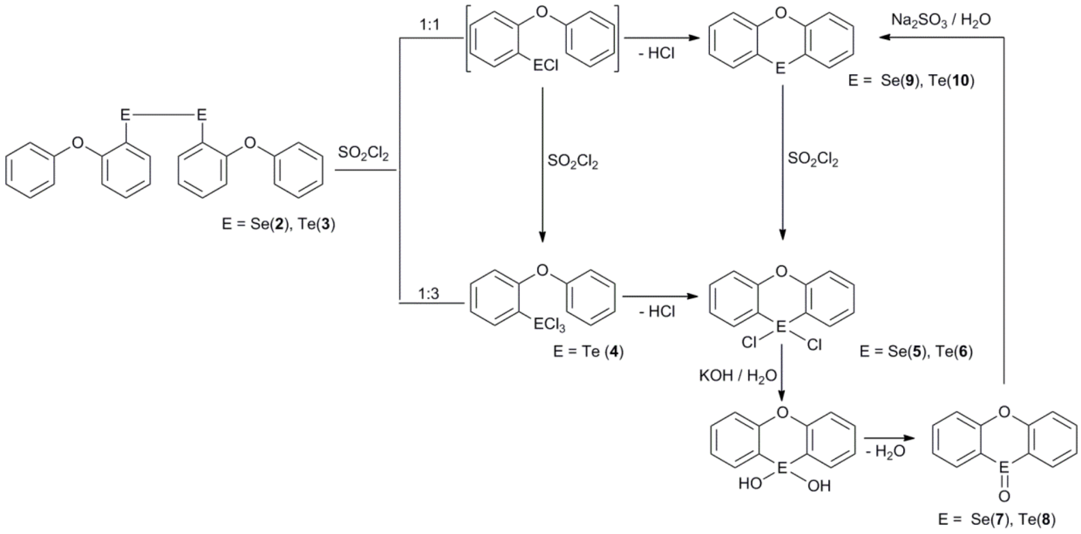
Compounds $[(C_6H_5)O(C_6H_4)]_2S_2$ (**1**), $[(C_6H_5)O(C_6H_4)]_2Se_2$ (**2**) and $[(C_6H_5)O(C_6H_4)]_2Te_2$ (**3**) were synthesized as shown in Scheme 1.3 and for compounds **2** and **3** suitable crystals for single-crystal X-ray diffraction could be obtained. In both cases, O···E interaction is observed, low under the van der Waals radii of the elements, generating *10–E–3* hypervalent species.



Scheme 1.3. General reaction scheme for the synthesis of the diorganodichalcogenides containing diphenyl ether.

Reactions of the diorganodichalcogenides with SO_2Cl_2

In an attempt to synthesize organochalcogen chlorides, the compounds **1** – **3** were reacted with SO_2Cl_2 in a 1: 1 molar ratio at room temperature. After the hydrolysis with a concentrated solution of KOH and further work-up, for the reaction between **2** with SO_2Cl_2 a mixture of two components was obtained, namely phenoxaselenine 10-oxide **7** and phenoxaselenine **9**. Both compounds could be separated based on their different solubility in THF and for **7** its molecular structure was determined by single-crystal X-ray diffraction, revealing at the selenium atom a trigonal pyramidal coordination geometry. For compounds **1** and **3** a complex mixture of products that could not be separated was obtained. Further, both **2** and **3** were reacted with SO_2Cl_2 under inert atmosphere and without further washing with KOH. In case of the diorganodichalcogenide **2**, an organoselenium dichloride **5** was obtained where at the selenium atom a see-saw coordination geometry appears. When reacting **3** with SO_2Cl_2 the main product was the organotellurium trichloride **4** where the coordination geometry at the chalcogen atom is of distorted octahedral one. From the same reaction, the corresponding organotellurium dichloride **6** is obtained as well, as identified from the ^{125}Te NMR spectrum. Therefore, the reaction pathway to the formation of **4** – **10** is given in Scheme 1.4.



Scheme 1.4. Proposed reaction pathway for the formation of species **4** – **10**

In order to understand why in the case of the reaction of **2** with SO_2Cl_2 under base hydrolysis a mixture of both phenoxaselenine **9** and phenoxaselenine 10-oxide **7** is obtained, it was proposed that the SO_2 that is generated in solution reacts with the excess of KOH to give the reducing agent K_2SO_3 and water. Therefore, compounds **5** and **6** were reacted with a concentrated solution of KOH to give in a quantitative yield compounds **7** and the equivalent compound **8**. Furthermore, the so-isolated **9** and **8** were reacted with a reducing agent, Na_2SO_3 to give compounds **9** and **10**.

Electrochemical studies of the oxidation process of diorganodichalcogenides with SO_2Cl_2

Some electrochemical experiments were performed in order to gain more insight regarding the oxidation mechanism of diorganidichalcogenides 2 and 3 with SO_2Cl2 and they were focused on the positive domain of potential. Both compounds present a peak at +1.95 V corresponding to the oxidation of the electrolyte and one at +1.5 V corresponding to the organic ligand. For the diorganodiselenide 2, a peak at +1.08 V can be correlated to the selenium atom. For 3, the peaks appear at +0.75 V, +1.1 V and +1.32 V and are irreversible. They can be attributed to the oxidation of the tellurium by means of a more complex process as for 2.

Unexpectedly, the Se(IV) compound 7 and the similar Te(IV) compound 6 could not be reduced in a reasonable potential range, although reduction was observed by the chemical behaviour in base hydrolytic conditions.

Conclusions

- The diorganodichalcogenides of type $[(C_6H_5)O(C_6H_4)]_2E_2$ [E = S (**1**), Se (**2**), Te (**3**)], were prepared and their oxidation reactions with SO_2Cl_2 were investigated. For compounds **2** and **3** their molecular structures were determined by single-cyrstal X-ray diffraction and, due to the intramolecular O→E (E = Se, Te) interactions, the compounds can be described as hypervalent *10−E−3* species.
- The reactions of these derivatives with SO_2Cl_2 in open atmosphere did not yield the expected organochalcogen chlorides – but for the diorganodiselenide **2** a mixture of phenoxaselenine-10-oxide (**7**) and phenoxaselenine (**9**) was obtained. In the case of compounds **1** and **3** a complex mixture of products resulted when similar reactions were performed.
- When the same reaction with SO_2Cl_2 was performed for **2** and **3** under inert conditions, the organoselenium dichloride **5** and respectively the organotellurium trichloride **4** were obtained. The single-crystal X-ray diffraction studies revealed dimeric associations in case of **4**, realized by Te···Cl intermolecular interactions, thus leading to a *14–Te–6* hypervalent species. In the crystal of **5** the molecules are associated in polymeric chains by H···Cl interactions.
- Further reactions of **2** and **3** with SO_2Cl_2 under base (NaOH) hydrolytic conditions were performed in order to explain the redox behavior of the organochalcogen species of this type and the formation of compounds **7** and **9**. A monomeric solid state structure was determined for **7** by single-crystal X-ray diffraction.
- Electrochemical studies were employed in order to identify the charge transfer processes that might take place when oxidizing **2** or **3** with SO_2Cl_2. No evidence of the *ECE* mechanism could be found for the investigated species, probably because the process was too rapid and the oxidation intermediates could not be evidenced.

- Among the organochalcogen compounds described in this chapter, **3** and **4** are for the first time reported and fully characterized in this work, while the other were only mentioned (**7**), or reported in the literature, but they were prepared by using different procedures or they were incompletely characterized before.

Organobismuth compounds

The chemistry of bismuth containing compounds has experienced a growing interest during last years, mainly due to the importance of such derivatives for different applications and of course, in order to gain insight in the fundamental knowledge regarding this field.

Bismuth is the heaviest of the pnicogens, with a mass of 208.9804 a.m.u. and the atomic number 83. Its electronic configuration of $[Xe]4f^{14}5d^{10}6s^{2}6p^{3}$ easily give rise to 3+ or 5+ oxidation states. Most of the compounds reported so far in the literature are of Bi^{3+} due to the fact that most commonly the three electrons^{-} from the *p* orbitals are those involved in bonding.

Literature data

The organometallic bismuth compounds can increase their valence by extended bonding. For organobismuth compounds, several hypercoordinated systems were already reported in the literature.

Organometallic compounds of type *8-Bi-3* [6] present themselves as generally having a trigonal pyramidal structure. Most of the triorganobismuth compounds fall in this category

The *10-Bi-4* species present at the metal atom a *pseudo* trigonal bipyramidal coordination geometry. The majority of the ionic bismuth compounds are in this category.

10-Bi-5 species present either a trigonal bipyramidal or a square-pyramidal coordination geometry. In order to identify which of these two geometries are best to describe the compounds, one must take a closer look at the τ_5 value. τ_5 is defined as the ratio $(\beta-\alpha)/60°$, $\beta > \alpha$, where β and α are the two greatest angles at the coordination center. If the τ_5 value is closer to 0, the structure might be described as square pyramidal, whereas if this value is closer to 1, the correct description is a trigonal bipyramid. In the case that these differences are exactly 0 or 1 then the structure can be discussed as an ideal one, but in most examples

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[6] H. Suzuki, T. Ogawa, N. Komatsu, Y. Matano, T. Murafuji, T. Ikegami, *Organobismuth Chemistry*, **2001**, Elsevier, Amsterdam, *First Edition.*

this is not the case.[7] Similarly, a τ_4 parameter is usually used to describe the coordination geometry in tetra coordinated metal complexes, as square-planar or tetrahedral.

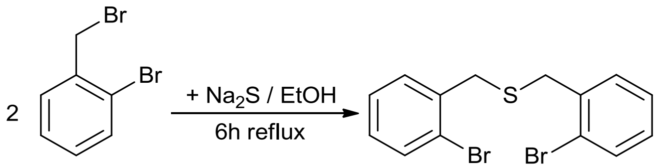
Organobismuth compounds containing a six coordinated metal atom can be described as *12-Bi-6* species.

When the bismuth atom is seven coordinated, *14-Bi-7* species are formed. Last but not least, few organometallic bismuth compounds can be described as *18-Bi-9* species.

Original contribution

Synthesis and characterization of diorganobismuth(III) compounds containing the $[(C_6H_4CH_2)_2S]$ fragment.

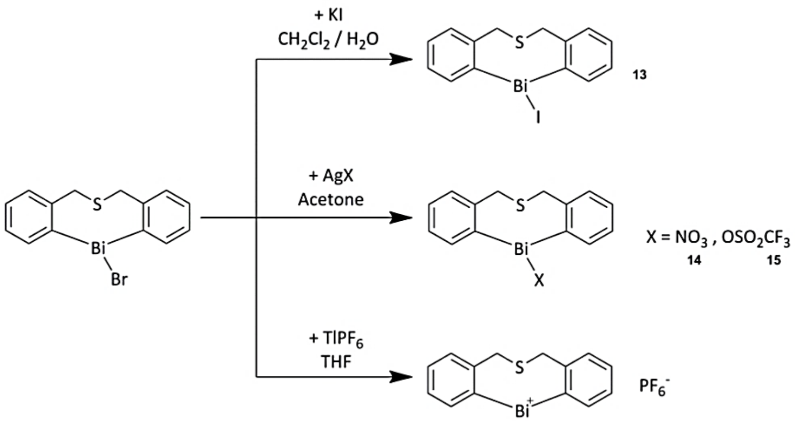
The organic ligand **11** was synthesized in high yields by a method described in the literature[8] (Scheme 2.1) and the purity of it was confirmed by NMR spectroscopy.



Scheme 2.1. Synthesis of bis(2-bromobenzyl)sulfane **11**.

The diorganobismuth(III) bromide **12** was synthesized by the reaction of the lithiated ligand with $BiBr_3$ at –78°C in Et_2O.

In order to investigate the influence of the anionic ligand on the transannular interaction a series of experiments were proposed, as shown in Scheme 2.2.



Scheme 2.2. Reaction scheme for the synthesis of thiabismocine(III) compounds with different inorganic ligands.

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[7] A. W. Addison, T. Nageswara Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.*, **1984**, 1349.

[8] S. Shimada, O. Yamazaki, T. Tanaka, Y. Suzuki, M. Tanaka, *J. Organomet.Chem.*, **2004**, *689*, 3012.

5 new compoundsm respectively $[(C_6H_4CH_2)_2S]BiBr$ (**12**), $[(C_6H_4CH_2)_2S]BiI$ (**13**), $[(C_6H_4CH_2)_2S]BiONO_2$ (**14**), $[(C_6H_4CH_2)_2S]BiOSO_2CF_3$ (**15**) and $[\{(C_6H_4CH_2)_2S\}Bi]^+PF_6^-$ were synthesized starting from the bis(2-bromobenzyl)sulfane ligand. Four of these compounds (**12–15**) were stable in solution as well as in solid state and could be fully characterized by NMR spectroscopy and single-crystal X-ray diffraction. The diorganobismuth hexafluorophosphate is highly sensitive to even traces of water and showed a fast decomposition in solution.

For compounds **14** and **15** the bidentate character of the ligands was demonstrated in solid state also by IR spectroscopy, where in the asymmetric vibration of the NO_2 and SO_3 groups a characteristic splitting was observed.

The influence of the ligands towards the S→Bi interaction was investigated both in solution and where possible, in solid state. A correlation between the chemical shift of the CH_2 protons and the experimentally determined S→Bi interaction is given in Table 2.9.

Table 2.1. Summary of chemical shifts for the CH_2 protons correlated with the transannular distance found in solid state for the thiabismocines.

Compounds R = $(C_6H_4CH_2)_2S$	H_a δ (ppm)	H_b δ (ppm)	d S→Bi (Å)
RBiI	4.43	4.18	2.853(5)
RBiBr	4.49	4.23	2.832(3)
$RBiONO_2$	4.69	4.41	2.765(3)
$[RBi]^+PF_6^-$	4.77	4.41	–
$RBiOSO_2CF_3$	4.87	4.58	2.674(1)

The correlation between the electronegativity of the ligand attached to bismuth and the transannular interaction can be easily observed and follows the trend predicted from the Hammett constant for the halides (for Br^- σ_m is 0.39 and for I^- σ_m is 0.35[9]) and this is reflected in the small differences between the transannular interaction in the crystal structure of the two compounds, 2.853 (**13**) and 2.832 (**12**) Å.

This character is reflected as well in the chemical shift of the AB spin system of the two CH_2 protons in the organic group. For the diorganobismuth bromide the resonances for these protons appear more deshielded than those from the iodide, as a consequence of the different electron withdrawing effect of the halogen that is transmitted through the transannular bond from the metal atom.

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[9] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.,* **1991**, *91*, 165

For the oxo-ligands, namely ONO_2^- and $CF_3OSO_2^-$, the transannular S→Bi interaction in the crystal structure is stronger than in the case of compounds **12** and 1**3**. The triflate moiety presents the strongest transannular interaction, in good agreement with the fact that OTf has the highest reported Hammett constant in this series, σ_m 0.56. For compound **15**, the resonances for the CH_2 groups in the ^1H NMR spectrum are the most deshielded, in the range where typically resonances for such protons appear in a thiabismocine cation[10], thus indicating that the bond between bismuth and oxygen might be at least partially ionic in solution.

The diorganobismuth(III) halides **12** and **13** can be described as *10-Bi-4* hypervalent species, with a see-saw coordination geometry about the metal, while compounds **14** and **15**, as a consequence of the bidentate behaviour of the inorganic ligands can be described as *12-Bi-5* hypervalent species, with a distorted trigonal bipyramidal coordination geometry.

Compounds **14** and **15** present π $Bi\cdots Ph_{centroid}$ interactions in the solid state and this fact can be associated with a weaker covalent bond between the inorganic ligand and the metal, that favours the formation of dimeric species which stabilize the bismuth atoms. In the case of the halides **12** and **13**, this Bi–X covalent bond is stronger and, therefore, dimeric associations appear in the molecular structure by means of secondary bismuth···halogen interactions.

DFT theoretical calculations on compounds **12** – **15** and $[(C_6H_4CH_2)_2S]BiCl$ showed a decreasing trend for the length of the transannular S→Bi interaction in the series **15** > **14** > $[(C_6H_4CH_2)_2S]BiCl$ > **12** > **13** which correlates very well with the decreasing ionic character of the Bi–X (X = Cl, Br, I, O).

Synthesis and characterization of diorganobismuth compounds containing the $C_6H_5CH_2N(CH_2C_6H_4)_2$ or $C_6H_5CH_2CH_2N(CH_2C_6H_4)_2$ fragments.

The starting organic ligand **16** was synthesized in high yields using a reported procedure[11] by an amine alkylation reaction between benzyl amine and 2–bromobenzyl bromide. Ligand **17** was prepared using a similar procedure, as described in Scheme 2.3.

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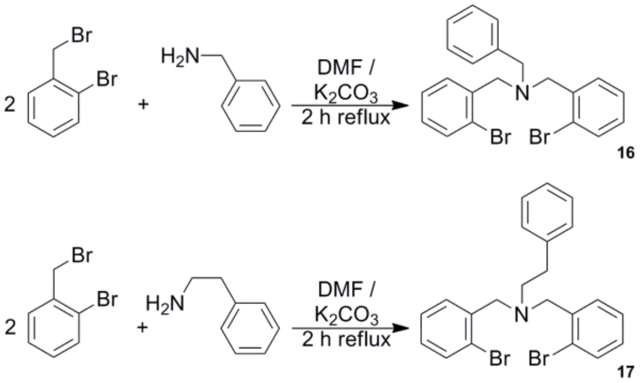
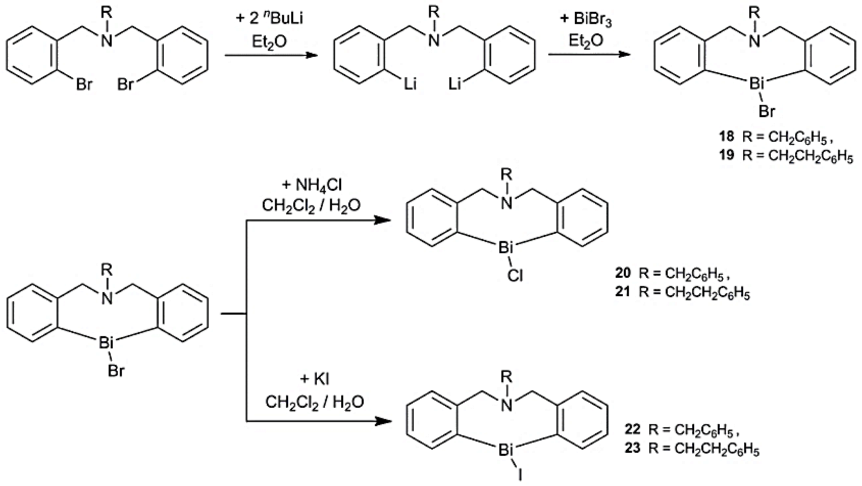
[10] T. Kotani, D. Nagai, K. Asahi, H. Suzuki, F. Yamao, N. Kataoka, T. Yagura, *Antimicrob. Agents Chemother.,* **2005**, *49*, 2729.

[11] F. H. Carré, R. J. P. Corriu, G. F. Lanneau, P. Merle, F. Soulairol, J. Yao, *Organometallics*, **1997**, *16*, 3878.



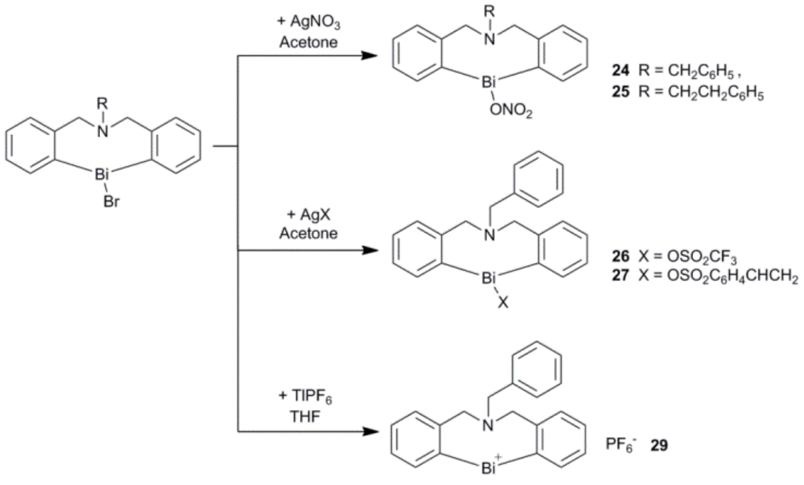
Scheme 2.3. Synthesis of the organic ligands **16** and **17**.

The bromides were used as starting materials in the synthesis of the corresponding chlorides (**20**, **21**) and iodides (**22**, **23**) (Scheme 2.4) and their synthesis was performed in a two phase system where the organometallic compound was dissolved in CH_2Cl_2 and the inorganic salt in water, followed by extraction. The chlorides are colorless solids, obtained in good (**21**) or very good yields (**20**), whereas the iodides were obtained as bright yellow solids in almost quantitative yields. All compounds are relatively stable in solution and as solids, but the iodides decompose after 2 months.



Scheme 2.4. Preparation of the azabismocine(III) halides **18-23**.

Further ligand exchange reactions were performed between the diorganobismuth(III) bromides and silver or talium salts of other ligands, like NO_3^-, $CF_3SO_3^-$, $CH_2CHC_6H_4SO_3^-$ or PF_6^- as shown in Scheme 2.5.



Scheme 2.5. Reaction scheme for the synthesis of azabismocine(III) compounds with nitrate, triflate, vinylsulfonate and PF_6^- ligands.

Catalytic activity of some azabismocines towards the oxidation of thiophenol to diphenyl disulfide

Cyclohexane and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (ionic liquid – IL) were used as solvents either pure or as a mixture of both. For these experiments, two different organobismuth compounds were tested. Firstly, the organic framework was varied by employing compounds having either one CH_2 moiety in the pendant arm or two CH_2 groups. Moreover, the substituent at the bismuth atom was either a halide, bromide for 1**8** and **19**, or an oxygen containing group, for **24** – **27**.

Between the halides, compound **19**, having two CH_2 groups, exhibits the best conversion, of 51%. Compound **18** is just slightly a better catalyst than NaOH, showing a conversion of only 21%. Interestingly, the organobismuth compounds containing the oxo ligands show better catalytic activity. The conversion decreases in the series from compound 24 > **26** > **25** > **27** and it goes from 100% > 94.8% > 92.9% > 86.1% after a reaction time of 5h.

Conclusions

This chapter presents the synthesis and characterization of 2 new classes of compounds starting from similar ligand systems. One class of compounds starts from *N,N*-bis(2-bromobenzyl)benzylamine, **16**, previously reported in literature, but not characterized and it contains **7** new diorganobismuth compounds, respectively the halides $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiX$ [X = Cl (**20**), Br (**18**), I (**22**)], as well as $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiONO_2$ (**24**), $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiOSO_2CF_3$ (**26**),

$[C_6H_5CH_2N(CH_2C_6H_4)_2]BiOSO_2C_6H_4(CHCH_2)$-4 (**27**) and $[C_6H_5CH_2N(CH_2C_6H_4)_2]Bi^+ PF_6^-$ (**29**).

The second class of compounds starts from *N,N*-bis(2-bromobenzyl)-2-phenylethanamine **17**, and contains a number of **4** new diorganobismuth compounds of type $[C_6H_5CH_2CH_2N(CH_2C_6H_4)_2]BiX$ [X = Cl (**21**), Br (**19**), I (**23**), ONO_2 (**25**)].

The starting diorganobismuth bromides **18** and **19** were used in a biphasic system to generate the iodides and the chlorides in good to very good yields.

Compounds containing oxygenated ligands were synthesized from the corresponding silver salts. A bidentate character was suggested by the IR spectroscopy, as the asymmetric vibrations of the ONO_2 and OSO_2 groups exhibit a characteristic splitting.

Compound **29** was synthesized starting from $TlPF_6$ and its structure was supported only by the NMR data, as no single-crystals suitable for X-ray diffraction could be obtained.

The influence of the substituents at the bismuth atom towards the transannular interaction N→Bi was investigated and a table of correlations between the chemical shift of the H_a and H_b protons from the CH_2 moieties and, where possible, the crystallographically determined distance N→Bi is presented. The results are given in Tables 2.2 and 2.3.

For the series containing one CH_2 group in the pendant arm, the correlation between the electronegativity of the substituent and the length of the transannular interaction follows in general the trend predicted from the Hammett constants. In the case of the halides, the differences in the length of the N→Bi bond are not so big. When changing to the oxygenated ligands, the strongest interaction is observed in case of compound **26**, which is in good agreement with the fact that the triflate moiety has the greatest Hammett constant of the series.

Table 2.2. Summary of chemical shifts of benzylic protons correlated with the transannular interaction found in solid state

Compound $R = C_6H_5CH_2N(CH_2C_6H_4)_2$	H_a δ (ppm)	H_b δ (ppm)	d N→Bi (Å)
RBiI	4.25	4.06	2.537(4)
RBiBr	4.30	4.10	2.531(4)
RBiCl	4.32	4.11	2.548(4)
$[RBi]^+PF_6^-$ *	4.89	4.53	—
$RBiONO_2$	4.47	4.26	2.463(7)
$RBiOSO_2C_6H_4CHCH_2$	4.48	4.22	2.454(4)
$RBiOSO_2CF_3$	4.59	4.39	2.402(3)

* Spectra registered in Acetone-d_6, while for the other compounds in $CDCl_3$

Table 2.3. Summary of chemical shifts of benzylic protons correlated with the transannular interaction found in solid state.

Compound R = $C_6H_5CH_2CH_2N(CH_2C_6H_4)_2$	H_{a+b} δ (ppm)	H_{15} δ (ppm)	H_{16} δ (ppm)	d N→Bi (Å)
RBiI	4.22	3.25	2.91	2.502(5)
RBiBr	4.26	3.26	2.91	2.531(1)
RBiCl	4.27	3.25	2.91	2.476(7)
$RBiONO_2$	4.39	3.35	2.93	2.479(5)

For the compounds containing two CH_2 groups in the pendant arm similar results are obtained and they are reflected as well in the chemical shift of the benzylic protons, that are more deshielded in the case of the nitrate compound **25** corresponding to the shortest transannular N→Bi interaction.

Except the compounds **24** and **25**, where the ONO_2 ligand is *O,O*-bidentate coordinated to bismuth, all the other compounds can be described as *10-Bi-4* hypervalent species, with a distorted see-saw coordination geometry. Compounds **24** and **25** are *12-Bi-5* hypervalent species with distorted trigonal bipyramidal coordination geometries, taking into account the secondary intramolecular O···Bi interaction.

Compounds **18** and **23** associate in dimeric pairs by means of Bi···halogen interactions and in case of **25** by Bi···O interactions with neighboring molecules. Compounds **20**, **22**, **24**, **26** and **27** associate as well in dimeric pairs but by means of π Bi···$Ph_{centroid}$ interactions. The strongest metal···$Ph_{centroid}$ interaction was found in case of compound **26** containing the triflate moiety as substituent at the metal atom, of 3.535 Å. One of the weakest metal···$Ph_{centroid}$ interaction was found in compound **22**, 4.136 Å, at the upper limit of such interactions previously reported.[12]

Compounds **18**, **19**, **24** – **27** were tested for the catalytic activity in the oxidation reaction of thiophenol to diphenyl disulfide. Compounds **24** – **27** showed high conversions both in cyclohexane and IL. Nevertheless, in IL better conversions were obtained in shorter time, *e.g.* for compound **25**, 100% conversion was reached in one hour.

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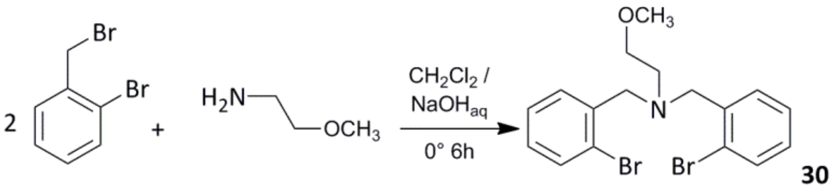
[12] a) A. A. Auer, D. Mansfeld, C. Nolde, W. Schneider, M. Schürmann, M. Mehring, *Organometallics*, **2009**, *28*, 5405.
b) I. Caracelli, J. Zuckerman-Schpector, I. Haiduc, E. R. T. Tiekink, *CrystEngComm*, **2016**, *18*, 6960.

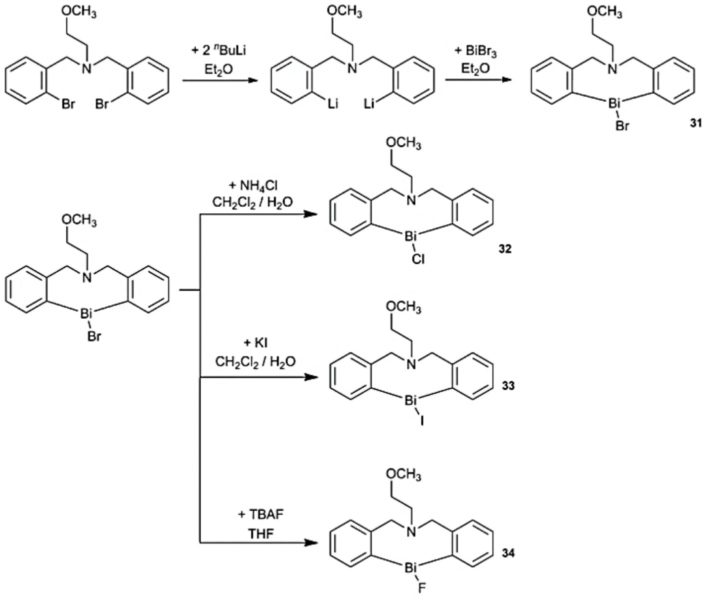
Synthesis and characterization of diorganobismuth compounds containing the $CH_3OCH_2CH_2N(CH_2C_6H_4)_2$ fragment.

The organic ligand **30** was synthesized with a high yield by reacting 2 equivalents of 2-bromobenzyl bromide with one equivalent of 2-methoxyethylamine in CH_2Cl_2 at 0° in the presence of a solution of NaOH in water.



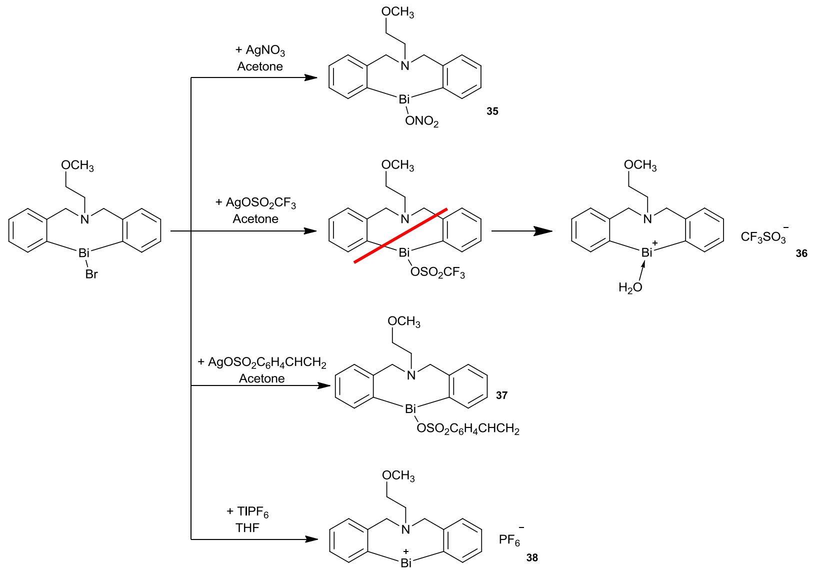
Scheme 2.6. Reaction scheme for the synthesis of the organic ligand **30**.

The ligand was then used to synthesize the bismuth bromide **31**, using a similar synthetic protocol as described for the bromides **18** and **19** (Scheme 2.7).



Scheme 2.7. Reaction scheme for the synthesis of azabismocine(III) halides containing the $NCH_2CH_2OCH_3$ moiety.

In order to investigate the influence of the substituent towards the transannular interaction and the intra- and intermolecular interactions of the compounds in the crystal structure, a series of diorganobismuth compounds with oxygenated ligands was synthesised.



Scheme 2.8. Synthesis of azabismocine(III) nitrate, triflate, sulfonate and hexafluorophosphate containing the $NCH_2CH_2OCH_3$ moiety.

Conclusions

8 new diorganobismuth(III) compounds of type containing the organic fragment $CH_3OCH_2CH_2N(CH_2C_6H_4)_2$, with a pendant arm capable to coordinate intramolecularly by O to the metal, were synthesized and structurally characterized, respectively the halides $[CH_3OCH_2CH_2N(CH_2C_6H_4)_2]BiX$ [X = F (**34**), Cl (**32**), Br (**31**), I (**33**)], $[CH_3OCH_2CH_2N(CH_2C_6H_4)_2]BiONO_2$ (**35**), $[\{CH_3OCH_2CH_2N(CH_2C_6H_4)_2\}Bi(H_2O)]^+\ OTf^-$ (**36**), $[CH_3OCH_2CH_2N(CH_2C_6H_4)_2]BiOSO_2C_6H_4(CHCH_2)$-4 (**37**) and $[\{CH_3OCH_2CH_2N(CH_2C_6H_4)_2\}Bi]^+\ PF_6^-$ (**38**).

Compounds **35**–**37** have been investigated in bulk in order to assess the bidentate character of the ligands by means of IR spectroscopy. In the case of the nitrate **35** no conclusion can be drawn as the asymmetric vibration of the NO_2 group partially overlaps with the fingerprint area of the ligand. The triflate **36** has an ionic structure, in which the coordination sphere about Bi is completed by a molecule of water. For the vinylsulfonate **37** the bidentate character of the ligand was suggested by IR spectroscopy, but the single-crystal X-ray diffraction studies revealed a monodentate coordination.

A correlation between the chemical shift of the CH_2 and the CH_3 protons and the experimentally determined N→Bi interaction is given in Table 2.4.

Table 2.4. Summary of chemical shifts for CH_2 and CH_3 protons correlated with the transannular interaction in solid state

Compound R = $CH_3OCH_2CH_2N(CH_2C_6H_4)_2$	H_7 δ (ppm)	H_8 δ (ppm)	H_9 δ (ppm)	$H_{methoxy}$ δ (ppm)	d N→Bi (Å)
RBiI	4.17	3.19	3.38	2.90	2.539(12)
RBiBr	4.21	3.20	3.37	2.90	2.507(8)
RBiCl	4.21	3.19	3.37	2.90	2.542(5)
RBiF*	4.09	3.12	3.35	2.88	2.583(6)
$[RBi]^+PF_6^-$*	4.71	3.48	3.66	2.86	—
$RBiONO_2$	4.33	3.29	3.37	2.88	2.433(13)
$RBiOSO_2CF_3$	4.38	3.38	3.38	2.90	2.416(3)
$RBiOSO_2C_6H_4CHCH_2$	4.30	3.27	3.32	2.86	2.424(4)

* Spectra were recorded in THF-d_6 and Acetone-d_6, respectively, while for the other compounds in $CDCl_3$.

No significant changes in the length of the trasnannular N→Bi interaction can be identified in the case of the halides. For the fluoride **34**, having the smallest Hammett's constant from the series of halides, the bond length between N and Bi is the longest. In the case of the oxygenated ligands, the weakest transannular interaction is found in the case of the nitrate, followed by the sulfonate and the strongest interaction is found for the ionic triflate, $[CH_3OCH_2CH_2N(CH_2C_6H_4)_2Bi(H_2O)]^+OTf^-$.

Except the compound **35**, containing a bidentate ONO_2 ligand, which can be described as a *14-Bi-6* hypervalent species, with a distorted pentagonal pyramidal coordination geometry around the bismuth atom, the other compounds can be described as *12-Bi-5* hypervalent species, with a distorted square pyramidal geometry around the metal.

The supramolecular assembly of the molecules is realized mainly by π Bi···$Ph_{centroid}$ interactions as shown for compounds **31**, **33**, **35** – **37.** The strongest interaction appears in compound **31** and is of 3.440 Å. For compound **38** no single-crystals suitable for X-ray diffraction could be obtained.