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Heterocyclic bismuth(III) compounds with transannular $N \rightarrow Bi$ interactions as catalysts for the oxidation of thiophenol to diphenyldisulfide

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The reactions between the diorganobismuth(III) bromides $[RCH_2N(CH_2C_6H_4)_2]BiBr$ $[R = C_6H_5$ (1), $C_6H_5CH_2$ (2)] and appropriate silver salts resulted in new diorganobismuth(III) compounds of the general formula $[RCH_2N(CH_2C_6H_4)_2]BiX$ $[R = C_6H_5, X = ONO_2$ (3), OSO_2CF_3 (4), $OSO_2C_6H_4$ (CHCH₂)-4 (5); $R = C_6H_5CH_2$, $X = ONO_2$ (6)], based on a butterfly-like tetrahydrodibenzo[c_rf][1,5]azabismocine heterocyclic framework. The new species were structurally characterized in solution by ¹H, ¹³C{H} and ¹⁹F{H} NMR and in solid state by IR spectroscopy and single-crystal X-ray diffraction. The nitrogen atom is intramolecularly coordinated to bismuth, thus resulting in hypercoordinated species of type *12-Bi-5* (3 and 6) and *10-Bi-4* (4 and 5). In addition, compound 4 shows bismuth… π arene and compounds 3 and 6 bismuth…oxygen intermolecular interactions, thus leading to dimers in solid state. These compounds were investigated as catalysts for the oxidation of thiophenol to diphenyl disulfide by using air as oxidizing agent, both in cyclohexane and in ionic liquid (1-butyl-1methylpyrrolidinium bis(trifluoromethanesulfonyl)imide), at temperatures below 100 °C, affording high reaction rates (TON 34.8, with 100% conversion after 5 h) and a total selectivity into the targeted product.

Introduction

The conversion of thiols to disulfides has attracted a continuously increased interest in recent years¹ due to the importance of disulfides in biology, mainly based on their antioxidant properties and their interconversion reactions in living systems,² fine chemicals synthesis, *e.g.* pharmaceuticals and pesticides,³ as well as in refinery processes and rubber vulcanization.⁴ Various methods, including catalysis (homogeneous,⁵ heterogeneous⁶ or photo-catalysis⁷), or non-catalytic oxidation procedures, *e.g.* with sodium periodate in a solid state reaction,⁸ or benzyltriphenylphosphonium peroxymonosulfate under reflux in acetonitrile⁹, as well as electrochemical techniques¹⁰ were employed (Table 1).

Constant efforts were made for the identification of

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appropriate systems consisting of the oxidant, solvent and catalyst, in order to increase the selectivity, i.e. to avoid the over-oxidation to by-products such as sulfoxides. thiosulfinates, thiosulfonates or sulfonic acids, but also the contamination with heavy metals or the toxicity, or to reduce the reaction time and the effective costs of the process.^{7,11} Thus, the replacement of halogens,¹² transition metal persulfate¹⁴ systems,¹³ containing ammonium or $Bu_3SnOMe/FeCl_3^{15}$ with air, molecular oxygen, H_2O_2 functionalized ionic liquids $[HSO_3N(C_2H_4OSO_3H)_3]^{11a}$ or even nitric oxide¹⁸ is highly desired. Among these, of special interest is the air oxidation which is a sustainable, cheap, easy to handle and an environmentally friendly process.¹⁹

Generally, chlorinated solvents (dichloromethane),²⁰ methanol, water, water–alcohol mixtures, or acetonitrile were used as a reaction medium in homogeneous processes. Different catalysts based on transition metals (Fe, Co, Pd, Pt, Au, Mo, Ru, Rh, etc.), despite their high selectivity and short reaction times,^{6a,21} are not always appropriate for pharmaceutical or biologically active products,²² mainly due to the toxicity of heavy metals. Therefore, heterogeneous systems using either nanoparticles of metal oxides (Fe₂O₃,^{11a} NiFe₂O₄,²³ Bi₂WO₆⁷), graphite oxide,^{6b} Fe(BTC) (BTC: 1,3,5-benzenetricarboxylate)^{6a} or iron phthalocyanine immobilized on graphene oxide²⁴ are preferred. Enzymes²⁵ and biomimetic iron(III)-tetraphenylporphyrin²⁶ were also investigated as selective catalysts in these reactions.

These state of the art examples demonstrate that there is still need for the optimization of the procedures for the

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oxidation of thiols to disulfides and for readily available, safe, stable and cheap catalysts. In this respect bismuth in the readily available, non-toxic and easy to handle oxidation states Bi(0) or Bi(III) has already demonstrated its capability as catalyst for a large variety of organic transformations including oxidation, reduction, C–C and C–E (E = O, N, S, halogen) bond formation.²⁷ Aromatic and aliphatic thiols were oxidized to disulfides with Bi(NO₃)₃ in high yields also,²⁸ but only few reports indicate organobismuth(III) compounds as catalysts,²⁹ due to a supposed low stability of the C–Bi bond.^{27d}

Bulky ligands³⁰ or organic groups bearing donor atoms capable for intramolecular coordination³¹ were used to stabilize main group metals, including bismuth in low oxidation states. Neutral or cationic hypercoordinated diorganobismuth(III) species based on а tetrahydrodibenzo[c,f][1,5]thiabismocine framework were reported as active species in Mannich reactions,³² or for the stereoselective synthesis of (*E*)- α , β -unsaturated ketones,³³ while compounds based on а tetrahydrodibenzo[c,f][1,5]azabismocine framework, e.g. ionic $[^{t}BuN(CH_{2}C_{6}H_{4})_{2}Bi]^{+}[B(C_{6}F_{5})_{4}]^{-}$ and neutral $[C_6H_{11}N(CH_2C_6H_4)_2]BiL$ (L = BF₄, OSO₂C₈F₁₇) were used in allylation reactions of aldehydes and Mukaiyama aldol reactions.34

A special attention was paid to the environmental impact of the solvents used in the catalytic processes^{35,36} and different alternatives to the organic solvents were proposed, including ionic liquids (ILs).³⁷

Besides other advantages, ILs contribute to the stabilization and the reuse of the catalyst and allow a good separation of the organic product by distillation. Selective catalytic oxidations, including the S–S coupling of thiols to disulfides took the advantage of using ILs.^{37a,38} They have also been used for the S–S coupling of thiols to disulfides in combination with various oxidizing agents in the following systems: [bmim][methylselenite] with air,³⁹ [bmim]Br with $K_2S_2O_8$,⁴⁰ [bmim][BF4]⁴¹ and [BPy]BF4⁴² with H₂O₂ or WO(O₂)₂·Phen·H₂O,⁴³ ([Hnmp]BF4] with H₂O₂,⁴⁴ [(CH₃)N(n-C₈H₁₇)₃]₂Mo₂O₁₁ and [(CH₃)N(n-C₈H₁₇)₃]₂W₂O₁₁ with H₂O₂,⁴⁵ ([C₄mim]Cl/2ZnCl₂ and [C₄mim]Cl/ZnCl₂), [CH₂COOHmim][HSO₄], [SO₃H–C₄mim][HSO₄], [Hmim][HSO₄] and [C₄mim][HSO₄] with H₂O₂.⁴⁶

We have recently reported diorganobismuth(III) halides of the type $[RCH_2N(CH_2C_6H_4)_2]BiX$ (R = C_6H_5 , $C_6H_5CH_2$, CH_3OCH_2 , X = halogen).⁴⁷ As a continuation of our studies regarding the compounds based on а tetrahydrodibenzo[c,f][1,5]azabismocine heterocyclic framework we used the bromides $RCH_2N(CH_2C_6H_4)_2$ BiBr [R = C_6H_5 (1), $C_6H_5CH_2$ (2)] to prepare the new species $[RCH_2N(CH_2C_6H_4)_2]BiX$ [R = C₆H₅, X = ONO₂ (3), OSO₂CF₃ (4), $OSO_2C_6H_4(CHCH_2)-4$ (5); R = $C_6H_5CH_2$, X = ONO_2 (6)]. Compounds 1 - 6 were investigated as catalysts in the oxidation with air of thiophenol to diphenyl disulfide in both cvclohexane and IL (1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide).

Table	1.	Perf	form	ance	s o	f	catalysts	reported	for	the	oxida	ation
of thic	Jc											

0	15.					
Entry	Catalysts	Yiel	TON	Source		
		d, %				
1	AI_2O_3	99	0.02	RSC Adv., 2013,		
				3 , 10680.		
2	Silica	95	8.2	RSC Adv., 2016,		
	Supported iron oxide			6 , 95753.		
	NiO/SiO ₂ nanocluster	99	198	Trans. Mat. Res.		
				Soc. Japan 2012,		
				37 , 177.		
3	Graphite oxide	100	0.3	Org. Biomol.		
				Chem., 2011, 9 ,		
				7292.		
	Cul	90	0.09	RSC Adv., 2013,		
				3 , 21369.		
4	Fe (III)/Nal	100	10	Synthesis 1999,		
				1 , 49.		
5	Cobalt-iron magnetic	100	2360	Appl. Catal., A		
	composites (Co0.5%)			2011, 392 , 151.		
6	Fe(BTC) BTC:1,3,5-	98	6.7	Chem.		
	benzenetricarboxylate			<i>Commun.,</i> 2010,		
-	F (070)	07		46 , 6476.		
/	Fe(BIC)	97	5.7	Cnem.		
		27	1.2	<i>Commun.</i> , 2012,		
		4	0.18	48 , 11275.		
0	$Fe(NO_3)_3 \cdot 9H_2O$	56	3.1			
8	1,3,2-oxazaphosphole	94	86	RSC Adv., 2015,		
0	Diagona combovoncido	100	2	5 , 45983.		
9	Diazenecarboxamide	100	Z	J. Cnem. Soc.,		
				Perkin Trans. 1,		
10	Manganaco(III) Cabiff	00	20	1998, 3917.		
10	hase complex	90	20	2007 8 697		

Results and discussion

Preparation and spectroscopic characterization

Diorganobismuth(III) compounds of the general formula $[RCH_2N(CH_2C_6H_4)_2]BiX$ $[R = C_6H_5, C_6H_5CH_2, X = ONO_2, OSO_2CF_3, OSO_2C_6H_4(CHCH_2)-4]$ based on a butterfly-like tetrahydro-dibenzo[*c*,*f*][1,5]azabismocine heterocyclic framework were prepared by ligand exchange reactions between the diorganobismuth(III) bromides **1** and **2** and the appropriate silver salt in a 1:1 molar ratio, as depicted in Scheme 1.



Scheme 1. Synthesis of diorganoBi(III) complexes 3 – 6.

The bismuth(III) compounds **3** – **6** are microcrystalline solids, soluble in common organic solvents. The ¹H, ¹³C{H} and ¹⁹F{H} NMR spectra are consistent with the presence of only one species in solution. The non-equivalent CH_2NCH_2 protons in the heterocyclic skeleton appear as an AB spin system in the

¹H NMR spectra, similarly with the situation found for the starting diorganobismuth(III) bromides **1** and **2**.⁴⁷

The IR spectra of the compounds **3** and **6** show strong, broad bands around 1445 cm⁻¹, characteristic for the $v_{as}(NO_2)$ stretching vibration,⁴⁸ thus suggesting an unisobidentate coordination of the anionic NO_3^- ligand, while the spectra of the compounds **4** and **5** show strong bands in the ranges 1240–1295, 1160–1170 and 1010–1020 cm⁻¹, which were assigned to the $v_{as}(SO_2)$, $v_s(SO_2)$ and v(SO) vibrations, respectively.⁴⁹

Single-crystal X-ray diffraction studies

Compounds **3** – **6** have similar molecular structures, with respect to the diorganobismuth(III) fragment, excepting that the crystal of **3** contains two independent molecules (**3a** and **3b**) in the asymmetric unit. Several differences appear in the coordination behavior of the oxo-ligands and in the types of intermolecular associations evidenced in the crystal structures. Thermal ellipsoids representations of the molecular structures of [**3**]₂, [**4**]₂, **5** and [**6**]₂ are depicted in Fig. 1 – 4. Relevant interatomic distances and bond angles for the new compounds **3** – **6**, as well as for the starting bromides **1** and **2**⁴⁷ are given in the supporting information (see ESI, Table S1).

Strong transannular N→Bi interactions (range 2.402(3) -2.479(5) Å, are found in compounds 3 - 6 and they are of a similar magnitude with those observed in the related $[RN(CH_2C_6H_4)_2]BiX$ (R = Ph, Cy; X = Cl, OC(O)CH_2CH_2GePh_3, BF_4 , 50,51 ^tBuN(CH₂C₆H₄)₂BiX (X = halogen)^{34b} or the starting diorganobismuth(III) bromides {2.531(4) Å in $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiBr$ (1) and 2.532(13) Å in $[C_6H_5CH_2CH_2N(CH_2C_6H_4)_2]BiBr$ (2),⁴⁷}, thus resulting in the formation of two five-membered NC₃Bi rings in each case, respectively Bi1C1C6C7N1 (1) and Bi1C14C9C8N1 (2) in 3a and 4-6 and Bi2C22C27C28N3 (1) and Bi2C35C30C29N3 (2) in 3b. These rings are not planar, but folded along the imaginary Bi1...C7 and Bi1...C8 axes in 3a and 4 - 6 and about the imaginary Bi2···C28 and Bi2···C29 axes in 3b.

Due to the planar chirality⁵² induced by the N \rightarrow Bi intramolecular coordination, the compounds crystallize as 1:1 mixtures of R^1 , R^2 and S^1 , S^2 isomers (the superscript indices "1" and "2" refer to the two five-membered rings, as designated above).

In **3** and **6** the NO₃ ligand is unisobidentate coordinated to bismuth, thus resulting in hypercoordinated *12-Bi-5* species.⁵³ In both compounds the molecules are associated in dimers by bridging NO₃ ligands which behave as bimetallic triconnective moieties in **3** (Fig. 1) and bimetallic tetraconnective moieties in **6** (Fig. 4).



Fig. 1. Thermal ellipsoids representation at 30% probability in a dimer of S^1, S^2 -**3a** and R^1, R^2 -**3b** isomers (hydrogen atoms are omitted for clarity).

In **3b** the benzyl group in the pendant arm is twisted in such a position that a Bi… π arene interaction of 3.895 Å between Bi2 and the phenyl ring of the pendant arm might also be considered.⁵⁴

In compounds **4** and **5** the CF₃SO₃ and the 4-(CH₂CH)C₆H₄SO₃⁻ ligands, respectively, are monodentate coordinated to bismuth by oxygen and these compounds can be described as hypercoordinated *10-Bi-4* species with a distorted see-saw coordination geometry about bismuth [O1–Bi1–N1 147.27(13)° in **4** and 144.79(14)° in **5**].

Strong Bi··· π arene interactions [Bi1···Cg1'(C9'-C14') 3.535 Å vs. 4.1 Å were evidenced and the upper value reported for other bismuth compounds displaying such interactions⁵⁴ results in dimeric associations in **4**.

A closer look at the crystal packing of the four compounds revealed further intermolecular interactions, thus leading to supramolecular networks in compounds **3** – **6**. But only in compound **3** the bismuth atoms in the molecules **3a** are involved in further associations of dimers by π Bi1…Cg1' interactions of 3.586 Å (see ESI, Fig. S1), thus determining a more congested environment about the metal centre, while in the crystals of **4** – **6** only non-classical hydrogen bonds, O…H or π H…Cg contacts, contribute to the supramolecular networks.

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Fig. 2. Thermal ellipsoids representation at 50% probability and atom

numbering scheme in a dimer of S^1, S^2-4 and R^1, R^2-4 isomers (hydrogen

Fig. 4. Thermal ellipsoids representation at 30% probability and atom numbering scheme in a dimer of R^1 , R^2 -**6** and S^1 , S^2 -**6** isomers (hydrogen atoms are omitted for clarity). Symmetry equivalent position -x, -y, -z is given by "prime".

atoms are omitted for clarity). Symmetry equivalent position 1-x, -y, 1-z is Catalyti



Fig. 3. Thermal ellipsoids representation at 30% probability and atom numbering scheme in R^1 , R^2 -5 isomer (hydrogen atoms are omitted for clarity).



In the absence of the catalyst some air oxidation of thiophenol to diphenyl disulfide (Scheme 2) occurred albeit with a low conversion (below 6% after 5 h), as can be seen from Fig. 5, irrespective of the solvent nature (cyclohexane or IL). This is in agreement with previous reports mentioning that in neutral media in which there are no radical initiators slow air oxidation occurs.⁵⁵



Scheme 2. Oxidative coupling of thiophenol to diphenyl disulfide.

Simple addition of NaOH led to an increase in the conversion to 16% after 5h, which might be explained by the fact that the autooxidation of thiols to disulfides, proceeding via the thyil radical (|RS|) and $^{-}O-O^{-}$ species, is enhanced in the presence of an excess of base.⁵⁵

In the presence of the diorganobismuth(III) bromides [RCH₂N(CH₂C₆H₄)₂]BiBr a further increase of the catalytic activity was observed, thus reaching a conversion of 21% for R = C₆H₅ (1) and more than double (51%) for R = C₆H₅CH₂ (2), corresponding to TON values of 7.3 and 17.8, respectively. These different behaviors might be explained by the observation that in solid state the bismuth atom in 1 is involved in weak Bi···Br (4.227 Å) and Bi···π arene (4.097 Å) intermolecular interactions (see ESI, Fig. S2), whilst in 2 the Bi is not involved in any intra- or intermolecular interactions, except the transannular N \rightarrow Bi one (see ESI, Fig. S3). The latter is present in both 1 and 2 and of a similar magnitude [2.531(4) Å in 1 and 2.532(13) Å in 2].⁴⁷

Therefore, it is likely to be a significant difference in the accessibility of the active site for the organic substrates to bind. Furthermore, the activity of the diorganobismuth(III) compounds **3** - **6** resulted in high conversions and TON.



Fig. 5. The activity of the heterocyclic bismuth(III) compounds 1 - 6 (the experiments were performed in cyclohexane).

After 5h the conversions (%)/TONs obtained were in the following order 3 (100/34.8) > 4 (94.8/33.0) > 6 (92.9/32.4) > 5 (86.1/30.0).

Table 2 compiles activity results of the compound ${\bf 4}$ for the oxidation of various thiols.

 Table 2. The oxidative coupling of several thiols to disulfides using compound 4.

Entry	Thiols	Conv. (%)	Sel. (%)	TON
1	Thiophenol	94.8	100	33
2	4-Methylbenzenethiol	100	100	35
3	1-Butanethiol	100	100	35
4	1-Octanethiol	66.4	100	23

The relative activity of these molecular catalysts should be associated to the polarizability of bismuth in the presence of different X^- ligands and with the Lewis acidity (Bi) / basicity (N) of the catalytic species.

DFT calculations revealed the variation of the positive charge on bismuth (q-Bi, Table 3) in the order 5 > 4 > 3 >> 1, while the negative charge on nitrogen varies in the order 4 > 5 > 3 >> 1 (q-N, Table 3). The latter sequence is correlated with the experimentally determined N \rightarrow Bi distances (4 < 5 < 3 << 1).

Anyway, the N \rightarrow Bi interatomic distances in compounds **3** – **6** are of a similar magnitude, but shorter than in the bromides **1** and **2**. This behaviour correlates well with the variation of the charge calculated for nitrogen and with the variation of the Hammett's constant for the substituents attached to bismuth, which is a measure of the electronic effects and the polarizability of the Bi-ligand bond (Table 3).⁵⁶

As a consequence, the increased catalytic activity of the complexes with oxygenated ligands in comparison with the diorganobismuth bromides is explained by the lower polar character of the Bi–Br bonds in comparison with the Bi–O bonds. In addition, the differences in the catalytic behavior of the complexes $\mathbf{3} - \mathbf{6}$ might be determined by the secondary interactions in the coordination sphere of bismuth and their influence on both the

polarizability of the metal-ligand bond and the accessibility of the organic substrate.

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Table	3.	N→Bi	transannular	interactions	(Å),	Hammett's	constants*	and
calcula	ate	d charg	e on Bi and N	in compound	s 1 a	nd 3 – 5 .		

	1	3	4	5
N→Bi	2.531(4)	2.473(8)	2.402(3)	2.454(4)
		2.453(7)		
Hammett's constant, $\sigma^{^{56a}}$	0.39	0.55	0.56	-
q-Bi	0.790	0.915	0.925	0.929
q-N	-0.240	-0.239	-0.232	-0.237

* Hammett's constants for compounds $1,\,3$ and 4 are given as previously reported in ref. 56a for Br, ${\sf ONO}_2$ and ${\sf CF}_3{\sf SO}_3.$

In case of compounds **3** and **6** it seems that the length of the aliphatic chain in the organic group attached to nitrogen does not influence the catalytic behaviour by itself, but it is responsible for the structural differences in the two compounds in solid state.

Changing the molecular solvent from cyclohexane to 1-butyl-1methylpyrrolidinium bis(trifluoromethanesulfonyl)imide) lead to an increase of the catalytic activity (Fig. 6).



Fig. 6. Time evolution of the conversion of thiophenol to disulfide in the presence of **2**, **5** and **6** as catalysts. The experiments were performed in cyclohexane (open element) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (close element).

It can be observed that complete conversion was reached for catalyst **6** in approx. 1h. It is noteworthy that this change in solvent did not affect the final selectivity to diphenyl disulfide. This increase in activity is thought to be due to the increased solubility of the molecular oxygen in the ionic liquid compared with the cyclohexane, as well as to the complete ionization of the catalyst in solution.⁵⁷

These experiments clearly demonstrate the positive influence of the IL as solvent. Moreover, the use of IL allowed a good recycling of the catalysts with only a small decrease in conversion from 92.9 to 85.8% for catalyst **4** over two consecutive reactions. This is in good agreement with previous reports on the stabilizing capacity of ILs in various catalytic reactions.⁵⁸

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Literature reported several mechanisms for this reaction. Based on EPR measurements Corma et al. concluded that on oxide heterogeneous catalysts the reaction is controlled by a radical pathway implying a homolytic S–H scission from the original thiol.⁵⁹ The same conclusion has been drawn by Garcia et al for MOF-type catalysts.⁶⁰ A radical mechanism has also been proposed using inorganic complexes.^{61,62}

Taking into account the experimental data collected in this study, a reaction pathway based on a two steps addition of PhSH to bismuth might be proposed (Fig. 7). In the first step it is formed a pentacoordinated Bi(III) species, with a trigonal bipyramidal coordination geometry, while the addition of the second PhSH molecule resulted in an octahedral Bi(III) species. We assume that the ONO₂ ligand acts as a monodentate moiety in the phenylthiolato bismuth(III) intermediates. In order to bring evidences for the proposed mechanism we performed a NMR tube scale reaction and we studied the *in situ* solution behavior of a mixture of compound **6** and thiophenol (1 : 2 molar ratio, in toluene-d₈) by a combination of ¹H NMR and MS experiments.



Fig. 7. Possible reaction pathway for the oxidation of thiophenol to diphenyl disulfide.



Fig. 8.¹H NMR spectra (toluene-d₈) of a reaction mixture of PhSH and compound **6** (*) showing the formation of Ph_2S_2 : (a) during the first 2 hours, at 20 °C.; (b) the solution behaviour at 80 °C; (c) a mixture of pure Ph_2S_2 and **6**.



Fig. 9. Detail of the aromatic region in the ¹H NMR spectra of a mixture of PhSH and compound **6**, showing the formation of Ph_2S_2 . (a) immediately after adding the solvent, at 20 °C, (b) after 2 hours at 20 °C, (c) after 24 hours at 20 °C, (d) at 80 °C, (e) again at 20 °C. Spectra **a** - **c** are recorded on a 600 MHz NMR spectrometer, while spectra **d** and **e** on a 400 MHz NMR spectrometer.

At room temperature the ¹H NMR spectrum suggested that only about 10% of the catalyst 6 has been solubilized (Fig. 8). During the first 2 h, it showed no change of the mixture (Figure 9, and ESI, Fig. S4), when only characteristic resonances for the pure PhSH and 6 were found in the spectrum. However, the solution turned to slightly yellow, thus indicating the formation of some bismuth organothiolates.⁶³ Also, after 2h, the ESI+ mass spectrum of the solution has shown a peak of very low intensity (1%) at m/z 618.17, thus suggesting the formation of the species $[\{C_6H_5CH_2CH_2N(CH_2C_6H_4)_2\}BiSPh^{\dagger}]$. The base peak at m/z 508.15 corresponds to the cation $[\{C_6H_5CH_2CH_2N(CH_2C_6H_4)_2\}Bi^{\dagger}]$ (see ESI, Fig. S7). After 24h the intensity of the peak at m/z 618.17 increased to about 20%, while the ¹H NMR spectrum has shown the decrease in intensity of the resonance corresponding to the PhSH proton in the alifatic region and the formation of Ph_2S_2 (see ESI, Figs. S4 – S6). We noticed that the C_6H_5 -ortho protons in Ph_2S_2 are strongly shifted at lower field in comparison with those in PhSH. The increase of the temperature up to 80 °C has been accompanied by several changes in the spectrum of the bismuth(III) complex, but in the range 20 -80 °C the resonance associated to the CH₂NCH₂ protons appears as an AB spin system, thus suggesting that nitrogen remains coordinated to bismuth. However, Ph₂S₂ has been detected only with a low intensity in the ESI+ mass spectrum, due to the poor ionization. To improve the ionization capacity of this species, we changed to APCI+, when a peak corresponding to $[Ph_2S_2^+]$ appeared at m/z 218.02 (43%), along with the cation at m/z 508.15 (see ESI, Fig. S8). At this point, the ¹H NMR spectrum of the final solution suggests the existence of at least two bismuth containing species, but unambiguously could be identified only the starting compound 6. To identify the nature of the insoluble species we added 5 mL of toluene and we heated the mixture at reflux (110 °C) for 15 min., with stirring, when the solution became clear. Then, decreasing again the temperature to 20 °C, the colourless precipitate was formed again and it has been identified by ¹H NMR as the starting catalyst 6. The APCI+ MS spectrum of the final solution shows a

peak at m/z 427.14 (52%), corresponding to the cation [(PhS)₂Bi^{*}] (Fig. S9), which might suggest the formation of an intermediate containing two phenylthiolato groups attached to the bismuth complex, thus confirming the pathway described in Fig. 7. This is also in line with the previous reports considering a radical mechanism.⁵⁹⁻⁶¹

Up to 70°C no NMR resonance characteristic for water formation has been observed. We attribute this fact to its physical adsorption on the remained solid catalyst, which only at higher temperature is desorbed (see ESI, Fig. S6).

The IR spectra of the pure compounds **4** and **6** show no significant differences of the bands assigned to the Bi complex in comparison with the solid separated after the oxidation of thiophenol in cyclohexane. We could only notice the formation of Ph_2S_2 and water (see ESI, Fig. S10).

Experimental

General

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Organic solvents were dried and distilled prior to use. The ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide, was prepared following standard procedures.⁶⁴ Initial, 1butyl-1-methylpyrrolidinium bromide [Bmpyrr][Br] was synthesized by mixing 1-methylpyrrolidine (200 mmoles) in acetone (75 mL) with equal molar amounts of 1-bromobutane in a round-bottomed flask. The reaction flask was immediately covered with aluminum foil. The mixture was stirred for 2 days until a white semi-solid was formed. The obtained solid was washed with cold acetone and separated by filtration. The anion exchange was performed further by using lithium bis(trifluoromethanesulfonimide) [LiN(CF₃SO₂)₂]. An aqueous solution of LiN(CF₃SO₂) (slight excess) was mixed with an aqueous solution of [Bmpyrr][Br] for 2h. The obtained ionic liquid [Bmpyrr][NTf₂] was extracted from the aqueous phase three times with dichloromethane. The solvent was removed using a rotary evaporator at 60 °C and the ionic liquid was dried for 24 h under high vacuum.

Experiments involving air sensitive compounds were carried out under argon atmosphere. Elemental analyses were performed on a Flash EA 1112 analyzer. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. ¹H, ¹³C{H} and $^{19}F{H}$ NMR spectra for compounds **3** – **6** were recorded in CDCl₃ on a Bruker 500 equipment, while the NMR spectra of the reaction mixture of PhSH and 6 were recorded at room temperature on a Bruker 600 and at higher temperature on a Bruker 400 equipment. The NMR spectra were processed with the MestReNova software.⁶⁵ The chemical shifts are reported in δ units (ppm) relative to TMS (1 H and 13 C) and CFCl₃ (19 F). The 1 H and 13 C chemical shifts were assigned based on 2D NMR experiments and they are given according to the numbering in Scheme 3. ESI+ and APCI+ mass spectra were recorded in CH₃CN on a LTQ Orbitrap - XL instrument. The IR spectra were recorded in the range 4000 - 400 cm⁻¹ on a Jasco spectrometer. Starting materials were commercially available or were prepared according to literature procedures, $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiBr$ (1) and $[C_6H_5CH_2CH_2N(CH_2C_6H_4)_2]BiBr$ (2).⁴⁷ The synthesis of silver 4-vinylbenzenesulfonate is given in the electronic supporting information.

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Scheme 3.

Synthesis of $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiONO_2$ (3)

A mixture of $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiBr$ (0.143 g, 0.249 mmol) and AgNO₃ (0.05 g, 0.294 mmol) in acetone (20 mL), was left under stirring, in the absence of light, for 2 h. The solvent was removed in vacuum and the remained solid was treated with CH₂Cl₂ (20 mL). AgBr was removed by filtration and from the clear solution, after the removal of the solvent, the title compound was isolated as a colorless solid. Yield: 0.155 g (93%). M.p. 151 °C (dec.). Anal. Calcd. for C₂₁H₁₉BiN₂O₃ (MW = 556.37): C 45.33, H 3.44, N 5.04; Found C 45.51, H 3.58, N 5.13. 1 H NMR (CDCl₃, 500 MHz): δ 4.08 (s, 2H, H₈), 4.36 (AB spin system with δ_{A} 4.26 and δ_{B} 4.47, 4H, H₇, ²J_{HH} 14.4 Hz), 7.30-7.32 (m, 2H, C₆H₅-ortho), 7.35 (dt, 2H, C₆H₄-H₄, ³J_{HH} 7.3, ⁴J_{HH} 1.3 Hz), 7.42-7.45 (m, 3H C₆H₅-*meta*+*para*) 7.53 (d, 2H C₆H₄-H₅, ³J_{HH} 8.02 Hz), 7.56 (t, 2H, C₆H₄-H₃, ³J_{HH} 7.3 Hz), 8.22 (d, 2H, C₆H₄-H₆, ³J_{HH} 7.1 Hz). ¹³C{H} NMR (CDCl₃, 125.72 MHz): δ 60.45 (*C*₈), 63.84 (*C*₇), 128.67 (C₄), 128.92 (C₃), 129.44 (C₆H₅-meta), 129.75 (C₆H₅-para), 131.16 (C₆H₅-ortho), 131.66 (C₅), 133.11 (C₆H₅-ipso), 138.39 (C₆), 148.97 (*C*₂), 180.3 (*C*₁). IR (v, cm⁻¹): 1453, 1436.

Compounds 4 – 6 were prepared similarly.

$[C_6H_5CH_2N(CH_2C_6H_4)_2]BiOSO_2CF_3(4)$

From $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiBr$ (0.188 g, 0.327 mmol) and AgOTf (0.089 g, 0.34 mmol) in acetone (20 mL), as a colorless solid. Yield: 0.210 g (94%). M.p. 155 °C (dec.). Anal. Calcd. for $C_{22}H_{19}BiF_3NO_3S$ (MW = 643.43): C 41.07, H 2.98, N 2.18%. Found C 40.91, H 2.77, N 2.09%. ¹H NMR (CDCl₃, 500 MHz): δ 4.13 (s, 2H, H₈), 4.49 (AB spin system with δ_A 4.39 and δ_B 4.59, 4H, H₇, ²J_{HH} 14.5 Hz), 7.28-7.30 (m, 2H, C₆H₅-*ortho*), 7.39 (dt, 2H, C₆H₄-H₄, ³J_{HH} 7.6, ⁴J_{HH} 1.4 Hz), 7.44-7.47 (m, 3H C₆H₅-*meta+para*) 7.61 (d, 2H C₆H₄-H₃, ³J_{HH} 7.7 Hz), 7.65 (t, 2H, C₆H₄-H₅, ³J_{HH} 7.3 Hz), 8.39 (d, 2H, C₆H₄-H₆, ³J_{HH} 7.5 Hz). ¹³C{H} NMR (CDCl₃, 125.72 MHz): δ 61.13 (C₈), 65.25 (C₇), 119.65 (q, CF₃, ¹J_{FC} 318.9 Hz), 128.92 (C₃), 129.02 (C₄), 129.73 (C₆H₅-*meta*), 130.23 (C₆H₅-*para*), 131.10 (C₆H₅-*ortho*), 132.34 (C₅), 132.74 (C₆H₅-*ipso*), 138.55 (C₆), 149.45 (C₂), 181.65 (C₁). ¹⁹F{H} NMR: δ -77.44. IR (v, cm⁻¹): 1299, 1197, 1020.

$[C_6H_5CH_2N(CH_2C_6H_4)_2]BiOSO_2C_6H_4CHCH_2-4$ (5)

From a mixture of $[C_6H_5CH_2N(CH_2C_6H_4)_2]$ BiBr (0.103 g, 0.179 mmol) and silver 4-vinylbenzenesulfonate (0.052g, 0.179 mmol) in acetone (20 mL), as a colorless solid. Yield: 0.118g (98%). M.p. 181 – 183 °C. Anal. Calcd. for $C_{29}H_{26}BiNO_3S$ (MW = 677.57): C 51.41, H 3.87, N 2.07%; Found: C 51.21, H 3.68, N 2.01%. ¹H NMR (CDCl₃, 500 MHz): δ 4.07 (s, 2H, H₈), 4.35 (AB spin system with δ_A 4.22 and δ_B 4.48, 4H, H_7 , $^2J_{HH}$ 13.6 Hz), 5.33 (d, 1H, CH=CH_AH_B, H_a, $^3J_{HH}$ 10.8 Hz), 5.82 (d, 1H, CH=CH_AH_B, H_B, $^3J_{HH}$ 17.6

ARTICLE

$[C_6H_5CH_2CH_2N(CH_2C_6H_4)_2]BiONO_2$ (6)

From $[C_6H_5CH_2CH_2N(CH_2C_6H_4)_2]BiBr$ (0.208 g, 0.353 mmol) and AgNO₃ (0.060 g, 0.353 mmol), as a colorless solid. Yield: 0.19 g (95%). M.p. 150 °C (dec.). Anal. calcd. for $C_{22}H_{21}BiN_2O_3$ (MW = 570.39): C 46.33, H 3.71, N 4.91%; Found: C 46.38, H 3.74, N 4.89%. ¹H NMR: δ 2.90 - 2.93 (m, 2H, CH₂, $CH_2C_6H_5$), 3.34 - 3.37 (m, 2H, CH₂, H₈), 4.39 (AB spin system with δ_4 4.33 and δ_8 4.45, 4H, H₇, ²J_{HH} 14.7 Hz), 7.02 (d, 2H, C_6H_5 -ortho, ³J_{HH} 7.2 Hz), 7.27 - 7.31 (m, 3H, C_6H_5 -meta+para), 7.35 (t, 2H, H₄, ³J_{HH} 7.3 Hz), 7.53 - 7.56 (m, 4H, H₃ + H₅), 8.17 (d, 2H, H₆, ³J_{HH} 7.5 Hz). ¹³C{H} NMR: δ 34.50 (C₉), 60.33 (C₈), 66.41 (C₇), 127.80 (C₆H₅-para), 128.47 (C₃), 128.59 (C₄), 128.90 (C₆H₅-ortho), 129.30 (C₆H₅-meta), 131.62 (C₅), 136.59 (C₆H₅-ipso), 138.13 (C₆), 149.10 (C₂), 181.59 (C₁). IR (v, cm⁻¹): 1451, 1443.

X-ray structure determination

Single-crystals of compounds **3** – **6** were obtained from a mixture of CH₂Cl₂ and n-hexane (1/5 v/v) at room temperature. The data were collected on an Oxford Gemini S (**3** and **4**, at 110 K) or a Smart Apex CCDC (**5** and **6**, at room temperature) diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The calculations were performed using the SHELXS-2013, SHELXL-2016-4⁶⁶ or the SHELXTL program.⁶⁷ The structures were solved by direct methods and refined by full-matrix least-square procedures on F^2 . All *non*-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions. Crystal and structural refinement data for the crystal structures of compounds **3** - **6** are given in ESI, Table S2. Intermolecular interactions were identified with PLATON.⁶⁸ The drawings were created with the Diamond software package.⁶⁹

Catalysis

The oxidation of thiophenol to diphenyl disulfide was performed in a glass batch reactor equipped with a condenser system. Thiophenol (0.001 moles) dissolved in either 10 mL 4 mL 1-butyl-1-methylpyrrolidinium cyclohexane or bis(trifluoromethanesulfonyl)imide was stirred at 600 rpm in a silicon bath at 100 °C under reflux. The catalyst in a loading of 5% wt. Bi (2.8 mol% Bi) from the reaction mixture was added after the stabilization of the temperature. In order to check the progress of the reaction, samples of 5 μ L were periodically removed from the reactor, analyzed by GC using a K072320 Termo-Quest chromatograph equipped with a FID detector and a capillary column of 30 m length and 0.324 mm in diameter and a DB-5 stationary phase. Highly pure N₂ (99.999%) was used as carrier gas. The reaction product was identified also by GS-MS, using a

GC/MS/MS VARIAN SATURN 2100 T spectrometer equipped with a CP-SIL 8 CB Low Bleed/MS column of 30 m length and 0.25 mm diameter.

NMR tube scale reaction

A mixture of $[C_6H_5CH_2CH_2N(CH_2C_6H_4)_2]BiONO_2$ (**6**) (0.036 g, 6.3 x 10⁻⁵ mmol), thiophenol (0.013 ml, 12.7 mmol) and toluene-d₈ (0.5 ml) was realized directly in the NMR tube. The solution became slightly yellow in approx. 10 min. Most of the compound **6** remained undisolved. The evolution of the oxidation reaction was followed by VT ¹H NMR in the range 20 – 80 °C and MS experiments.

Theoretical Calculations

The geometry optimizations and frequency calculations on compounds **1** and **3** - **5** were performed with Gaussian 09,⁷⁰ Revision E.01 using B3LYP functional,⁷¹ and def2-TZVP basis set.⁷² The dispersion corrections were accounted using D3 version of Grimme's dispersion with Becke-Johnson damping.⁷³ Cartesian coordinates of the calculated molecular structures **1** and **3** - **5** are given in ESI, Tables S3 - S6.

Electronic Supplementary Information

CCDC 1520802 (3), 1520801 (4) 1520800 (5) and 1520799 (6) contain the supplementary crystallographic data for the investigated compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The supplementary material also contains the crystal and structural refinement data for the crystal structures of 3 - 6, interatomic distances and bond angles in compounds 1 - 6, Figures representing the coordination sphere of Bi in the crystals of 1 - 3, Figures representing selected ¹H NMR and MS spectra, as well as cartesian coordinates of the calculated molecular structures 1 and 3 - 5.

Conclusions

Diorganobismuth(III) compounds of type $[C_6H_5CH_2N(CH_2C_6H_4)_2]BiX$ [X = Br, ONO₂, OSO₂CF₃, OSO₂C₆H₄ $(CHCH_3)-4].$ based on a butterfly-like tetrahydrodibenzo[c,f][1,5]azabismocine heterocyclic framework, with anionic ligands with different electron-withdrawing ability proved to be efficient catalysts for the oxidation of thiophenol to diphenyl disulfide under mild conditions with high conversions and chemoselectivity. The catalytic activity in cyclohexane was observed to increase going from the starting diorganobismuth(III) bromides to the derivatives with oxygenated ligands, as a consequence of the stronger electron-withdrawing character of the latter systems. This behaviour was also correlated with a decrease of the $N{\rightarrow}Bi$ distance by changing Br (about 2.531 Å) with oxygenated ligands [range 2.402(3) - 2.479(5) Å]. It is clear that the overall catalytic activity is strongly influenced by a combination of factors including the acid/base character of the diorganobismuth(III) complex, the polarizability of the Bi-X (X = O, Br) bond and the accessibility to the metal centre.

8 | J. Name., 2012, 00, 1-3

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Journal Name

Catalytic experiments carried out in 1-butyl-1methylpyrrolidinium bis(trifluoromethanesulfonyl)imide showed a positive influence of the ionic liquid leading to higher reaction rates with the same selectivity to diphenyl disulfide. This effect is explained by the higher solubility of oxygen in the ionic liquid than in cyclohexane, as well as by the ionization of the catalytic species promoted by the IL.

Taking into account the calculated charge on bismuth (0.790 for Br and over 0.9 for the oxygenated ligands), as well as the experimental catalytic results, it might be concluded that the increased polarity of the Bi–O bond compared to the Bi–Br one, make the complexes with oxygenated ligands more suitable for catalysis, either in cyclohexane or in ionic liquid.

The ¹H NMR and ESI+ MS experiments carried out for a 1 :2 (molar ratio) mixture in toluene- d_8 solution support a two steps reaction pathway, involving the intermediary formation of diorganobismuth(III) phenylthiolates.

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Notes and references

- (a) U. Pathak, L.K. Pandey, S. Mathur, Synth. Commun., 2009, 39, 2923; (b) R.J. Cremlyn (Ed.), An Introduction to Organosulfur Chemistry, Wiley & Sons, New York, 1996; (c) A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Commun., 2010, 46, 6476.
- 2 (a) P.C. Jocelyn, *Biochemistry of the Thiol Group*, Academic Press, New York, 1977; (b) Y. Kanda, T. Fukuyama, *J. Am. Chem. Soc.*, 1993, **115**, 8451; (c) G. Pattenden, A. Shuker, *J. Chem. Soc. Perkin Trans.*, 1992, **1**, 1215; (d) E. Block, *Angew. Chem. Int. Edn. Engl.*, 1992, **31**, 1135.
- 3 (a) Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang, Y. Yang, *Chem. Soc. Rev.*, 2014, **43**, 3480; (b) F. Cavani, *Catal. Today*, 2010, **157**, 8.
- 4 A. Talla, B. Driessen, N.J.W. Straathof, L.-G. Milroy, L. Brunsveld, V. Hessel, T. Noel, *Adv. Synth. Catal.*, 2015, **357**, 2180; (b) S. Dharmarathna, C. K. Kingondu, L. Pahalagedara, C.-H. Kuo, Y. Zhang, S.L. Suib, *Appl. Catal. B*, 2014, **147**, 124.
- 5 J.-E. Bäckvall, (Ed), *Modern Oxidation Methods*, Wiley-VCH, Hoboken, NJ, 2011.
- 6 (a) A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Commun., 2010, 46, 6476; (b) D.R. Dreyer, H.-P. Jia, A.D. Todd, J. Geng, C. W. Bielawski, Org. Biomol. Chem., 2011, 9, 7292.
- 7 Y.P. Bhoi, D.P. Rout, B.G. Mishra, J. Clust. Sci., 2015, 27, 267.
- 8 M. Montazerozohori, S. Joohari, B. Karami, N. Haghighat, *Molecules*, 2007, **12**, 694.

- 9 A.R. Hajipour, S.E. Mallakpour, H. Adibi, J. Org. Chem., 2002, 67, 8666.
- 10 S.L.S. Leite, V.L. Pardini, H. Viertler, *Synth. Commun.*, 1990, **20**, 393.
- (a) A. Sabet, A. Fakhraee, M. Ramezanpour, N. Alipour, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering 2014, 8, 1184; (b) V. Cimpeanu, V.I. Pârvulescu, P. Amoros, D. Beltran, S. Johnson, C. Hardacre, Chem-Eur J., 2004, 10, 4640; (c) V. Cimpeanu, A.N. Parvulescu, V.I. Pârvulescu, D.T. On, S. Kaliaguine, J.M. Thompson, C. Hardacre, J. Catal., 2005, 232, 60.
- 12 (a) T. Aida, T. Akasaka, N. Furukawa, S. Oae, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1441; (b) J.R. Schaeffer, C.T. Goodhue, H.A. Risley, R.E. Stevens, *J. Org. Chem.*, 1967, **32** 392.
- (a) T.J. Wallace, J. Org. Chem., 1966, **31**, 3071; (b) J. Choi, N. M. Yoon, J. Org. Chem., 1995, **60**, 3266; (c) P. Salehi, A. Farrokhi, M. Gholizadeh, Synth. Commun., 2001, **31**, 2777; (d) N.A. Noureldin, M. Caldwell, J. Hendry, D.G. Lee, Synthesis, 1998, **11**, 1587.
- 14 R.S. Varma, H.M. Meshram, R. Dahiya, *Synth. Commun.*, 2000, **30**, 1249.
- 15 S. Tsuneo, O. Junzo, N. Hitosi, *Tetrahedron Lett.*, 1990, **31**, 3591.
- 16 K.-T. Liu, Y.-C. Tong, Synthesis, 1978, 669.
- 17 B.J. Evans, J.T. Doi, W.K. Musker, J. Org. Chem., 1990, 55, 2337.
- 18 (a) W.A. Pryor, D.F. Church, C.K. Govindan, G. Crank, J. Org. Chem., 1982, 47, 156; (b) N. Iranpoor, H. Firouzabadi, A.-R. Pourali, Tetrahedron, 2002, 58, 5179.
- (a) H. Golchoubian, F. Hosseinpoor, *Catal. Commun.*, 2007, 8, 697; (b) M. Kirihara, K. Okubo, T. Uchiyama, Y. Kato, Y. Ochiai, S. Matsushita, A. Hatano, K. Kanamori, *Chem. Pharm. Bull.*, 2004, 52, 625; (c) M. Kirihara, Y. Asai, S. Ogawa, T. Noguchi, A. Hatano, Y. Hirai, *Synthesis*, 2007, 3286; (d) M. Chakraborty, P.C. Mandal, S. Mukhopadhyay, *Polyhedron*, 2012, 45, 213; (e) M. Hayashi, K. Okunaga, S. Nishida, K. Kawamura, K. Eda, *Tetrahedron Lett.*, 2010, 51, 6734; f) C. Tidei, M. Piroddi, F. Galli, C. Santi, *Tetrahedron Lett.*, 2012, 53, 232.
- 20 (a) M. Montazerozohari, B. Karami, M. Azizi, Arkivoc, 2007, 1, 99; (b) M. Zolfigol, F. Shirini, K. Zamani, E. Ghofrani, S. Ebrahimi, Phosphorus Sulfur Silicon Relat. Elem., 2004, 179, 2177; (c) M.A. Zolfigol, Tetrahedron, 2001, 57, 9509.
- 21 (a) H. Egami, T. Katsuki, J. Am. Chem. Soc., 2007, 129, 8940;
 (b) K. Jeyakumar, D.K. Chand, Tetrahedron Lett., 2006, 47, 4573;
 (c) R. Sanz, R. Aguado, M.R. Pedrosa, F.J. Arnaiz, Synthesis, 2002, 856;
 (d) A. Corma, H. Garcia, Chem. Soc. Rev., 2008, 37, 2096.
- 22 (a) A. Saxena, A. Kumar, S. Mozumdar, J. Mol. Catal. A: Chem., 2007, 269, 35; (b) E.J. Lenardao, R.G. Lara, M.S. Silva, R.G. Jacob, G. Perin, Tetrahedron Lett., 2007, 48, 7668; (c) M.A. Walters, J. Chaparro, T. Siddiqui, F. Williams, C. Ulku, A. L. Rheingold, Inorg. Chim. Acta, 2006, 359, 3996; (d) M.A. Zolfigol, Tetrahedron, 2001, 57, 9509.
- 23 A.M. Kulkarni, U.V. Desai, K.S. Pandit, M.A. Kulkarni, P.P. Wadgaonkar, *RSC Adv.*, 2014, **4**, 36702.
- 24 P. Kumar, G. Singh, D. Tripathi, S.L. Jain, *RSC Adv.*, 2014, 4, 50331.
- 25 M. Sridhar, S.K. Vadivel, U.T. Bhalerao, *Synth. Commun.*, 1998, **28**, 1499.
- 26 B. Karami, M. Montazerozohori, M. Moghadam, M.H. Habibi, K. Niknam, Turk. J. Chem., 2005, 29, 539.
- 27 (a) J. Luan, L. Zhang, Z. Hu, *Molecules*, 2011, 16, 4191; (b) H. Gaspard-Iloughmane, C.L. Roux, *Eur. J. Org. Chem.*, 2004, 2517; (c) N.M. Leonard, L.C. Wieland, R.S. Mohan, *Tetrahedron*, 2002, 58, 8373; (d) H. Suzuki, Y. Matano (Eds.), *Organobismuth Chemistry*, Elsevier, Amsterdam, 2001. (e) T. Ollevier, *Org. Biomol. Chem.*, 2013, 11, 2740 and references

This journal is © The Royal Society of Chemistry 20xx

therein; (f) T. Ollevier (Ed.), *Bismuth-Mediated Organic Reactions*, Springer-Verlag, Berlin, Heidelberg, 2012.

- 28 M.M. Khodaei, I. Mohammadpoor-Baltork, K. Nikoofar, Bull. Korean Chem. Soc., 2003, 24, 885.
- 29 (a) R. Qiu, Y. Chen, S.-F. Yin, X. Xu, C.-T. Au, RSC Adv., 2012, 2, 10774; (b) H.R. Kricheldorf, Chem. Rev., 2009, 109, 5579.
- 30 H.J. Breunig, N. Haddad, E. Lork, M. Mehring, C. Mügge, C. Nolde, C.I. Raţ, M. Schürmann, Organometallics, 2009, 28, 1202.
- 31 C. Silvestru, H.J. Breunig, H. Althaus, *Chem. Rev.*, 1999, **99**, 3277.
- 32 (a) R. Qiu, S. Yin, X. Zhang, J. Xia, X. Xu, S. Luo, *Chem. Commun.*, 2009, 4759; (b) R. Qiu, S. Yin, X. Song, Z. Meng, Y. Qiu, N. Tian, X. Xu, S. Luo, F.-R. Dai, C.-T. Au, W.-Y. Wong, *Dalton Trans.*, 2011, **40**, 9482.
- (a) R. Qiu, Y. Qiu, S. Yin, X. Xu, S. Luo, C.-T. Au, W.-Y. Wong, S. Shimada, *Adv. Synth. Catal.*, 2010, **352**, 153; (b) R.H. Qiu, Y. M. Qiu, S.F. Yin, X.X. Song, Z.G. Meng, X.H. Xu, X.W. Zhang, S.L. Luo, C.-T. Au, W.-Y. Wong, *Green Chem.*, 2010, **12**, 1767.
- 34 (a) X.W. Zhang, S.F. Yin, R.H. Qiu, J. Xia, W. L. Dai, Z.Y. Yu, C.T. Au, W.Y. Wong, *J. Organometal. Chem.*, 2009, **694**, 3559; (b) X.W. Zhang, R.H. Qiu, N.Y. Tan, S.F. Yin, J. Xia, S.L. Luo, C.T. Au, *Tetrahedron Lett.*, 2010, **51**, 153.
- 35 I.T. Horváth, P.T. Anastas, Chem. Rev., 2007, 107, 2169.
- 36 J.H. Clark, S.J. Tavener, Org. Process Res. Dev., 2007, 11, 149.
- 37 (a) V.I. Parvulescu, C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615;
 (b) H. Olivier-Bourbigou, L. Magna, D. Morvan, *Appl. Catal. A.-Gen.*, 2010, **373**, 1; (c) R. Hayes, G.G. Warr, R. Atkin, *Chem. Rev.*, 2015, **115**, 6357; (d) N.V. Plechkovaa, K.R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.
- 38 (a) G. Chatel, R.D. Rogers, ACS Sustainable Chem. Eng., 2014,
 2, 322; (b) W. Qian, E. Jin, W. Bao, Y. Zhang, Angew. Chem. Int. Ed., 2005, 44, 952; (c) D. Betz, P. Altmann, M. Cokoja,
 W.A. Herrmann, F.E. Kühn, Coord. Chem. Rev., 2011, 255, 1518; (d) S.M. Coman, M. Florea, V.I. Parvulescu, V. David, A. Medvedovici, D. de Vos, P.A. Jacobs, G. Poncelet, P.Grange, J. Catal., 2007, 249, 359.
- S. Thurow, V.A. Pereira, D.M. Martinez, D. Alves, G. Perin, R. G. Jacob, E.J. Lenardão, *Tetrahedron Lett.*, 2011, 52, 640.
- 40 A.R. Hajipour, M. Mostafavi, A.E. Ruoho, *Phosphorus Sulfur*, 2009, **184**, 1920.
- 41 S.M.S. Chauhan, A. Kumar, K.A. Srinivas, *Chem. Commun.*, 2003, 2348.
- 42 D. Zhao, Y. Wang, Erhong Duan, Molecules, 2009, 14, 4351.
- 43 W. Zhu , H. Li , X. Jiang , Y. Yan , J. Lu , J. Xia, Energ. Fuel., 2007, 21, 2514.
- 44 D. Zhao, J. Wang, E. Zhou, Green. Chem., 2007, 9, 1219.
- 45 W. Zhu, G. Zhu, H. Li, Y. Chao, Y. Chang, G. Chen, C. Han, J. Mol. Catal. A.-Chem., 2011, 347, 8.
- 46 G. Yu, J. Zhao, D. Song, C. Asumana, X. Zhang, X. Chen, Ind. Eng. Chem. Res., 2011, 50, 11690.
- 47 A. M. Toma, A. Pop, A. Silvestru, T. Rüffer, H. Lang, M. Mehring, *Dalton Trans.*, 2017, 46, 3953-3962.
- 48 (a) H.J. Breunig, M.G. Nema, C. Silvestru, A.P. Soran, R.A. Varga, *Dalton Trans.*, 2010, **39**, 11277; (b) R.P. Oertel, R.A. Plane, *Inorg. Chem.*, 1968, **7**, 1192.
- 49 Y. Matano, T. Miyamatsu, H. Suzuki, Organometallics, 1996, 15, 1951.
- 50 X.-W. Zhang, J. Xia, H.-W. Yan, S.-L. Luo, S.-F. Yin, C.-T. Au, W.-Y. Wong, *J. Organomet. Chem.*, 2009, **694**, 3019.
- 51 S. Shimada, O. Yamazaki, T. Tanaka, Y. Suzuki, M. Tanaka, J. Organomet. Chem., 2004, 689, 3012.
- 52 IUPAC Nomenclature of Organic Chemistry, Pergamon Press, Oxford, 1979.
- 53 The N-X-L nomenclature system has been previously described: N valence shell electrons about a central atom X with L ligands. C. W. Perkins, J. C. Martin, A. J. Arduengo III,

W. Lau, A. Alegria and K. Kochi, J. Am. Chem. Soc., 1980, 102, 7753.

- 54 (a) A. A. Auer, D. Mansfeld, C. Nolde, W. Schneider, M. Schürmann, M. Mehring, *Organometallics*, 2009, 28, 5405;
 (b) I. Caracelli, J. Zukerman-Schpector, I. Haiduc and E.R.T. Tiekink, *CrystEngComm*, 2016, 18, 6960.
- 55 P.V. Ioannou, Main Group Chemistry, 2013, **12**, 125.
- 56 (a) C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
 (b) K. Ohkata, S. Takemoto, M. Ohnishi and K. Akiba, *Tetrahedron Lett.*, 1989, **30**, 4841.
- 57 I. Bahadur, K. Osman, C. Coquelet, P. Naidoo, D.Ramjugernath, J. Phys. Chem. B, 2015, 119, 1503.
- 58 O.D. Pavel, P. Goodrich, L. Cristian, S.M. Coman, V.I. Pârvulescu, C. Hardacre, *Catal. Sci. Technol.*, 2015, **5**, 2696.
- 59 A. Corma, T. Rodenas and M.J. Sabater, *Chem. Sci.*, 2012, **3**, 398.
- 60 A. Dhakshinamoorthy, A.M. Asiri, J.R. Herance, H. Garcia, Catal. Today, 2016, https://doi.org/10.1016/j.cattod.2017.01.018
- 61 C. Esmieu, M. Orio, L. Le Pape, C. Lebrun, J. Pécaut, S. Ménage and S. Torelli, *Inorg. Chem.*, 2016, **55**, 6208.
- 62 P.K. Shyam, Y.K. Kim, C. Lee, H.-Y. Jang, *Adv. Synth. Catal.* 2016, **358**, 56.
- 63 (a) G. G. Briand, A. Decken, N. M. Hunter, G. M. Lee, J. A. Melanson, E. M. Owen, *Polyhedron*, 2012, **31**, 796; (b) P. Simon, R. Jambor, A. Ruzicka, L. Dostal, *Organometallics*, 2013, **32**, 239.
- 64 D. Zhao, Z. Fei, R. Scopelliti, P. Dyson, J. Inorg. Chem., 2004, 43, 2197.
- 65 MestReC and MestReNova, Mestrelab Research S.L., A Coruña 15706, Santiago de Compostela.
- 66 G.M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, **64**, 112.
- 67 G.M. Sheldrick, SHELXTL 5.1, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, Siemens Analytical X-ray Instruments, Madison, WI, 1990.
- 68 PLATON (a) A. L. Spek, J. Appl. Cryst., 2003, 36, 7; (b) A.L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr. 2009, 65, 148; (c) A.L. Spek, Acta. Cryst C., 2015, 71, 9.
- 69 DIAMOND-Visual Crystal Structure Information System, Crystal Impact: Postfach 1251, D-53002 Bonn, Germany, 2001.
- 70 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 09, Revision E.01, Gaussian, Inc., Wallingford CT, 2013.
- 71 A.D. Becke, J. Chem. Phys., 1993, 98, 5648.
- 72 F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297.
- 73 S. Grimme, S. Ehrlich, L. Goerigk, J. Comp. Chem., 2011, **32**, 1456.

10 | J. Name., 2012, 00, 1-3

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Aerial oxidation of thiophenol to diphenyl disulfide proceeds with high reaction rates, total conversion and selectivity in ionic liquids by using diorganobismuth(III) catalysts based on a tetrahydro-dibenzo[*c*,*f*][1,5]azabismocine heterocyclic framework.



J. Name., 2013, 00, 1-3 | 11