Homogeneous Catalysis

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

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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 this coupling reaction. 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 = Z+ + X−) under mild reaction conditions, which is a key feature for potential catalytic applications via radical pathways.[2,5] 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)(Ar = C₆H₅−2,6-(C₆H₅−2,6-iPr)₂; Pn = Sn, Sb, Bi)₃]. Such findings have paved the way for new catalytic applications of well-defined, molecular complexes of heavy p-block elements in radical reactions.[2,5] 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.[3,6a] In this context, the radical dehydrocoupling of SiPh₃ and TEMPO with [Bi(NON₃)₆]⁺ yields the radical cyclo-isomerisation of δ-iodo-olefins with Ph₃Bi-Mn(CO)₅ have recently been reported (Scheme 1; TEMPO = (tetramethyl-piperidin-1-yl)-oxyl; NON₃ = O(SiMe₃)₃). 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) vanadates (BiVO₄), halides perovskites (Cs₅Bi₂Br₁₀), and an oxybromide (Bi₄O₃Br₆(OH)₃) have been exploited in photocatalytic transformations. Catalysed types of reactions include the degradation of organic dyes such as methyl orange, antibiotics such as tetracycline, and biocides such as triclosan, as well as CH activation of aliphatic and aromatic hydrocarbons, transfer (de)hydrogenation of alcohols/ketones, and olefin polymerisation.[3,6] 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.[4] 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(NON₃)₆]⁺, a dibismuthane, and a cationic bismuth carbamoyl [(RBI-C(NO)NR₂)₃]⁺. 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 bis-muthane 1-Mn(CO)₅ and diphenylisulfide, (SPH₂)₂ (Scheme 2, [a])
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 B1–Se1 and Bi1–Te1 bond length in the expected range[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 B1–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, 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 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

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: B1–C1, 2.284(11); B1–C14, 2.303(10); B1–Se1, 2.7285(11); B1–S1, 2.966(3); C1–B1–C14, 97.9(3); C1–B1–Se1, 90.0(3); S1–B1–Se1, 157.23(6). 2-TePh: B1–C1, 2.288(3); B1–C14, 2.289(3); B1–Te1, 2.9296(3); B1–S1, 3.0007(7); C1–B1–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). Isosvalue = 0.03.

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

| # | Cat. | Silane | n | Cond. | Conversion [%][a] |
|---|------|--------|---|-------|------------------|
| 1 | 2-SPH | S1 (Ph) | 1 | 23 °C | <1 (P1) |
| 2 | 2-SPH | 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-SPH | S1 (Ph) | 1 | 80 °C | 9 (P1) |
| 6 | 2-TePh | S1 (Ph) | 1 | 80 °C | 9 (P1) |
| 7 | None | S1 (Ph) | 1 | hv | 10 (P1) |
| 8 | 2-SPH | S1 (Ph) | 1 | hv | 93 (51% P1, 20% P1') |
| 9 | 2-SPH | S1 (Ph) | 1 | hv | 65 (39% P1, 13% P1') |
| 10 | 2-TePh | S1 (Ph) | 1 | hv | 13 (P1) |
| 11 | 2-SPH | S1 (Ph) | 2 | hv | 64 (% P1, 87% P1') |
| 12 | 2-SPH | S3 (Ph) | 1 | hv | 63 (P3) |
| 13 | 2-SPH | S3 (Ph) | 2 | hv | 97 (P3) |
| 14 | 2-SPH | S2 (nHex) | 2 | hv | 64 (69% P2, 29% P2') |
| 15 | 2-SPH | S4 (Ph/Me) | 2 | hv | 54 (P4) |
| 16 | 2-SPH | S5 (Bu) | 2 | hv | 64 (58% P2, 34% P2') |
| 17 | 4 | S1 (Ph) | 1 | 23 °C | 4 (P1) |
| 18 | 4 | S1 (Ph) | 1 | hv | >99 (52% P1, 24% P1') |
| 19 | 5 | S1 (Ph) | 1 | 23 °C | <1 (P1) |
| 20 | 5 | S1 (Ph) | 1 | hv | 48 (P1) |

[a] Conversion of TEMPO, determined by ¹H NMR spectroscopic analysis of siloxanes S1–S5 and P1–P4 (also see Supporting Information).[20] b Con- version of S3 and S4 to P3 and P4. [c] The TEMPO that is part of S4 is also fully converted (Supporting Information).
was obtained as a red solid from the reaction of 3 with in situ-generated Na(OTEMP). Single-crystal X-ray diffraction analysis revealed X–O1 bond lengths (B1–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). This is also in agreement with the presence of a B1–Si bonding interaction, which is expected for a sufficiently electronegative anionic substituent X” bound to [Bi(C₄H₄CH₂)₂S]⁺. 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(C₄H₄CH₂)₂S(OTEMP)⁺] ↔ [Bi(C₄H₄CH₂)₂S⁺] + TEMPO⁺, appeared tempting. 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, indicating that it is in fact due to trace impurities of TEMPO in the sample, which could not be removed by repeated recrystallisations (Figure S12, Supporting Information).

Scheme 3. a) Synthesis of compounds 4 and 5; i: Na(OTEMP), rt, THF, 2 h; ii: PhSH2, 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: B1–C1, 2.274(8); B1–C14, 2.271(9); B1–O1, 2.184(5); B1–S1, 2.936(2); N1–O1, 1.459(8); C11–B1–C14, 91.5(3); C1–B1–O1, 92.3(3); B1–O1–N1, 106.1(4); S1–B1–O1, 159.7(6); C2/C/O–N1/C/O, 333.9(6); 5: B1–C1, 2.262(7); B1–C14, 2.289(7); B1–B1’, 3.021(5); C1–B1–C14, 104.8(3); C1–B1–B1’, 91.5(8); C1–B1–C1‘, 180.

Preliminary investigations into the substrate scope of this reaction showed 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). This corresponds to species with the sum formulae [C₄H₄B1cN(SiMe₃)₂]⁺ (calc. m/z = 578.1925) and [C₃H₂B1cS]⁺ (calc. m/z = 843.1000), which were assigned to protonated derivatives of the bismuth tempoxide [Bi(C₄H₄CH₂)₂S(OTEMP)]⁻ and the dibismuthane [Bi(C₄H₄CH₂)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).
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, symmetry and a non-polar Bi–Bi bond (3.02 Å), resulting in the absence of Bi–S1 interactions (Scheme 3).[30]

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[2(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, 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 Services structure.

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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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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 Supporting Information).

[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 $[\text{Bi(CSiMe}_3\text{CH}_2)_2]_2 \rightarrow 2[\text{Bi(CSiMe}_3\text{CH}_2)_2]^\cdot$ could not be detected by EPR spectroscopy (ref. [2b]).

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