An efficient and facile one-pot synthesis of structurally unique 2,4,6-tris(arylchalcogeno)-1,3,5-triazine and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzene

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Dedicated to Professor Ram Charan Mehrotra (UOR) on his 82nd birthday

Abstract—An efficient one-pot synthesis of a novel class of 2,4,6-tris(arylchalcogeno)-1,3,5-triazine (sulfur, selenium and tellurium) and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzene (sulfur and selenium)-containing ligands has been developed based on the reaction of 2,4,6-trichloro-1,3,5-triazine and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene with the corresponding arylchalcogenide anions generated in aqueous tetrahydrofuran.

There has been significant interest in the design and synthesis of robust organic ligands based on triazine and trimethylbenzene anchors due to their unique applications in organic synthesis, enantiodifferentiating coupling reagents, catalysis, molecular tectonics, polymeric materials and in analytical and coordination chemistry. We also became interested in developing synthetic methodology for multifunctional organochalcogen (S, Se and Te) donors in order to create non-hydrogen-bonded networks, whereby chalcogen atoms could play an important role in the design and synthesis of highly diverse spatially arranged single components that may exhibit self-organizing properties through chalcogen-chalcogen interactions. In fact, the directional forces between chalcogen centres may lead to interesting structures when the chalcogen atoms are incorporated into fairly rigid ring systems. For these reasons, we paid attention to the synthesis of 2,4,6-tris(arylchalcogeno)-1,3,5-triazines and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzene.

Keywords: Arylchalcogen; Triazine; Sulfur; Selenium; Tellurium.
Cl\(\text{REER} \xrightarrow{\text{NaBH}_4/\text{THF}} \text{NaOH} / 0{^\circ}\text{C}}

Scheme 1.

In compound 2 we encountered Te- •-Te distances of the order of 3.937 Å which is less than the van der Waals distance\(^1\) (Te- •-Te = 4.40 Å). The distances between Te(1)-Te(2), Te(2)-Te(3) and Te(3)-Te(1) are 5.778, 5.810, and 6.033 Å, respectively, which further indicate that the triazine ring is distorted and forces the orientations of the two phenyltelluro rings towards each other. The substituted telluriums at the 2,4,6-positions are in close proximity with the nitrogens of the 1,3,5-triazine ring. Nevertheless, the atomic distances are worth mentioning (Te(1) •-N(1), Te(2) •-N(2) and Te(3) •-N(3) are 3.015, 2.942, and 2.871 Å, respectively) and are larger than the sum of their covalent radii but significantly shorter than the sum of the corresponding van der Waals radii (3.61 Å).\(^1\)

In summary, we have demonstrated a new and facile method for the reduction of diaryldiselenide or ditelluride with sodium borohydride in aqueous tetrahydrofuran for the generation of arylselenolate or tellurolate anions. Regrettably, the reduction of R\(_2\)Se\(_2\) or R\(_2\)Te\(_2\) has never received great attention in organic chalcogen chemistry due to its poor reactivity. However, addition of a few drops of water in tetrahydrofuran (aqueous THF) makes the reaction quite facile and generates arylselenolate or tellurolate ions, within a few minutes, which are both stable and easy to handle. We have also demonstrated a general, versatile and high yielding method for the construction of an aryl-heteroatom bond by preparing novel classes of 2,4,6-tris(arylchalcogeno)-1,3,5-triazines and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzenes (sulfur, selenium and tellurium based robust ligands). Compounds 1-8 are quite appealing building blocks for the synthesis of metal complexes.

![Figure 1. Crystal structure of [(PhTe)\(_3\)C\(_3\)N\(_3\)] and crystal packing along the a-axis.](image-url)
where the S, Se and Te atoms may participate in bonding with metal ions. We are currently involved in examining their applications in creating extended-reach structures and results will be reported in due course.

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References and notes


9. Typical procedure for the synthesis of 2. To a stirred solution of diphenylditelluride (2.05 g, 5mmol) and sodium hydroxide (0.040g, 10mmol) in aqueous THF (20mL + 0.2mL H2O) under N2 (g) and cooled to 0°C was added NaBH4 (0.419g, 11mmol) carefully. The orange-yellow colour of the ditelluride disappeared within a few minutes. The resulting mixture was allowed to warm to room temperature over 0.25 h. To the clear solution thus formed was added 2,4,6-trichloro-1,3,5-triazine (0.615g, 3.33mmol) in anhydrous THF (10mL). The reaction mixture was stirred for 2h at room temperature and reaction completion was monitored by thin layer chromatography. The reaction mixture was concentrated to dryness and treated with saturated NH4Cl solution (10 mL) and extracted with chloroform (3x20mL). The combined organic extracts were washed with water (2x20mL) and dried (MgSO4) and concentrated to afford a colourless oil. This was washed with diethyl ether to yield the desired product of sufficient analytical purity. Diethyl ether washings also produced crystals of the desired species of X-ray quality on evaporation of the diethyl ether at room temperature. mp 98°C. Elemental analysis for C31H35N7Te2: (%): C 36.44; H, 2.18; N, 6.07; found: C 36.32, H 2.03 and N 5.91. FAB-MS: m/z 699 for [M + H]+. 1H NMR (300 MHz, CDCl3, d): 4.73-7.01 (m, 9H, m- and p-Ph), 7.74-7.63 (m, 6H, o-Ph). 13C NMR (75MHz, CDCl3) d: 172.42, 139.23, 129.29, 128.76, 114.23.

10. (a) Tani, H.; Inamasu, T.; Suzuki, H. Heterocycles 1992, 34, 341-347; (b) This complicated procedure involved the reaction of diaryldichalcogenide using sodium metal in THF for reduction to generate arylchalcogenolate anions and required 36h refluxing followed by extraction and purification by column chromatography.

11. Selected bond lengths (Å) and angles (°): N(1)-C(1) 1.334(9), N(2)-C(2) 1.325(8), N(3)-C(3) 1.328(9), N(1)-C(3) 1.338(8), N(2)-C(1) 1.325(9), N(3)-C(3) 1.330(8), Te(1)-C(1) 2.112(6), Te(2)-C(2) 2.111(7), Te(3)-C(3) 2.100(7), C(1)-N(2)-C(2) 115.16(6), C(3)-N(1)-C(1) 112.86(6), C(3)-N(3)-C(2) 114.6(6), N(1)-C(3)-N(3) 126.4(6), N(1)-C(1)-N(2) 126.3(6), N(2)-C(2)-N(3) 124.8(7). Crystallographic data for compound 2 have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 242546. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (+44-1223-336408; e-mail: deposit@ccdc.cam.ac.uk) or www.ccdc.cam.ac.uk).

