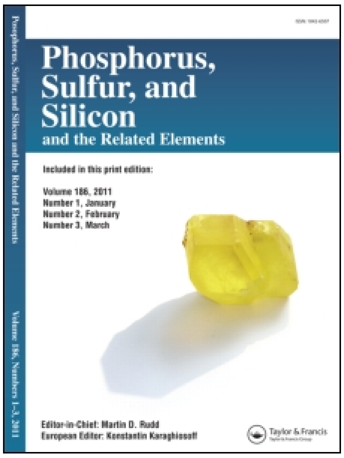

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New Aspects in the Chemistry of Aromatic and Fluoroaromatic Selenium and Tellurium Compounds: Similarities and Diversities

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Polyfluorinated aromatic selenium and tellurium compounds are synthesized and their chemistry and properties discussed. Besides the standard characterization by spectroscopic methods, several crystal structures were obtained. Improved syntheses for the starting materials were presented for the known $(C_6F_5Se)_2$ (**1**), C_6F_5SeCl (**2**), $(C_6F_5)_2Se$ (**3**), $(C_6F_5)_2Te$ (**4a**) and new $(R_F)_2Te$ (**4b-d**, $R_F = 4\text{-}CF_3C_6F_4$, $2,6\text{-}C_6F_2H_3$ and $4'\text{-}(4\text{-}CF_3C_6F_4O)C_6F_4$). Some chemistry of the corresponding Se/Te(IV) derivatives, obtained by oxidation of **3** and **4**, as well as nucleophilic substitution reactions of **2** is described with a particular focus on pseudohalide species. An unusual perfluorophenyl migration is observed for the reaction of diaryltellurium(IV) dihalide (Cl, Br) with cyanide leading to triaryltelluronium chloride/bromide. The synthesis and thorough characterization of the first diaryltellurium(IV) diazides is presented.

Keywords: pentafluorophenylseleneny1 derivatives; diarylselenium/tellurium dihalides; selenium/tellurium azides; ^{77}Se and ^{125}Te NMR; X-ray structure determination

Pentafluorophenyl selenium and tellurium compounds, such as the diselenide **1**, selenenyl chloride **2**, selenide **3** and telluride **4a** have been known for 30 years.[1,2] Different routes to **3** and **4a** as well as improved methods for the preparation of **1**, **2** and **3** were reported more recently.[3,4] We were able to determine the crystal structures of **3**,[4] **4a** (Figure 1) and $(CF_3C_6F_4)_2Te$ (**4b**).

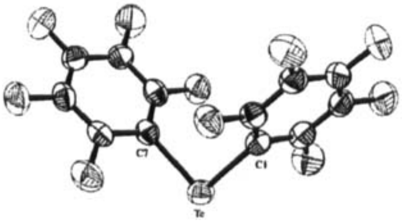
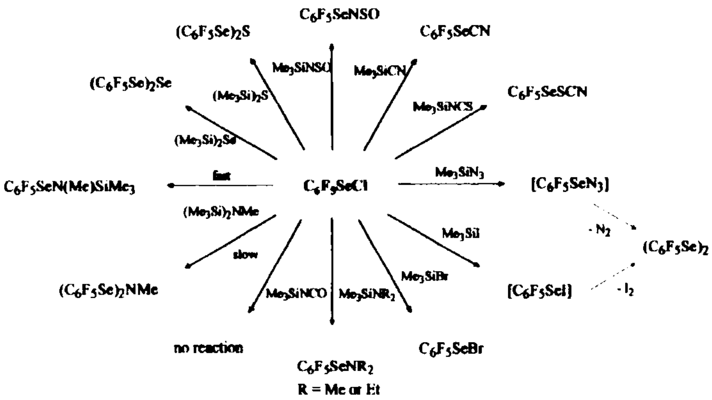


FIGURE 1. Molecular structure of $(C_6F_5)_2Te$ (**4a**)

The following scheme illustrates reactions of **2** with a variety of trimethylsilyl nucleophiles leading to new pentafluorophenylselenenyl derivatives.



In addition to the crystal structure of the selenocyanate C_6F_5SeCN, [4] the structure of the bis(selenenyl) sulfide $(C_6F_5Se)_2S$ was determined (Figure 2).

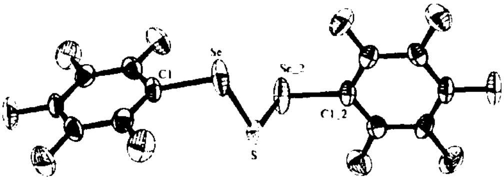


FIGURE 2 Molecular structure of $(C_6F_5Se)_2S$

Oxidation of **3** with 3-chloroperbenzoic acid yields the selenoxide $(C_6F_5)_2SeO$, which was previously reported as a hydrolysis product [5] from the fluorination of **3**. Chlorination in liquid chlorine gives the extremely unstable dichloride $(C_6F_5)_2SeCl_2$, which immediately upon removal of excess chlorine reforms **3**. Evidence for the formation of this dichloride was found by NMR spectroscopy.

The crystal structure of the selenoxide shows interesting SeO interactions leading to hexamers (Figure 3).

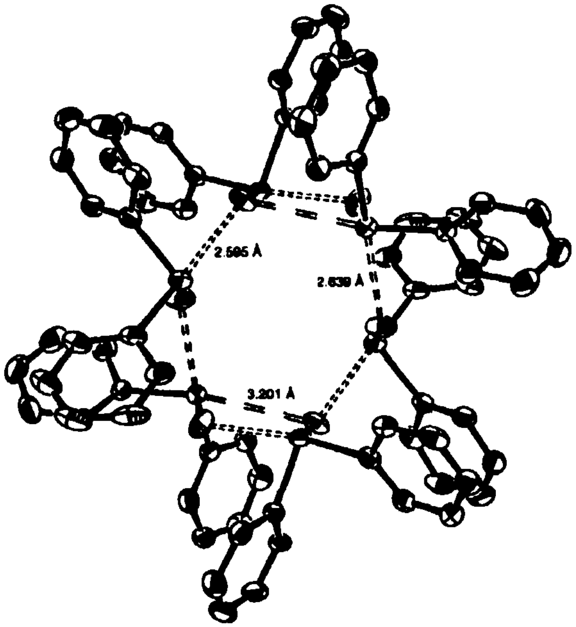


FIGURE 3 Molecular structure of $(C_6F_5)_2SeO$, fluorine atoms omitted for clarity

Oxidation of the tellurides **4a-d** with XeF_2, SO_2Cl_2 and Br_2 gives the corresponding diaryltellurium(IV) difluorides/dichlorides/dibromides in quantitative yields. The crystal structures of the series $(C_6F_2H_3)_2TeX_2$ (X = F (Figure 4), Cl, Br) and of $(CF_3C_6F_4)_2TeF_2$ have been determined in addition to the already reported structures of $(C_6F_5)_2TeX_2$ (X = F, Cl, Br).[6,7]

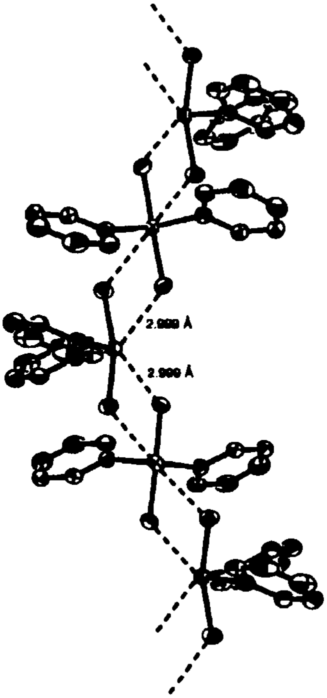


FIGURE 4 Molecular structure of $(C_6F_2H_3)_2TeF_2$ displaying intermolecular TeF interactions (ring hydrogen and fluorine atoms omitted for clarity)

An unusual behaviour is observed in the reaction of diaryltellurium dichlorides and dibromides with cyanide reagents. Treatment with silver cyanide in chloroform or bromoform over prolonged periods (2-20 d) resulted in the migration of an aryl group to a second molecule to give the corresponding telluronium chloride and bromide in reasonable yields. The mechanism for this reaction is not yet understood and the formation of the desired diaryltellurium dicyanide has never been detected. With trimethylsilyl cyanide this reaction is even slower. The exact nature of one of the products was revealed by X-ray crystallography (Figure 5).

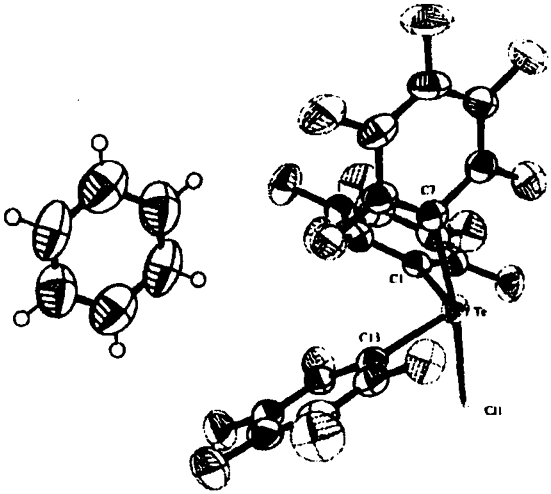
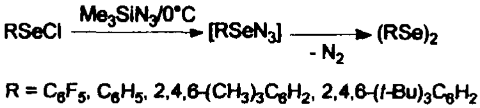


FIGURE 5 Molecular structure of $(C_6F_5)_3TeCl \cdot C_6H_6$

A study of the reactivity of arylselenenyl chlorides towards trimethylsilyl azide revealed the unstable nature of arylselenenyl azides which were detected by NMR spectroscopy at low temperatures. Elimination of nitrogen resulted in the formation of stable diselenides.



$$RSeCl \xrightarrow{Me_3SiN_3/0°C} [RSeN_3] \xrightarrow[- N_2]{} (RSe)_2$$

$R = C_6F_5, C_6H_5, 2,4,6\text{-}(CH_3)_3C_6H_2, 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$

The proposed isolation and spectroscopic data of mesitylselenenyl azide could not be confirmed.[8]

The reaction of $(C_6F_5)_2SeF_2$ with Me_3SiN_3 resulted in immediate (with $(C_6F_5)_2SeO$ slower) reduction to $(C_6F_5)_2Se$ and evolution of nitrogen. However, a different behaviour is observed in the reaction of diaryltellurium(IV) difluorides with Me_3SiN_3. Here the corresponding diazides are formed and isolated at ambient temperature as relatively stable crystalline materials.

$$R_2TeF_2 \xrightarrow{Me_3SiN_3/25^\circ C} R_2Te(N_3)_2$$

$$R = C_6F_5,\ C_6H_5$$

The crystal structures of bis(pentafluorophenyl)tellurium(IV) diazide (Figure 6) and its nonfluorinated analogue (Figures 7) display interesting structural differences in the arrangement of the azide groups relative to the phenyl rings. In the fluorinated tellurium azide the azide groups are bent away from the pentafluorophenyl substituents probably because of steric reasons and electrostatic repulsions between free electron pairs of fluorine and nitrogen. In the nonfluorinated analogue the azide groups are bent towards the phenyl substituents.

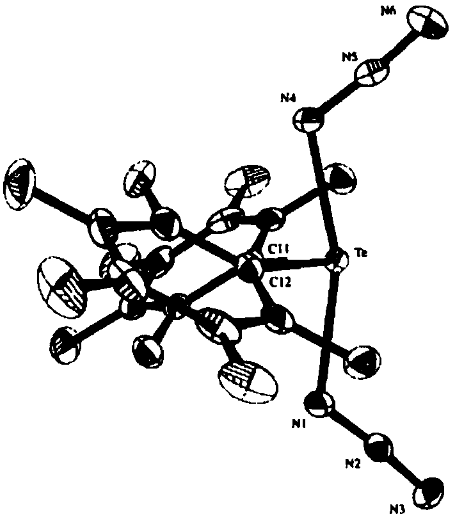


FIGURE 6 Molecular structure of $(C_6F_5)_2Te(N_3)_2$

Both compounds exhibit intermolecular TeN interactions in the range of 3.1-3.5 Å which are shorter than the sum of their van der Waals radii (3.70 Å). Whereas for $(C_6F_5)_2Te(N_3)_2$ coordination of one N_γ nitrogen to two tellurium atoms occurred, for $(C_6H_5)_2Te(N_3)_2$ a coordination of one N_α nitrogen to one tellurium atom has been found.

The substituent influence of pentafluorophenyl selenium-tellurium compounds on the chemical shift of the $^{77}Se/^{125}Te$ resonance is displayed in Table 1. A general low field shift is observed when selenium or tellurium is in the oxidation state +IV.

TABLE 1. ^{77}Se and ^{125}Te NMR shifts (25 °C) [ppm] of C_6F_5Se/Te compounds[a]

	^{77}Se	^{125}Te	
C_6F_5SeOOH [b]	1215	1080	$(C_6F_5)_2TeF_2$
$(C_6F_5Se)_2NCH_3$	972	807	$(C_6F_5)_2Te(N_3)_2$
$(C_6F_5)_2SeO$	915	665	$(C_6F_5)_2TeCl_2$
$C_6F_5SeN_3$ [c]	911	626	$(C_6F_5)_2TeBr_2$
C_6F_5SeNSO	830	390	$(C_6F_5)_3TeBr$
C_6F_5SeCl	801	384	$(C_6F_5)_3TeCl$
$C_6F_5SeN(CH_3)_2$	768	307	$(C_6F_5Te)_2$
$(C_6F_5)_2SeF_2$ [b]	694	296	$(C_6F_5)_2Te$
$C_6F_5SeN(CH_3)SiMe_3$	679		
$C_6F_5SeN(CH_2CH_3)_2$	633		
C_6F_5SeBr	619		
$(C_6F_5Se)_2S$	510		
C_6F_5SeSCN	482		
$(C_6F_5Se)_2Se$	421*		
$(C_6F_5Se)_2$	373		
C_6F_5SeCN	184		
$(C_6F_5)_2Se$	122		
$(C_6F_5Se)_2Hg$ [d]	55		
$C_6F_5SeSiMe_3$	–60		

[a] $CDCl_3$. [b] CD_3CN. [c] not isolated, 0 °C. [d] C_6D_6. * SeSeSe $\delta = 815$

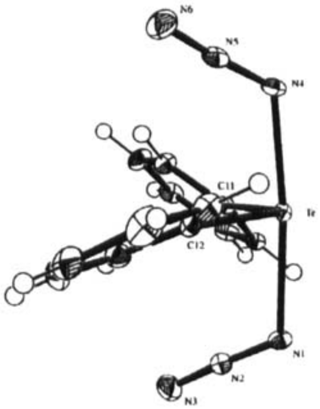


FIGURE 7 Molecular structure of $(C_6H_5)_2Te(N_3)_2$

ACKNOWLEDGMENTS

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