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# An efficient synthesis and structural aspects of hexakis (arylseleno)benzenes and hexakis(arylselenomethyl)benzenes

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Respectfully dedicated to Professor Tej Narayan Srivastava, who passed away on 27 December 2003

**Abstract**—An efficient synthesis and structural aspects of a novel class of selenium bearing hexa-hosts by the reaction of hexafluorobenzene or hexakis(bromomethyl) benzene with $RSe^-$ ions is demonstrated. However, under identical reaction conditions, our attempts to prepare tellurium analogues by the reaction of $RTe^-$ (R = Ph or *p*-$CH_3C_6H_4$-) with hexafluorobenzene or hexakis(bromomethyl)benzene to obtain $(RTe)_6C_6$ and $(RTeCH_2)_6C_6$ proved to be difficult.
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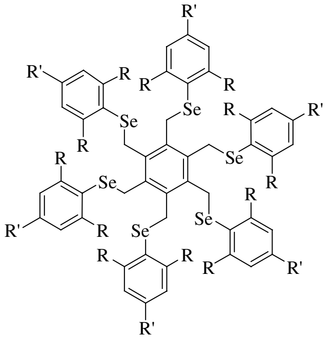
Currently considerable efforts are being devoted to the synthesis of hexasubstituted benzene derivatives with 1,3,5- or 2,4,6-substitution pattern, leading to characteristically preorganized systems and a wide range of inclusion behavior has been established for hexa-host type molecules.[1] Certain structural features present in host compounds, such as size, shape, and the symmetry of the host molecule, can maximize opportunities for inclusion complex formation. Furthermore, the modification of a known host might lead to new hosts with properties significantly different from those of the parent in terms of both cavity size and selective inclusion behavior. In this regard a wide range of hexa-hosts containing either oxygen[2] or sulfur[1,3] have been studied in detail for their multimolecular inclusion behavior. In contrast, comparatively little work has appeared concerning the structurally related selenium analogues.[4,5] For example, the investigations on $(PhSe)_6C_6$, $(PhSeCH_2)_6C_6$, and $(p^tBuC_6H_4SeCH_2)_6C_6$ are limited to their synthesis and the structures of the resulting products remain unexplored despite the fact that these systems might exhibit self-organizing properties and may create useful nonhydrogen-bonded networks through chalcogen···chalcogen interactions.



R' = R = H **1** ; R' = Me, R = H **2** ; R' = OMe, R = H **3** ;
R' = R = Me **4** ; R' = R = $CHMe_2$ **5** ; R' = R = $CMe_3$ **6**

Our curiosity regarding the structures of these hexa-hosts was stimulated by our continuing interest in the search for potential organoselenium or tellurium-containing molecules whereby the chalcogen atoms could play an important role in the design and synthesis of highly diverse spatially arranged single components with a view to creating nonhydrogen-bonded networks. In the present study a new and different strategy is employed for the selenium-containing hexa-hosts, the main objective being the design and synthesis of new hosts with no direct structural relationship to any other host. Sodium areneselenolate ions,[6] can be generated in situ by the reduction of the corresponding diaryldiselenide in aqueous THF with sodium borohydride at 0 °C. A 'problem' we encountered immediately was that $NaBH_4$

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*Keywords*: Selenium; Hexa-host; Inclusion complexes; X-ray structure.

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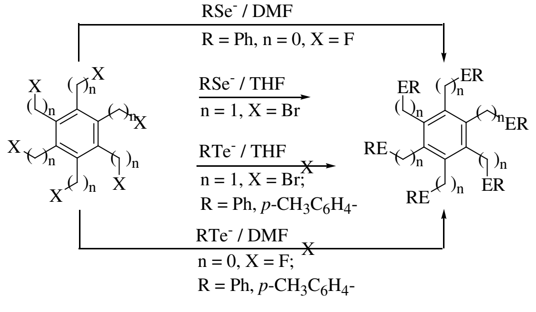
was not very soluble in anhydrous THF. However, the addition of a few drops of water to the anhydrous THF apparently facilitated dissolution (giving clear solutions as observed), and generated the corresponding $ArSe^-$ anion.[7] It reacted cleanly with hexabromomethylbenzene and, after completion of the reaction, the product in solution was recovered by conventional aqueous workup in excellent yields (>90%) and high purity. In particular, compound **2** was easily isolated as white crystals after removal of the solvent.[8] We also attempted the synthesis of hexakis(phenylseleno)benzene [$(PhSe)_6C_6$] **7** via a modified route. The synthesis of the first example of hexakis(phenylseleno)benzene has been reported in the literature; it was prepared by the reaction of PhSeNa with $C_6Cl_6$ in HMPA at ambient temperature for four days, furnishing a 51% yield of hexakis(phenylseleno)benzene.[4] This compound can easily be obtained by the reaction of 1 mol of hexafluorobenzene with 6 mol of the $PhSe^-$ anion generated in situ for a stoichiometric and complete reaction.[9] However, under identical conditions, our attempts to prepare tellurium analogues by the reaction of $RTe^-$ (R=Ph or *p*-$CH_3C_6H_4$-) with hexakis(bromomethyl)benzene and hexafluorobenzene to afford $(RTe)_6C_6$ and $(RTeCH_2)_6C_6$ proved to be difficult and recovery of $R_2Te_2$ from the reaction mixture was the typical outcome (Scheme 1).

Compounds (**1**–**7**) are crystalline in nature and poorly soluble in common organic solvents when freshly prepared and the solubility further decreased after crystallization. They can be crystallized from a solution of benzene or toluene. Physicochemical and spectral studies are in good agreement with the proposed stoichiometry. $^1H$ and $^{13}C$ NMR spectral data showed no unusual features, suggesting in all cases, the equivalence of the $RE^-$ groups as well as the ring carbons indicating symmetrical structures. The electrospray mass spectral (ES-MS) technique was found to be quite helpful in establishing structures on the basis of fragmentations. Although the parent molecular ion peaks were not observed, in each case the loss of one arylseleno group was always observed from the parent ion and the resulting signals were attributable to the consecutive loss of the arylseleno groups as part of their fragmentation pattern.[10] The stepwise fragmentation pattern further confirms the symmetrical nature of the product. Single crystal X-ray diffraction studies of the compound $(PhSeCH_2)_6C_6$ **1** revealed that the molecule crystallizes in a monoclinic, *C*2/*c*, space group.[11] The distribution of the side-chain phenylseleno units of compound **1** was regular as they were arranged alternatively above and below the central benzene ring plane (*ababab* conformation, *a* = above and *b* = below).



**Scheme 1.** Reagents and conditions: E = Se, *n* = 1, R=Ph **1** (90%); *p*-$CH_3C_6H_4$ **2** (92%); MeO–$C_6H_4$ **3** (95%); 2,4,6-$Me_3C_6H_2$ **4** (92%); 2,4,6-$^iPrC_6H_2$ **5** (91%); 2,4,6-$^tBuC_6H_2$ **6** (93%); E = Se, *n* = 0, R=Ph **7** (91%).

In summary, we have demonstrated that multi-selenium aromatic compounds can be synthesized easily. The hexa-host compounds of oxygen and sulfur have been prepared and encouragingly formed a number of inclusion complexes with solvent molecules and are capable of binding metal cations in solution as well. However, we could not find any inclusion phenomenon in our systems. Due to their sterically congested structures, they might be regarded as building blocks for larger π-conjugated systems aiming at star-shaped molecules with new properties. We are currently involved in examining their applications and results will be reported in due course.

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7. On the basis of many experiments, we finally established that the reaction was most satisfactorily run in THF at temperatures around 0 °C with the molar ratios between the reactants ($Ar_2Se_2$:$NaBH_4$:NaOH) being 1:2.2:2.2 in anhydrous THF containing 2% water.
8. To a cooled (0 °C) and stirred solution of ($p$-$CH_3C_6H_4)_2Se_2$ (1.02 g, 3 mmol) and sodium hydroxide (0.25 g, 6.6 mmol) in aqueous THF (20 mL + 0.2 mL $H_2O$) under $N_2$(g), was added $NaBH_4$ (0.419 g, 6.6 mmol) (exothermic) in pinches. The yellow color of the selenol was soon generated and then gradually faded to a colorless solution (usually taking only a few minutes). This was allowed to warm to room temperature over 0.5 h. The clear colorless solution thus formed was treated with hexabromomethylbenzene (0.32 g, 2.2 mmol), which was added as a solid in portions. The reaction mixture was stirred for 6 h at room temperature and was then diluted with aqueous $NH_4Cl$ solution followed by extraction with chloroform (3×25 mL). The combined organic extracts were washed with water and brine and dried over anhydrous $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated to dryness on a rotary evaporator to give **2** as essentially white crystals in >90% yield.
9. To a stirred solution of diphenyldiselenide (0.94 g, 3 mmol) in DMF (10 mL) at 0 °C under an $N_2$ atmosphere was added sodium hydride (60% dispersion in mineral oil, 0.12 g, 3 mmol) in pinches. After the liberation of $H_2$ gas had ceased, the reaction mixture was stirred for an additional 30 min. To this mixture, a solution (0.94 g, 0.5 mmol) of hexafluorobenzene in 5 mL of DMF was added dropwise over 15 min, and the resulting reaction mixture was stirred for an additional 2 h. It was then poured into 100 mL of ice-water, and the white precipitate formed was filtered and dried overnight in air yielding 0.92 g (91%) of the desired compound. Crystallization from chloroform/diethyl ether mixture (50:50) yielded colorless crystals.
10. For compound **2**, $[M-(SeC_6H_4-CH_3\text{-}p)]^+$ [$m/z = 1006.54$ (calcd 1007.68)], $[M-2(SeC_6H_4-CH_3\text{-}p)]^+$ [$m/z = 836.47$ (calcd 838.60)], $[M-3(SeC_6H_4-CH_3\text{-}p)]^+$ [$m/z = 668.38$ (calcd 669.52)], $[M-4(SeC_6H_4-CH_3\text{-}p)]^+$ [$m/z = 498.37$ (calcd 500.44)], $[M-5(SeC_6H_4-CH_3\text{-}p)]^+$ [$m/z = 330.42$ (calcd 331.55)].
11. Diffraction measurements were made on a Siemens smart Apex CCD diffractometer with graphite-monochromated Mo K$\alpha$ ($\lambda = 0.7107$ Å) radiation at room temperature. The crystal structure was solved by direct methods using the SHELXTL package. Semi-empirical absorption correction was applied using the SAD ABS program. All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were located using geometrical constraints. The heaviest atoms were located first and the remaining atoms were deducted from subsequent Fourier difference syntheses. The final cycle of full-matrix least-squares refinement on $F^2$ was based on 4848 observed reflections and 329 variable parameters and converged with unweighted and weighted agreement factors of: $R1 = \Sigma||F_0|-|F_C||/\Sigma$—$|F_0|| = 0.0366$ for $3193 F_0 > 4\text{sig}(F_0)$ and 0.0588 for all 4848 data; $wR2 = [\Sigma(w(F_0^2 - F_C^2)^2)/\Sigma w(F_0^2)^2]^{1/2} = 0.0772$. Compound **1**, colorless cubes (0.50×0.10×0.05 mm) is monoclinic, $C_{48}H_{42}Se_6$, space group $C2/c$, $a$ = 10.7433(11) Å, $b$ = 25.979(3) Å, $c$ = 15.3594(16) Å, $\alpha = 90.00°$, $\beta = 102.271(2)°$, $\gamma = 90.00,°$, $V = 4188.79$ Å.[3]