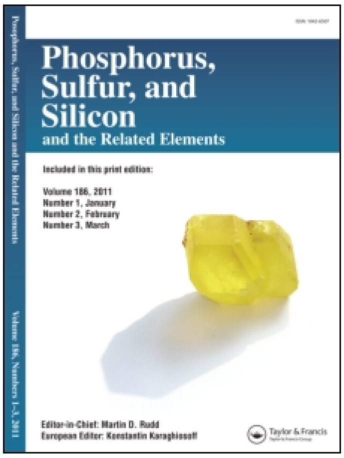

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The Reaction of Organo-Selenium and -Tellurium Compounds with Dihalogens, Interhalogens, and Pseudohalogens

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The Reaction of Organo-Selenium and -Tellurium Compounds with Dihalogens, Interhalogens, and Pseudohalogens

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Adducts of selenium and tellurium donor molecules with dihalogens, interhalogens, and pseudohalogens exhibit a remarkable structural diversity. Some interesting examples of these materials and key factors influencing their formation, structures, and bonding are discussed.

Keywords Charge-transfer; dihalogen complexes; selenium; tellurium

INTRODUCTION

The extremely varied solid-state structures of adducts of Group 16 donors with dihalogen and interhalogen acceptors have only recently been elucidated.[1,2] The donor atom (Se, Te), organic substituents, reaction stoichiometry, and in some cases, the solvent permittivity can influence the solid-state structure of the adduct. An overview of the common adduct types, and some recent advances in this area, are given here.

CHARGE-TRANSFER (CT) COMPLEXES

Adducts formed between a donor and (usually) I_2, IBr, or ICl extreme lengthening of the I—X bond may occur. There is a *grey area* in which it

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Dedicated to the late Prof. C. A. McAuliffe (1941–2002).

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is difficult to categorise the adduct as CT, ionic with cation-anion interactions, or possessing 3c-4e bonds. For example, we describe Me_2SeI_2 as a CT species [d(I—I) = 2.916 (3) Å],[1] but du Mont, on the basis of d (Se—I) [2.768 (3) Å] invokes a 3c–4e or "triiodide" model.[2]

SEE-SAW ADDUCTS

Formed *via* reacting R_2E with X_2 (X = Cl, Br, I). In some cases secondary bonding as observed for Me_2SeCl_2,[1] distorts the geometry at selenium towards octahedral.

POLYIODIDE AND *EXTENDED SPOKE* STRUCTURES

The *extended spoke* structures of mbts.$2I_2$ and mbts.2IBr (mbts = *N*-methylbenzothiazole-2-selone) are surprisingly different.[1] The former is interpreted by Devillanova as $[RSe—I]^+$ interacting with I^-, which, in turn, interacts with I_2, whereas in mbts.2IBr an essentially covalent Se—I bond interacts with $IBr_2{}^-$.

T-SHAPED ADDUCTS

e.g. $(Me_2N)_3PSeBr_2$[3] and mbts.Br_2,[1] rarer for I_2/IBr acceptors. 1,2-bis-(3-methyl-imidazolin-2-ylium iodobromoselenamide) ethane[3] contains both ionic $[C—SeI]^+\cdots Br^-$ and covalent I—Se—Br structural motifs in two independent molecules within the same asymmetric unit.

"TRUE" COVALENT S—I BONDS

Unperturbed covalent Se—I bonds, such as in 2,4,6-*tris*(tert-butyl)-phenyl(iodo)selenide,[4] are rare. $(Ph_2Se_2I_2)_2$,[1] prepared from Ph_2Se_2/I_2 is a centrosymmetric dimer with one selenium atom of each diselenide acting as a donor towards I_2 with the other atom acting as a very weak acceptor. Changing the chalcogen produces another isomeric form of the *PhEI* moiety. The Ph_2Te_2/I_2 reaction produces *square* $Ph_4Te_4I_4$, which exhibits long Te—Te bonds [3.125 (2)–3.175 (2) Å] *c.f.* 2.705 (1) Å for Ph_2Te_2. $I\cdots I$ contacts create an extended structure.

NEW ADDUCT MOTIFS

$PhSeX_3$ (X = Cl, Br)

Ph_2Se_2 reacts with SO_2Cl_2 or Br_2 to give $PhSeX_3$. In $PhSeBr_3$, molecules are linked through a long Br—Br bond [3.0046 (12) Å]. Notably, this structure illustrates molecular square-based pyramidal geometry at Se, a charge-transfer interaction, and discrete Br^- anions in the lattice. Dibromine bond fission has occurred, which adds Br(1) and Br(4) across the selenium atom. In addition a Br—Br bond is retained in the structure despite being lengthened. The terminal bromine in this CT arrangement bridges to a bromine in an adjacent molecule, giving a polymeric array. $PhSeCl_3$ exhibits a polymeric structure where molecules are linked *via* bridging chlorine atoms with square based pyramidal geometry at Se *c.f.* $PhTeX_3$ (X = Cl, Br).[5]

$Ph_4Se_4X_4$ (X = Cl, Br)

Prepared from Ph_2Se_2/X_2, $Ph_4Se_4X_4$ are isostructural with $Ph_4Te_4I_4$. In $Ph_4Se_4Br_4$ (Figure 1) the Se_4 unit forms *via* weak Se—Se bonds [3.004 (2)–3.051 (2) Å], *c.f.* 2.287 (2) Å in Ph_2Se_2. These squares are further linked by long Br$\cdots$Br contacts [3.693 (2)–3.798 (2) Å], just within the van der Waals radius for two bromine atoms (3.9 Å), giving a network of Se_4 and Br_4 squares.

$R_3PSe(R)X$ (X = Br, I)

In common with $Ph_2Se_2I_2$, $Ph_4Se_4Br_4$ acts a source of *PhSeX*. We described the first example of an noninternally chelating RSeI coordination with a donor, $Ph_3PSe(Ph)I$, as a CT adduct containing PhSe,$^{-1}$ based on the geometry at selenium and the great similarity with Ph_3PI_2,[1] long considered a CT compound. Support for our hypothesis was provided by $(Me_2N)_3PSe(Ph)I$, in which P—Se—I = 114.5 (2)°, with a long Se—I contact, 3.825 (1) Å.

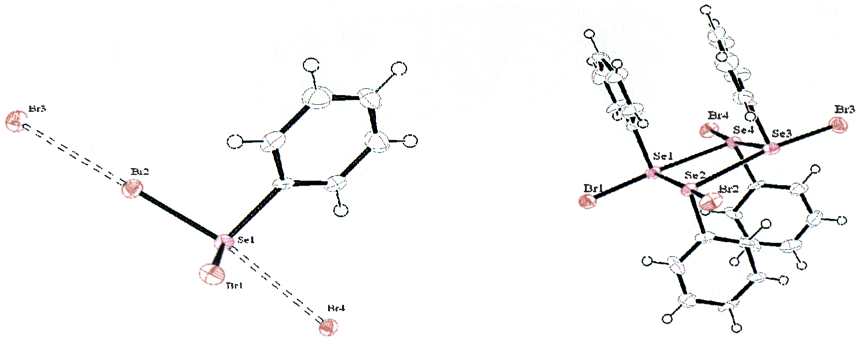

FIGURE 1

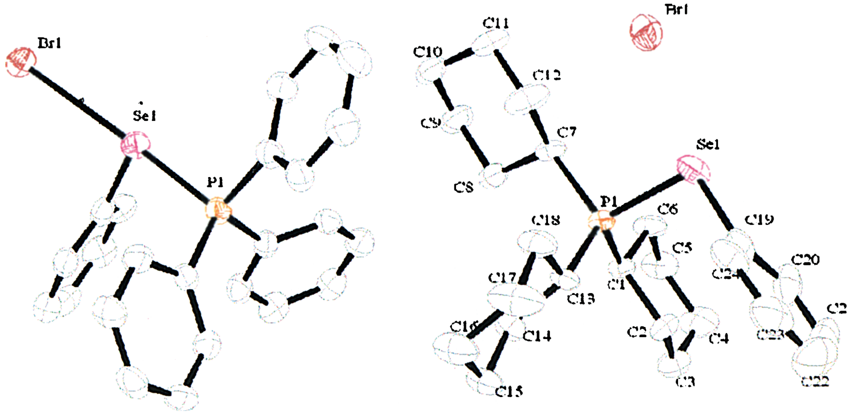

FIGURE 2 Structure of R_3 PSe(Ph)Br.

$Ph_4Se_4Br_4/PR_3$ Systems

$Ph_3PSe(Ph)Br$ (Figure 2) and $Me_3PSe(Ph)Br$ have a distorted T-shaped geometry at Se and an essentially linear P—Se—Br bond. $Cy_3PSe(Ph)Br$ has an ionic structure with negligible cation-anion contacts, a short P—Se bond and a bent geometry at Se.

$Me_3PSe(Ph)I.CH_2Cl_2$ *vs* $Me_3PSe(Ph)Br$

Se—X contact is much longer for iodide compared to bromide. In $Me_3PSe(Ph)I$, phosphorus is *cis* to iodine, but *trans* to bromine in $Me_3PSe(Ph)Br$. The situation is complicated by the CH_2Cl_2 molecule, which significantly interacts with the selenium center in $Me_3PSe(Ph)I.CH_2Cl_2$.

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