

Homogeneous Catalysis

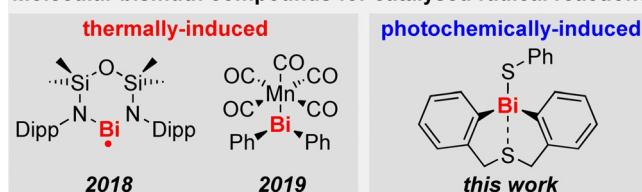
Well-Defined, Molecular Bismuth Compounds: Catalysts in Photochemically Induced Radical Dehydrocoupling Reactions

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

Abstract: A series of diorgano(bismuth)chalcogenides, [Bi(di-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 = (tetramethyl-piperidin-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 ($Z-X \rightleftharpoons Z^{\cdot} + X^{\cdot}$) 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≡Sn bond in (SnAr)₂ and the Pn–Pn bonds in (Pn(CSiMe₃CH₂)₂)₂ (Ar = C₆H₃-2,6-(C₆H₃-2,6-*i*Pr₂)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 SiPhH₃ and TEMPO with [Bi(NON^{Dipp})][•] and the

Molecular bismuth compounds for catalysed radical reactions



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

radical cyclo-isomerisation of δ -iodo-olefins with Ph₂Bi–Mn(CO)₅ have recently been reported (Scheme 1; TEMPO = (tetramethyl-piperidin-1-yl)-oxyl; NON^{Dipp} = O(SiMe₂N^{Dipp})₂, Dipp = 2,6-*i*Pr₂C₆H₃).^[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 (Bi₂O₃),^[8] titanates (Bi₄Ti₃O₁₂),^[9] vanadates (BiVO₄),^[10] halide perovskites (Cs₃Bi₂Br₉),^[11] and an oxybromide (Bi₂₄O₃₁Br₁₀(OH)₈)^[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})][•], 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.

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

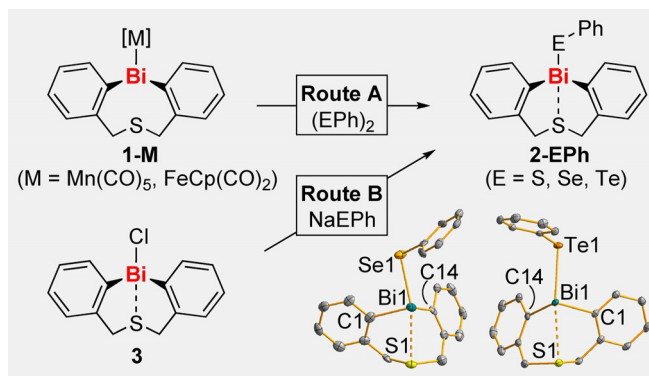
We recently reported preliminary results on the synthesis of the diorgano(bismuth)thiolate **2-SPh** from transition metal bismuthane **1-Mn(CO)₅** and diphenyldisulfide, (SPh)₂ (Scheme 2,

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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 = C₅H₅. 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).

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%, Supporting Information). 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, Supporting Information, 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 sulfur atom of the ligand backbone, S1, as recently reported for the sulfur 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 mol⁻¹ (Supporting Information). 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 Supporting Information). 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 Supporting Information). 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*-anti-bonding 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

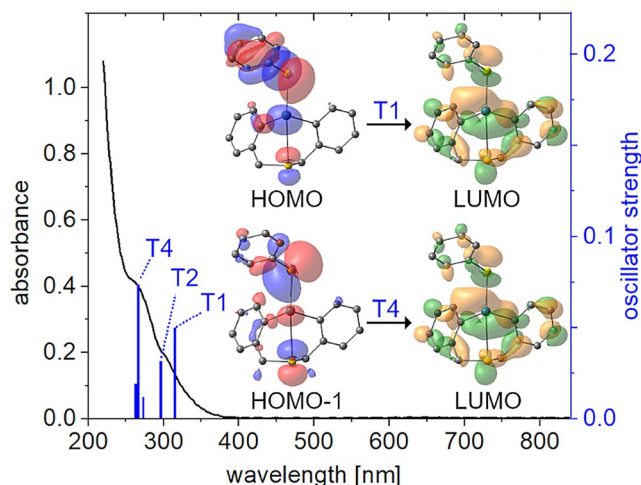


Figure 1. Experimental UV/Vis spectrum of **2-SPh** in THF (solid black line), five lowest energy calculated transitions (blue bars), and molecular orbitals involved in the two calculated absorptions with highest intensity (A1 and A4). Isovalue = 0.03.

Table 1. Bismuth species in the catalysed dehydrocoupling reaction of TEMPO with PhSiH₃ (**S1**) or Ph₂SiH₂ (**S2**).

$\begin{array}{c} n \text{ equiv. TEMPO} \\ + \\ \text{R}_2\text{SiH}_3 \text{ or } \text{R}_2\text{SiH}_2 \\ \text{S1, S2} \quad \text{S3-S5} \end{array} \xrightarrow[\text{- 0.5 H}_2]{\text{10 mol\% cat.}} \begin{array}{c} \text{R}_2\text{SiH}_2(\text{OTEMP}) \text{ (P1, P2)} \\ + \\ \text{R}_2\text{SiH}(\text{OTEMP})_2 \text{ (P1', P2')} \\ \text{or} \\ \text{R}_2\text{SiH}(\text{OTEMP}) \text{ (P3-P5)} \end{array}$					
#	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	hν	10 (P1)
8	2-SPh	S1 (Ph)	1	hν	93 (53% P1 , 20% P1')
9	2-SePh	S1 (Ph)	1	hν	65 (39% P1 , 13% P1')
10	2-TePh	S1 (Ph)	1	hν	13 (P1)
11	2-SPh	S1 (Ph)	2	hν	94 (13% P1 , 87% P1')
12	2-SPh	S3 (Ph ₂)	1	hν	63 (P3)
13	2-SPh	S3 (Ph ₂)	2	hν	97 (P3) ^[b]
14	2-SPh	S2 (nHex)	2	hν	64 (69% P2 , 29% P2')
15	2-SPh	S4 (Ph/Me)	2	hν	54 (P4) ^[b]
16	2-SPh	S5 (tBu ₂)	2	hν	0 (P5)
17	4	S1 (Ph)	1	23 °C	4 (P1)
18	4	S1 (Ph)	1	hν	> 99 (52% P1 , 24% P1') ^[c]
19	5	S1 (Ph)	1	23 °C	< 1 (P1)
20	5	S1 (Ph)	1	hν	48 (P1)

[a] Conversion of TEMPO, determined by ¹H NMR spectroscopic analysis of silanes **S1–S5** and **P1–P4** (also see Supporting Information).^[20] [b] Conversion of **S3** and **S4** to **P3** and **P4**. [c] The TEMPO that is part of **4** is also fully converted (Supporting Information).

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

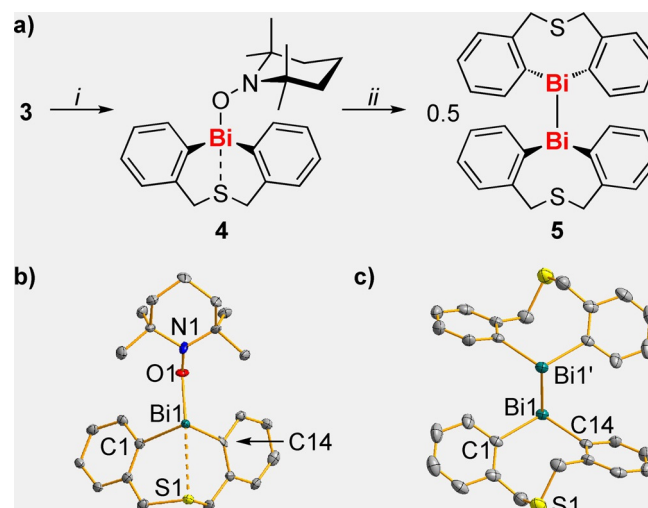
product **P1** were detected, but the product formations are in agreement with stoichiometric regimes (entries 4–6). Following our UV/Vis spectroscopic and (TD-)DFT analyses of compounds **2-EPh**, these bismuth chalcogenides were also tested as dehydrocoupling catalysts under *photochemical* conditions. Indeed, **2-EPh** proved to be catalytically active under irradiation with a mercury vapour lamp (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 sulfur 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, H₂, was detected by ¹H 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 Ph₂SiH₂ (**S3**): with one equivalent of TEMPO, 63% yield of **P3** was 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})], which was recently reported to catalyse the reaction of **S1** with TEMPO in a thermally-induced transformation (e.g.: 10 mol% [Bi(NON^{Dipp})], 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(SiMe₃)₂}(thf)₂, which has been shown to catalyse thermally-initiated dehydrocoupling reactions of **S1** and **S3** with TEMPO: while Mg{N(SiMe₃)₂}(thf)₂ is catalytically more selective in addressing only one Si–H bond of PhSiH₃, that is, 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, that is, in the overall reaction of **S1** or **S3** with two equiv TEMPO (**S1**: 10 mol% Mg{N(SiMe₃)₂}(thf)₂, 80 °C, 6 d, 96% yield, **S3**: 10 mol% Mg{N(SiMe₃)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 Supporting Information).

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 (Supporting Information).^[23] This corresponds to species with the sum formulae [C₂₃H₃₁BiNOS]⁺ (calc. *m/z* = 578.1925) and [C₂₈H₂₅Bi₂S₂]⁺ (calc. *m/z* = 843.1000), which were assigned to protonated derivatives of the bismuth tempoxide [Bi(C₆H₄CH₂)₂S(OTEMP)] (**4**) and the dibismuthane [Bi(C₆H₄CH₂)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 3 b).^[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(C₆H₄CH₂)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(C₆H₄CH₂)₂S(OTEMP)] ⇌ [Bi(C₆H₄CH₂)₂S]⁺ + TEMPO[•], 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, Supporting Information).

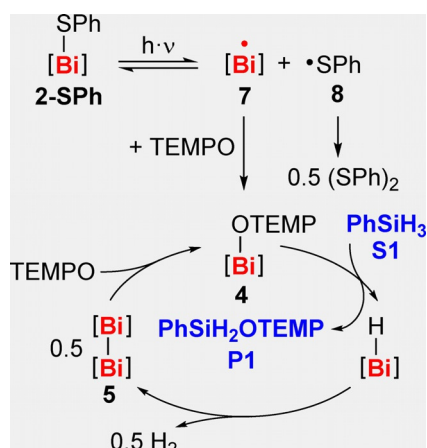
Compound **5** was obtained as a red solid from the reaction of **4** with PhSiH₃. NMR spectroscopic reaction monitoring revealed the formation of PhSiH₂(OTEMP) and H₂, suggesting a mechanism via the short-lived bismuthane



Scheme 3. a) Synthesis of compounds **4** and **5**; i: Na(OTEMP), r.t. THF, 2 h; ii: PhSiH₃, 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); Σ C/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.

[HBi(C₆H₄CH₂)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 (Supporting Information).^[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 3 c).^[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 (Supporting Information). 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 Supporting Information).



Scheme 4. Tentatively suggested catalytic cycle for dehydrocoupling of **S1** with TEMPO to give **P1**, catalysed by **2-SPh** (for further details see Supporting Information). [Bi] = [Bi(C₆H₄CH₂)₂S].

In summary, we have demonstrated that the easily accessible and storable diorgano(bismuth)thiolate [Bi(C₆H₄CH₂)₂S(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.

Experimental Section

Crystallographic data: Deposition numbers 1990330, 1990331, 1990332, and 1990333 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of interest

The authors declare no conflict of interest.

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

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