Chemistry
A European
Journal

Chemistry
Europe
European Chemical
Societies Publishing

Accepted Article

Title: Well-defined, molecular bismuth compounds: catalysts in photochemically-induced radical dehydrocoupling reactions

Authors: Jacqueline Ramler, Ivo Krummenacher, and Crispin Lichtenberg

To be cited as: *Chem. Eur. J.* 10.1002/chem.202002219

Link to VoR: https://doi.org/10.1002/chem.202002219

WILEY-VCH

Well-defined, molecular bismuth compounds: catalysts in photochemically-induced radical dehydrocoupling reactions

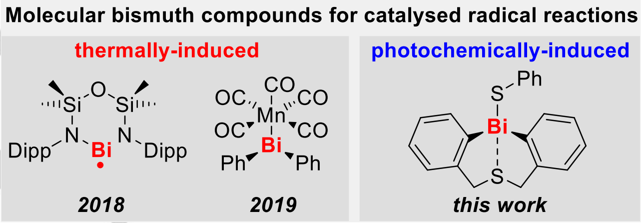
Jacqueline Ramler,[a] Ivo Krummenacher,[a,b] and Crispin Lichtenberg*[a]

[a] J. Ramler, Dr. I. Krummenacher, Priv.-Doz. Dr. C. Lichtenberg
Institute of Inorganic Chemistry
Julius-Maximilians-University Würzburg
Am Hubland, 97074 Würzburg, Germany
E-mail: crispin.lichtenberg@uni-wuerzburg.de
[b] Dr. I. Krummenacher
Institute of Sustainable Chemistry & Catalysis with Boron
Am Hubland, 97074 Würzburg, Germany

Supporting information for this article is given via a link at the end of the document.

Abstract: A series of diorgano(bismuth)chalcogenides, [Bi(aryl)EPh], has been synthesised and fully characterised (E = S, Se, Te). These molecular bismuth complexes have been exploited in homogeneous *photochemically*-induced radical catalysis, using the coupling of silanes with TEMPO as a model reaction (TEMPO = (tetramethylpiperidin-1-yl)-oxyl). Their catalytic properties are complementary or superior to those of known catalysts for these coupling reactions. Catalytically competent intermediates of the reaction have been identified. Applied analytical techniques include NMR, UV/vis, and EPR spectroscopy, mass spectrometry, single-crystal X-ray diffraction analysis, and (TD-)DFT calculations.

Covalent bonds Z–X with a heavy p-block element Z as one of the bonding partners show low homolytic bond dissociation energies due to inefficient spatial and energetic overlap of the relevant atomic orbitals.[1] This allows access to reversible homolytic bond dissociations ($Z–X \rightleftarrows Z^{\bullet} + X^{\bullet}$) under mild reaction conditions, which is a key feature for potential catalytic applications via radical pathways.[2] For instance, equilibrium scenarios have been reported for the homolysis of the $Sn\equiv Sn$ bond in $(SnAr)_2$ and the Pn–Pn bonds in $(Pn(CSiMe_3CH_2)_2)_2$ (Ar = C_6H_3-2,6-(C_6H_3-2,6-$i$$Pr_2$)$_2$; Pn = Sb, Bi).[3,4] Such findings have paved the way for new catalytic applications of well-defined, molecular complexes of heavy p-block elements in radical reactions.[2c] Among potential catalysts of this kind, bismuth compounds in particular are attractive synthetic targets due to characteristics such as low cost, (relatively) low toxicity, and prospects for recyclability.[5,8a] In this context, the radical dehydrocoupling of $SiPhH_3$ and TEMPO with $[Bi(NON^{Dipp})]^{\bullet}$ and the radical cyclo-isomerization of δ-iodo-olefins with $Ph_2Bi–Mn(CO)_5$ have recently been reported (Scheme 1; TEMPO = (tetramethylpiperidin-1-yl)-oxyl; NON^{Dipp} = $O(SiMe_2N^{Dipp})_2$, Dipp = 2,6-$i$$Pr_2C_6H_3$).[6,7] While these reactions are thermally-initiated, photochemically-induced transformations represent an important complementary approach to radical catalysis. Indeed, a range of inorganic bismuth compounds such as (nanostructured) oxides (Bi_2O_3),[8] titanates ($Bi_4Ti_3O_{12}$),[9] vanadates ($BiVO_4$),[10] halide perovskites ($Cs_3Bi_2Br_9$),[11] and an oxybromide ($Bi_{24}O_{31}Br_{10}(OH)_{\delta}$)[12] have been exploited in photocatalytic transformations. Catalysed types of reactions include the degradation of organic dyes such as methyl orange,[9] antibiotics such as tetracycline,[10] and biocides such as triclosan,[8b] as well as CH activation of aliphatic and aromatic hydrocarbons,[11] transfer (de)hydrogenation of alcohols/ketones,[12] and olefin polymerisation.[8a] These applications of bismuth compounds in heterogeneous catalysis suggest that photochemical strategies might also be applicable for well-defined, molecular bismuth compounds under homogeneous conditions. Indeed, the light-sensitivity of molecular bismuth complexes such as organobismuthanes, dibismuthanes, bismuth amides, and related species has been phenomenologically reported in some cases.[13] The direct involvement of bismuth functional groups in visible light absorption has been demonstrated through TD-DFT calculations and UV/vis spectroscopy for the bismuth radical $[Bi(NON^{Dipp})]^{\bullet}$, a dibismuthane, and a cationic bismuth carbamoyl ($[RBi–C(O)NR'_2]^+$).[4a,14,15,16] However, applications of well-defined molecular bismuth compounds in photochemically-initiated, catalysed radical reactions have not been reported to date.

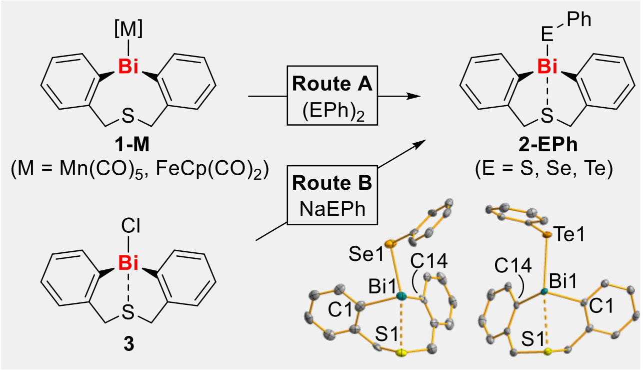


Scheme 1. Well-defined, molecular bismuth compounds for catalysed radical reactions: species applied in thermally- vs. photochemically-induced transformations.

We show here that an easily accessible, storable, molecular organo(bismuth) thiolate is catalytically active in photochemically-induced radical dehydrocoupling reactions.

We recently reported preliminary results on the synthesis of the diorgano(bismuth)thiolate **2-SPh** from transition metal bismuthane **1-Mn(CO)₅** and diphenyldisulfide, $(SPh)_2$ (Scheme 2,

10.1002/chem.202002219



Scheme 2. Synthesis of compounds **2-EPh** via routes A and B and molecular structures of **2-SePh** and **2-TePh** in the solid state. Cp = C_5H_5. Displacement parameters are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): **2-SePh**: Bi1–C1, 2.284(11); Bi1–C14, 2.303(10); Bi1–Se1, 2.7285(11); Bi1–S1, 2.966(3); C1–Bi1–C14, 97.9(3); C1–Bi1–Se1, 90.0(3); S1–Bi1–Se1, 157.23(6). **2-TePh**: Bi1–C1, 2.288(3); Bi1–C14, 2.289(3); Bi1–Te1, 2.9296(3); Bi1–S1, 3.0007(7); C1–Bi1–C14, 96.98(9); C1–Bi1–Te1, 93.92(7); S1–Bi1–Te1, 161.818(14).

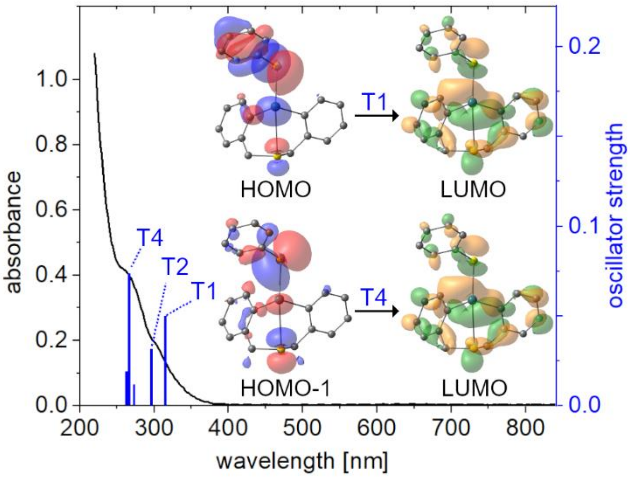


Figure 1. Experimental UV/vis spectrum of **2-SPh** in THF (solid black line), five lowest energy calculated transitions (blue bars), and molecular orbitals involved in the two calculated absorptions with highest intensity (A1 and A4). Iso-value = 0.03.

Route A).[6] Here, we extend this approach to the heavier homologues **2-SePh** and **2-TePh**, which could be obtained in high yields (>90%, Supp. Inf.). In addition, compounds **2-EPh** were also synthesised in a straightforward, transition-metal-free salt elimination protocol via Route B and fully characterised (Scheme 2, Supp. Inf., E = S, Se, Te). Single-crystal X-ray diffraction analysis of **2-SePh** and **2-TePh** confirmed Bi1–Se1 and Bi1–Te1 bond length in the expected ranges[17] and bonding interactions between Bi1 and the sulphur atom of the ligand backbone, S1, as recently reported for the sulphur analogue **2-SPh**.[6,18] According to NBO analyses, these Bi1⋯S1 interactions are realised through n(S1)→σ*(Bi–EPh) bonding with the corresponding deletion energies ranging from 18.2 to 21.3 $kcal\cdot mol^{-1}$ (Supp. Inf.). In order to evaluate the potential of compounds **2-EPh** to be applied in photochemical reactions, they were analysed by UV/vis spectroscopy and (TD-)DFT calculations. The results are qualitatively identical and discussed here for **2-SPh** (for details see Supp. Inf.). The experimental UV/vis spectrum of **2-SPh** in THF shows two absorption features centred around 307 and 264 nm with an onset at ca. 380 nm (Figure 1). These absorption bands were correlated with five singlet-singlet transitions T1-T5, three of which show larger oscillator strengths (T1 (315 nm), T2 (296 nm), T4(266 nm)). T1, T2, and T4 correspond to a HOMO/LUMO (T1, 88%), HOMO/LUMO+1 (T2, 78%), and HOMO-1/LUMO (T4, 59%) transition, respectively (Figure 1 and Supp. Inf.). While the HOMO and the HOMO-1 show contributions to Bi–SPh σ-bonding,[19] the LUMO and LUMO+1 show contributions to Bi–SPh σ*-antibonding interactions. These analyses suggest that compounds **2-EPh** should be susceptible to photochemical Bi–EPh bond cleavage, rendering them candidates for photocatalytic applications.

We thus turned our attention towards the dehydrocoupling of phenylsilane (**S1**) with TEMPO to give siloxides **P1** and **P1’** (see reaction scheme in Table 1). This reaction has recently been investigated as a model reaction for *thermally*-initiated radical catalysis with main group compounds in pivotal studies by the groups of Hill[20] and Coles.[7] In benzene solution at 23 °C with a reaction time of 1 d, 10 mol% of compounds **2-EPh** proved to be not catalytically active (entries 1-3). At an elevated temperature of 80 °C, small amounts of the coupling product **P1** were detected, but the product formations are in agreement with stoichiometric regimes (entries 4-6). Following our UV/vis spectroscopic and (TD-)DFT analyses of compounds **2-EPh**, these bismuth chalcogenides were also tested as dehydrocoupling catalysts under *photochemical* conditions. Indeed, **2-EPh** proved to be catalytically active under irradiation with a mercury vapour lamp

Table 1. Bismuth species in the catalysed dehydrocoupling reaction of TEMPO with $PhSiH_3$ (**S1**) or Ph_2SiH_2 (**S2**).

$$\begin{array}{c} \text{n equiv. TEMPO} \\ + \\ RSiH_3 \ \textit{or} \ R_2SiH_2 \\ \textbf{S1, S2} \quad \textbf{S3-S5} \end{array} \xrightarrow[\text{1 d, benzene} \\ -\ 0.5\ H_2]{\text{10 mol\% cat.}} \begin{array}{c} RSiH_2(OTEMP)\ (\textbf{P1, P2}) \\ +\ RSiH(OTEMP)_2\ (\textbf{P1', P2'}) \\ \textit{or} \\ R_2SiH(OTEMP)\ (\textbf{P3-P5}) \end{array}$$

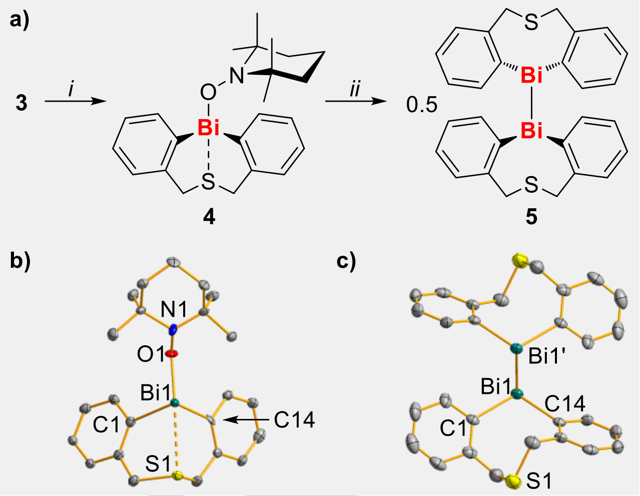
#	cat.	silane (R or R_2)	n	cond.	conversion [%][a]
1	**2-SPh**	**S1** (Ph)	1	23 °C	<1 (**P1**)
2	**2-SePh**	**S1** (Ph)	1	23 °C	<1 (**P1**)
3	**2-TePh**	**S1** (Ph)	1	23 °C	<1 (**P1**)
4	**2-SPh**	**S1** (Ph)	1	80 °C	3 (**P1**)
5	**2-SePh**	**S1** (Ph)	1	80 °C	9 (**P1**)
6	**2-TePh**	**S1** (Ph)	1	80 °C	9 (**P1**)
7	None	**S1** (Ph)	1	h·v	10 (**P1**)
8	**2-SPh**	**S1** (Ph)	1	h·v	93 (53% **P1**, 20% **P1’**)
9	**2-SePh**	**S1** (Ph)	1	h·v	65 (39% **P1**, 13% **P1’**)
10	**2-TePh**	**S1** (Ph)	1	h·v	13 (**P1**)
11	**2-SPh**	**S1** (Ph)	2	h·v	94 (13% **P1**, 87% **P1’**)
12	**2-SPh**	**S3** (Ph_2)	1	h·v	63 (**P3**)
13	**2-SPh**	**S3** (Ph_2)	2	h·v	97 (**P3**)[b]
14	**2-SPh**	**S2** (*n*Hex)	2	h·v	64 (69% **P2**, 29% **P2’**)
15	**2-SPh**	**S4** (Ph/Me)	2	h·v	54 (**P4**)[b]
16	**2-SPh**	**S5** (*t*Bu_2)	2	h·v	0 (**P5**)
17	**4**	**S1** (Ph)	1	23 °C	4 (**P1**)
18	**4**	**S1** (Ph)	1	h·v	>99 (52% **P1**, 24% **P1’**)[c]
19	**5**	**S1** (Ph)	1	23 °C	<1 (**P1**)
20	**5**	**S1** (Ph)	1	h·v	48 (**P1**)

a: conversion of TEMPO, determined by ^1H NMR spectroscopic analysis of silanes **S1-S5** and **P1-P4** (also see Supp. Inf.).[20] b: conversion of **S3** and **S4** to **P3** and **P4**. c: the TEMPO that is part of **4** is also fully converted (Supp. Inf.).

(entries 7-10). While the background reaction and the tellurium compound **2-TePh** only led to low yields of the desired coupling products, good (65%) and excellent conversions (93%) could be obtained with the homologous selenium (**2-SePh**) and sulphur species (**2-SPh**). This trend was ascribed to the photosensitivity of **2-EPh**, which increases with increasing atomic numbers of E, and to the higher reactivity of selenium and tellurium containing by-products (with the potential to undergo unselective side reactions).[21] The by-product dihydrogen, H_2, was detected by ^{1}H NMR spectroscopy. With **2-SPh** as a catalyst and two equivalents of TEMPO, 94% conversion was obtained in 1 d reaction time, necessarily with a clear preference for the double substitution product **P1'** (entry 11). **2-SPh** is also active as a catalyst for dehydrocoupling of the less reactive substrate Ph_2SiH_2 (**S3**): with one equivalent of TEMPO, 63% yield of **P3** were obtained under standard photochemical conditions (entry 12). Near-quantitative conversion of **S3** to **P3** in 1 d was obtained by using n = 2 equivalents of TEMPO (entry 13). These results demonstrate for the first time the high potential of well-defined molecular bismuth compounds for the exploitation in photochemically-induced catalytic bond forming events via radical pathways. In terms of catalytic activity, the bismuth thiolate **2-SPh** clearly outperforms the bismuth radical compound $[Bi(NON^{Dipp})]^{\bullet}$, which was recently reported to catalyse the reaction of **S1** with TEMPO in a thermally-induced transformation (e.g.: 10 mol% $[Bi(NON^{Dipp})]^{\bullet}$, 70 °C, 1.7 d reaction time, 10% conversion (formation of **P1**);[22] *cf.* entries 8, 11).[7] Furthermore, the catalytic activity of **2-SPh** can compete with that of the magnesium amide $Mg\{N(SiMe_3)_2\}_2(thf)_2$, which has been shown to catalyse thermally-initiated dehydrocoupling reactions of **S1** and **S3** with TEMPO: while $Mg\{N(SiMe_3)_2\}_2(thf)_2$ is catalytically more selective in addressing only one Si–H bond of $PhSiH_3$, i.e. reaction of **S1** with 1 equiv. TEMPO (10 mol% cat., 60 °C 1 d, 99% yield of **P1**; *cf.* entry 8), **2-SPh** is catalytically more active in addressing Si–H bonds of secondary silanes, i.e. in the overall reaction of **S1** or **S3** with two equiv. TEMPO (**S1**: 10 mol% $Mg\{N(SiMe_3)_2\}_2(thf)_2$, 80 °C, 6 d, 96% yield, **S3**: 10 mol% $Mg\{N(SiMe_3)_2\}_2(thf)_2$, 80 °C, 4 d, 99% yield; *cf.* entries 11, 13). Concerning the mode of initiation of the reaction (thermally vs. photochemically), our approach is complementary to those previously reported for the dehydrocoupling of TEMPO with silanes.[7,20]

Preliminary investigations into the substrate scope of this reaction show reduced catalytic activities for silanes bearing one or more alkyl substituents (entries 14-16 and Supp. Inf.).

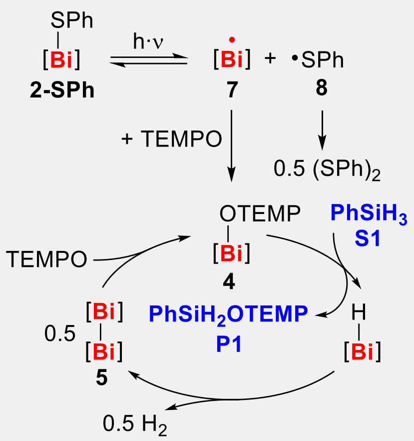
In order to identify potential intermediates of the catalysed reactions, a reaction mixture obtained under our standard catalytic conditions (e.g. entry 8) was analysed by high-resolution mass spectrometry. Signals of m/z = 578.1922 and 843.1000 were detected (Supp. Inf.).[23] This corresponds to species with the sum formulae $[C_{23}H_{31}BiNOS]^+$ (calc. m/z = 578.1925) and $[C_{28}H_{25}Bi_2S_2]^+$ (calc. m/z = 843.1000), which were assigned to protonated derivatives of the bismuth tempoxide $[Bi(C_6H_4CH_2)_2S(OTEMP)]$ (**4**) and the dibismuthane $[Bi(C_6H_4CH_2)_2S]_2$ (**5**), respectively. Both compounds were synthesised in independent approaches, isolated, and fully characterised (Scheme 3). Compound **4** was obtained as a colourless solid from the reaction of **3** with in-situ-generated Na(OTEMP). Single-crystal X-ray diffraction analysis revealed X–O1 bond lengths (Bi1–O1, 2.18 Å; N1–O1, 1.46 Å) and an angle sum around N1 (333.9°), which point towards this complex being best described as a bismuth tempoxide species (Scheme 3b).[3b,7,24,25] This is also in agreement with the presence of a Bi1···S1 bonding interaction, which is expected for a sufficiently electronegative anionic substituent X^- bound to $[Bi(C_6H_4CH_2)_2S]^+$.[6,18] EPR spectroscopic investigations revealed a very weak resonance indicating the presence of trace amounts (0.3%) of TEMPO in solution. Since the NMR spectroscopic and elemental analysis of **4** gave no hints at the presence of impurities, the postulation of an equilibrium scenario $[Bi(C_6H_4CH_2)_2S(OTEMP)] \rightleftharpoons [Bi(C_6H_4CH_2)_2S]^{\bullet} + TEMPO^{\bullet}$, appeared tempting.[3b,7] However, powder EPR spectra of **4** and the temperature-dependence of the EPR signals of **4** in solution clearly ruled out an equilibrium scenario in the range of –60 to +20 °C,[26] indicating that it is in fact due to trace impurities of TEMPO in the sample, which could not be removed by repeated re-crystallisations (Figure S12, Supp. Inf.).



Scheme 3. a) Synthesis of compounds **4** and **5**; i: Na(OTEMP), r.t. THF, 2 h; ii: $PhSiH_3$, 60 °C, benzene, 4 d. b,c) Molecular structures of **4** and **5** in the solid state. Displacement parameters are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): **4**: Bi1–C1, 2.274(8); Bi1–C14, 2.271(9); Bi1–O1, 2.184(5); Bi1–S1, 2.936(2); N1–O1, 1.459(8); C1–Bi1–C14, 91.5(3); C1–Bi1–O1, 92.3(3); Bi1–O1–N1, 106.1(4); S1–Bi1–O1, 159.76(15); ΣC/O–N1–C/O, 333.9(6). **5**: Bi1–C1, 2.262(7); Bi1–C14, 2.289(7); Bi1–Bi1', 3.0211(5); C1–Bi1–C14, 104.8(3); C1–Bi1–Bi1', 91.59(18); C1–Bi1–Bi1'–C1', 180.

Compound **5** was obtained as a red solid from the reaction of **4** with $PhSiH_3$. NMR spectroscopic reaction monitoring revealed the formation of $PhSiH_2(OTEMP)$ and H_2, suggesting a mechanism via the short-lived bismuthane $[HBi(C_6H_4CH_2)_2S]$.[27,28] Once compound **5** is precipitated, its solubility in common organic solvents is very poor. NMR spectroscopic data could only be obtained at elevated temperature in pyridine (Supp. Inf.).[29] Single-crystal X-ray diffraction analysis confirmed the expected molecular structure with C_i symmetry and a non-polar Bi–Bi bond (3.02 Å), resulting in the absence of Bi1···S1 interactions (Scheme 3c).[6]

Combined UV/vis spectroscopic and (TD-)DFT analyses of **4** and **5** suggest that they should be susceptible to photochemically-induced Bi–O/Bi–Bi bond cleavage (Supp. Inf.). In agreement with these results, isolated compounds **4** and **5** proved to be catalytically competent in the photochemically-induced dehydrocoupling of **S1** with TEMPO (Table 1, entries 17-20). While quantitative yields were obtained with **4**, the lower yield of 48% obtained with **5** was ascribed to the poor solubility of the isolated species. The mechanism of the catalysed reactions presented in this work is certainly complex and potentially involves resting states and parallel reaction pathways. In order to rationalise the catalytic reaction, a tentatively suggested catalytic cycle involving all compounds that were isolated or detected in catalytic experiments is shown in Scheme 4 (for further details, see Supp. Inf.).



Scheme 4. Tentatively suggested catalytic cycle for dehydrocoupling of **S1** with TEMPO to give **P1**, catalysed by **2-SPh** (for further details see Supp. Inf.). [Bi] = [Bi($C_6H_4CH_2$)$_2$S].

In summary, we have demonstrated that the easily accessible and storable diorgano(bismuth)thiolate [Bi($C_6H_4CH_2$)$_2$S(SPh)] (**2-SPh**) allows for the first application of a well-defined molecular bismuth compound as a catalyst in a homogeneous *photochemical* approach. In the radical dehydrocoupling of silanes with TEMPO, **2-SPh** shows a much higher catalytic activity than previously reported bismuth compounds and is competitive with a previously reported magnesium species. The new approach is complementary to existing ones in terms of reaction initiation (thermal vs. photochemical), opening up perspectives for orthogonal synthetic strategies. TD-DFT calculations gave insights into the initiating step of the reaction and catalytically competent intermediates have been isolated and characterised.

Acknowledgements

Funding through the Fonds der Chemischen Industrie, the Universitätsbund Würzburg, the University of Würzburg, and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. C. L. thanks Prof. Holger Braunschweig for continuous support.

Keywords: bismuth • chalcogens • radical reactions • dehydrocoupling • photocatalysis

[1] a) Y.-R. Luo, Bond Dissociation Energies. In CRC Handbook of *Chemistry and Physics*, 89th ed.; Ed.: D. R. Lide, CRC Press/Taylor and Francis: Boca Raton, FL, 2009; b) S. J. W. Price and A. F. Trotman-Dickenson, *Trans. Faraday Soc.* **1958**, *54*, 1630-1637; c) D. P. Mukhopadhay, D. Schleier, S. Wirsing, J. Ramler, D. Kaiser, E. Reusch, P. Hemberger, T. Preitschopf, I. Krummenacher, B. Engels, I. Fischer, C. Lichtenberg, *Chem. Sci.* **2020**, DOI: 10.1039/D0SC02410D.

[2] a) A. Studer and D. P. Curran, *Angew. Chem. Int. Ed.* **2016**, *55*, 58-102; b) C. Lichtenberg, *Angew. Chem. Int. Ed.* **2016**, *55*, 484-486; c) C. Lichtenberg, *Chem. Eur. J.* **2020**, doi: 10.1002/chem.202000194.

[3] a) T. Y. Lai, L. Tao, R. D. Britt, P. P. Power, *J. Am. Chem. Soc.* **2019**, *141*, 12527-12530; b) S. Ishida, F. Hirakawa, K. Furukawa, K. Yoza, T. Iwamoto, *Angew. Chem. Int. Ed.* **2014**, *53*, 11172-11176.

[4] For isolable bismuth radicals see: a) R. J. Schwamm, J. R. Harmer, M. Lein, C. M. Fitchett, S. Granville, M. P. Coles, *Angew. Chem. Int. Ed.* **2015**, *54*, 10630-10633; b) C. Ganesamoorthy, C. Helling, C. Wölper, W. Frank, E. Bill, G. E. Cutsail III, S. Schulz, *Nat. Commun.* **2018**, *9*, 87.

[5] a) J. M. Bothwell, S. W. Krabbe, R. S. Mohan, *Chem. Soc. Rev.* **2011**, *40*, 4649-4707; b) R. Mohan, *Nat. Chem.* **2010**, *2*, 336. c) R. Qiu, Y. Qiu, S. Yin, X. Song, Z. Meng, X. Xu, X. Zhang, S. Luo, C.-T. Au, W.-Y. Wong, *Green Chem.* **2010**, *12*, 1767-1771.

[6] J. Ramler, I. Krummenacher, C. Lichtenberg, *Angew. Chem. Int. Ed.*, **2019**, *58*, 12924-12929.

[7] R. J. Schwamm, M. Lein, M. P. Coles, C. M. Fitchett, *Chem. Commun*. **2018**, *54*, 916-919.

[8] a) K. Hakobyan, T. Gegenhuber, C. S. P. McErlean, M. Müllner, *Angew. Chem. Int. Ed,* **2019**, *58*, 1828-1832; b) M. Weber, T. Rüffer, F. Speck, F. Göhler, D. P. Weimann, C. A. Schalley, T. Seyller, H. Lang, M. Mehring, *Inorg. Chem.,* **2020**, *59*, 3353-3366; c) L. Zhou, W. Wang, H. Xu, S. Sun, M. Shang, *Chem. Eur. J.* **2009**, *15*, 1776-1782; *d*) H. Cheng, B. Huang, J. Lu, Z. Wang, B. Xu, X. Qin, X. Zhang and Y. Dai, *PhysChemChemPhys* **2010**, *12*, 15468-15475.

[9] W. F. Yao, X. H. Xu, H. Wang, J. T. Uhou, X. N. Yang, Y. Zhang, S. X. Shang, B. B. Huang, *Appl. Catal. B Environ.* **2004**, *52*, 109-116.

[10] M. Tayebi, A. Tayyebi, T. Soltani and B.-K. Lee, *New J. Chem*. **2019**, *43*, 9106-9115.

[11] Y. Dai, C. Pidevin, C. Ochoa-Hernández, A. A. Auer, H. Tüysüz, *Angew. Chem. Int. Ed.* **2020**, *59*, 5788-5796.

[12] Y. Dai, C. Li, Y. Shen, S. Zhu, M. S. Hvid, L.-C. Wu, J. Skibsted, Y. Li, J. W. H. Niemantsverdriet, F. Besenbacher, N. Lock, R. Su, *J. Am. Chem. Soc.* **2018**, *140*, 16711-16719.

[13] a) A. J. Ashe III, E. G. Ludwig Jr., J. Oleksyszyn, *Organometallics* **1983**, *2*, 1859-1866; b) J. Lorberth, W. Massa, S. Wocadlo, I. Sarraje, S.-H. Shin, X.-W. Li, *J. Organomet. Chem.* **1995**, *485*, 149-152; c) W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, M. E. Green, D. C. R. Hockless, N. C. Norman, *Inorg. Chem.* **1991**, *30*, 4680-4682; d) J. M. Wallis, G. Müller, H. Schmidbaur, *J. Organomet. Chem*. **1987**, *325*, 159-168; e) . Lichtenberg, F. Pan, T. P. Spaniol, U. Englert, J. Okuda, *Angew. Chem. Int. Ed.* **2012**, *51*, 13011-13015.

[14] a) J. Ramler, J. Poater, F. Hirsch, B. Ritschel, I. Fischer, F. M. Bickelhaupt, C. Lichtenberg, *Chem. Sci.* **2019**, *10*, 4169-4176; b) B. Ritschel, J. Poater, H. Dengel, F. M. Bickelhaupt, C. Lichtenberg, *Angew. Chem. Int. Ed.* **2018**, *57*, 3825-3829.

[15] Also see ref. [3b] for comparison.

[16] K. Y. Monakhov, T. Zessin and G. Linti, *Eur. J. Inorg. Chem.* **2010**, 322-332.

[17] a) F. Calderazzo, A. Morvillo, G. Pelizzi, R. Poly, F. Ungari, *Inorg. Chem.*, **1988**, *27*, 3730-3733; b) P. Šimon, R. Jambor, A. Růžička, L. Dostál, *Organometallics* **2013**, *32*, 239-248; c) J. Ramler, C. Lichtenberg, *Chem. Eur. J.* **2020**, DOI: 10.1002/chem.202001674.

[18] Also see: A. Toma, C. I. Raţ, A. Silvestru, T. Rüffer, H. Lang, M. Mehring, *J. Organomet. Chem.* **2016**, *806*, 5-11.

[19] There are also significant contributions of a sulphur-centred lone pair to the HOMO and the HOMO-1.

[20] D. J. Liptrot, M. S. Hill, M. F. Mahon, *Angew. Chem. Int. Ed*. **2014**, *53*, 6224-6227.

[21] a) J.-J. Aleman-Lara, E. Block, S. Braverman, M. Cherkinsky, M. B. C. de la Plata, *Sulfur, Selenium, and Tellurium, Science of Synthesis*, vol. 39, Houben-Weyl, 2014; b) S. M. Horvat, C. H. Schiesser, *New J. Chem*. **2010**, *34*, 1692-1699.

[22] Data read out from Figure S7 of ref. [7].

[23] Bismuth radicals are challenging to detect EPR spectroscopically, which has been ascribed to fast relaxation as a result of large spin-orbit coupling (ref. [2b]). For example, the bismuth radical that is formed in the

equilibrium reaction [Bi(CSiMe$_3$CH$_2$)$_2$]$_2$ $\rightleftharpoons$ 2 [Bi(CSiMe$_3$CH$_2$)$_2$]$^\bullet$ could not be detected by EPR spectroscopy (ref. [2b]). The EPR spectroscopic detection of a bismuth radical that may be a reactive species in the catalytic experiments presented in this work would thus be surprising, since it would be expected to be very short-lived and present only in very low concentrations. Nevertheless, attempts to detect bismuth radical species by irradiating **2-SPh** or **4** during EPR spectroscopic experiments were undertaken, but proved to be unsuccessful (for details see Supp. Inf.).

[24] G. C. Forbes, A. R. Kennedy, R. E. Mulvey, P. J. A. Rodger, *Chem. Commun*. **2001**, 1400-1401.

[25] Z. Turner, *Inorg. Chem*. **2019**, *58*, 14212-14227.

[26] This equilibrium scenario may well be accessible at elevated temperatures, since the homolytic cleavage of the Bi–O bond in **4** is only mildly endergonic (ΔG = +12.0 kcal·mol^{-1}) according to DFT calculations (Supp. Inf.).

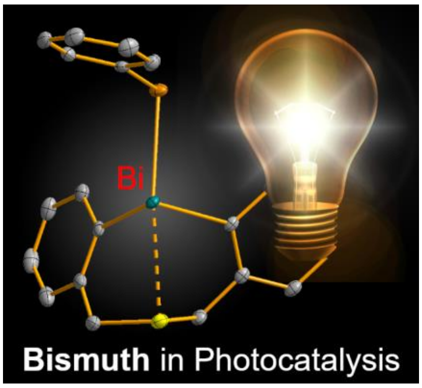
[27] a) G. Balázs, H. J. Breunig, E. Lork, *Organometallics* **2002**, *21*, 2584-2586; b) G. Balázs, H. J. Breunig, E. Lork, *Z. Naturforsch.* **2005**, *60b*, 180-182; c) R. J. Schwamm, M. Lein, M. P. Coles, C. M. Fitchett, *Angew. Chem. Int. Ed*. **2016**, *55*, 14798-14801.

[28] A sole example of an isolable secondary bismuthane has been reported: N. J. Hardman, B. Twamley, P. P. Power, *Angew. Chem. Int. Ed.* **2000**, *39*, 2771-2773.

[29] A poor solubility of the related species [Bi(C$_6$H$_4$CH$_2$)$_2$NMe]$_2$ is suggested by the use of 100 mL THF for the extraction of 59 mg of this compound: S. Shimada, J. Maruyama, Y.-K. Choe, T. Yamashita, *Chem. Commun* **2009**, 6168-6170.

Entry for the Table of Contents

Insert graphic for Table of Contents here.



Well-defined molecular bismuth with Bi–EPh functional groups are catalytically active in the photochemical dehydrocoupling of silanes with TEMPO (E = S, Se, Te). Their properties are complementary or superior to those of other main group catalysts for these reactions.

Institute and/or researcher Twitter usernames: @Uni_WUE