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Cristian G. Hrib^a; Wolf- W. du Mont^a; Jörg Jeske^a

^a Institut fuer Anorganische und Analytische Chemie, Technische Universitaet Braunschweig, Braunschweig, Germany

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Phosphine Selenide Arenetellenyliodide Complexes and Telluroselenophosphonium Salts

Cristian G. Hrib, Wolf-W. du Mont, and Jörg Jeske

Institut fuer Anorganische und Analytische Chemie, Technische
Universitaet Braunschweig, Braunschweig, Germany

Trialkylphosphine selenides $t\text{Bu}_n\text{iPr}_{3-n}\text{PSe}$ ($n = 3, 2, 1, 0$) and bidentate phosphine selenides (dppmSe_2 , dppeSe_2) react with arenetellurenyl iodides (RTeI) furnishing complexes $t\text{Bu}_n\text{iPr}_{3-n}\text{PSeTe(R)I}$ ($\text{R} = p\text{-tolyl}$, $p\text{-anisyl}$, mesityl [Mes]), $\text{dppm}[\text{SeTe(Mes)I}]_2$ and $\text{dppe}[\text{SeTe(Mes)I}]_2$ that contain Se-Te(R)-I moieties (10-Te-3). $\text{Dppe}[\text{SeTe(Mes)I}]_2$ exhibits supramolecular soft-soft interactions by “T-stacking” of the Se-Te(R)-I functions in the solid. When trialkylphosphine selenides $t\text{Bu}_n\text{iPr}_{3-n}\text{PSe}$ react with two equivalents of RTeI , novel trialkyl(aryltelluroseleno)phosphonium diiodotellurate(II) salts are formed. In solid $[(t\text{Bu}_2\text{iPrPSeTe-}p\text{-Tol})^+(p\text{-TolTeI}_2)^-]$ the Te atom from the $(p\text{-TolTeI}_2)^-$ anion behaves as soft donor towards the formally uncharged Te atom in the cation $(t\text{Bu}_2\text{iPrPSeTe-}p\text{-Tol})^+$ exhibiting a novel type of $\text{Te}\cdots\text{Te}$ anion→cation donor-acceptor interaction ($\text{Te}\cdots\text{Te}$ 318 pm). Loss of mesityl groups in course of reactions with MesTeI led to a unique iodotelluroselenophosphonium salt $\{[(\text{iPr}_3\text{PSeTeI})^+]_2(\text{TeI}_6)^{2-}\}$ with chelating cation-anion $\text{Te}^{\text{II}}\cdots\text{I-Te}^{\text{IV}}$ contacts, to the six-membered chelate complex $\text{dppmSe}_2\text{TeI}_2$ with a square planar $\text{cis-Se}_2\text{TeI}_2$ group, and to $\text{dppeSe}_2\text{TeI}_2$ with $\text{trans-Se}_2\text{TeI}_2$ groups in a helical chain structure.

Keywords Cation-anion interactions; donor-acceptor complexes; phosphonium salts; soft-soft interactions; supramolecular structures; tellurium iodides

INTRODUCTION

Reactions of phosphine selenides (R_3PSe) with iodine lead to 1:1 adducts, that crystallize, depending on their substitution pattern, as molecular species ($\text{R}_3\text{PSe-I-I}$) or as ionic compounds $[(\text{R}_3\text{PSe})_2\text{I}^+]\text{I}_3^{1-4-}$; with excess of iodine, iodoselenophosphonium salts $[\text{R}_3\text{PSeI}^+]\text{I}_x^-$ can be generated.^{4a,b} Our study on R_3PSe arenetellurenyl iodide (RTeI) complexes was stimulated by current work on R_3PSe adducts

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Address correspondence to Wolf-W. du Mont, Institut fuer Anorganische und Analytische Chemie, Technische Universitaet Braunschweig, Hagenring 30, 38106 Braunschweig, Germany. E-mail: w.du-mont@tu-bs.de

with bromine and iodine that exhibit remarkable supramolecular soft-soft networks in the solid state.^{4b-6} Our observation, that chelate ligands dppmSe_2 [bis(diphenylphosphino)methane-diselenide] and dppeSe_2 [bis(diphenylphosphino)ethane-diselenide] gave unsoluble adducts with Br_2 and I_2 , and that crystal structures could not be determined, led us to consider RTeI as iodine-related electrophiles. Aryl groups should help to control solubilities of the adducts and ^{125}Te -NMR should be a useful probe in solution. R_3PSe complexes of an arenetellurenyl chloride and a related bromide have been characterized earlier, but any NMR spectra of such complexes have not appeared in literature.⁷

REACTIONS

Reactions of ligands $t\text{Bu}_n i\text{Pr}_{3-n}\text{PSeTe}$ with RTeI ($\text{R} = p\text{-tolyl}$, $p\text{-anisyl}$, mesityl [Mes]) lead to monomeric complexes $t\text{Bu}_n i\text{Pr}_{3-n}\text{PSeTe}(\text{R})\text{I}$. With excess of RTeI , abstraction of an iodide anion from the 1:1 complexes occurs and aryltelluroselenophosphonium aryldiiodotellurate(II) salts are formed.⁸ The structure shown in Figure 1a exhibits a unique kind of $\text{Te} \cdots \text{Te}$ interaction (318 pm) between two-coordinated (8-Te-2) and T-shaped (10-Te-3) atoms. Thermal decomposition of a 1:2 product with loss of a mesityl (2,4,6-trimethylphenyl) substituent furnished the crystalline compound $(i\text{Pr}_3\text{PSeTeI})_2\text{TeI}_6$ in which two of the unusual cations $(i\text{Pr}_3\text{PSeTeI})^+$ are stabilized through iodine-bridging soft-soft interactions with a distorted TeI_6^{2-} anion (Figure 1b).

In solid $\text{dppeSe}_2[\text{Te}(\text{I})\text{Mes}]_2$ the bidentate phosphine selenide ligand dppeSe_2 is bridging two T-shaped $\text{SeTe}(\text{I})\text{Mes}$ moieties (Figure 2) in a centrosymmetric binuclear complex. The molecules are packed in a way that allows side-on intermolecular soft-soft interactions in pairs of approximately linear Se-Te-I units, thus linking the molecules to

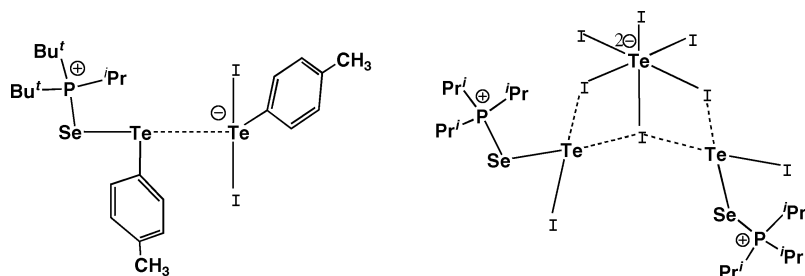


FIGURE 1 a, b: Cation-anion interactions in (telluroseleno)phosphonium salts.

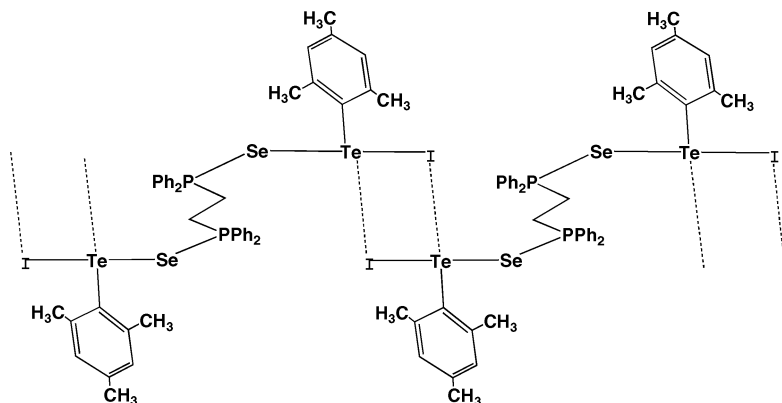


FIGURE 2 T-stacking in $\text{dppeSe}_2(\text{MesTeI})_2$.

chain-like supramolecular arrays. The “T-T” $\text{Te} \cdots \text{I}$ distances (399 pm) are in the order of the sum of van der Waals radii.

From bidentate phosphine selenides dppmSe_2 and dppeSe_2 two different kinds of 1:1 complexes with tellurium diiodide were also isolated: $\text{dppmSe}_2\text{TeI}_2$ is a molecular six-membered chelate complex (12-Te-4) (Figure 3a) that exhibits intermolecular $\text{Se} \cdots \text{I}$ and $\text{Se} \cdots \text{Se}$ contacts (Figure 3b), whereas $\text{dppeSe}_2\text{TeI}_2$ crystallises as helical coordination polymer containing bridging dppmSe_2 ligands between *trans*- TeI_2 moieties.⁹

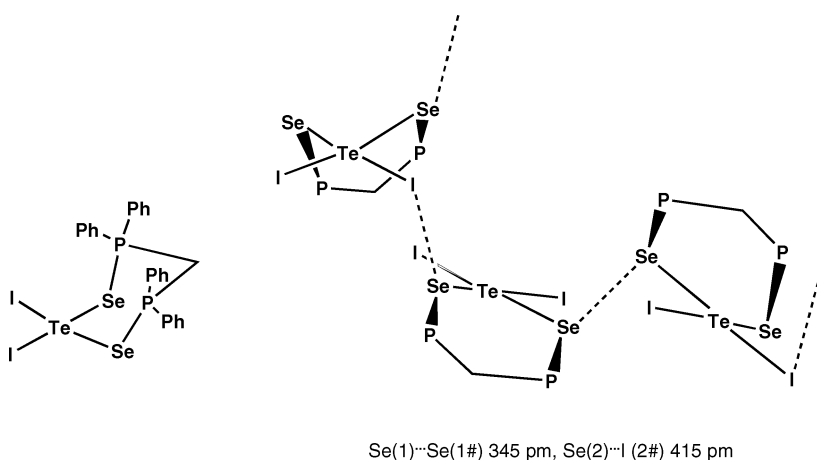


FIGURE 3 (a) Molecular structure of $\text{dppmSe}_2\text{TeI}_2$; and (b) weak intermolecular $\text{Se} \cdots \text{I}$ and $\text{Se} \cdots \text{Se}$ contacts.

NMR-Spectra

Mixtures of R_3PSe with $R_3PSe-Te(R)I$ or of $R_3PSe-Te(R)I$ with $[R_3PSeTe(R)]^+$ exhibit averaged ^{31}P - and ^{77}Se -NMR signals, i.e., that stable complexes $R_3PSe-RTeI$ and cations $[R_3PSeTe(R)]^+$ behave kinetically labile with respect of R_3PSe ligand exchange.^{8,9} $^1J(^{77}Se, ^{31}P)$ decreases and ^{77}Se -NMR doublets are shifted to higher frequency (down-field) in the range



CONCLUSIONS

Structures data of mono- and bidentate phosphine selenide tellurenyl iodide complexes have been determined. Excess tellurenyl iodide acts as iodide scavenger leading to aryltelluroselenophosphonium aryldiiodotellurate(II) salts. Side reactions with loss of mesityl groups led to phosphine selenide telluriumdiiodide complexes and to a very particular iodotelluroselenophosphonium salt. ^{31}P , ^{77}Se and ^{125}Te NMR spectra reveal, that stable complexes $R_3PSe-Te(R)I$ and cations $[R_3PSeTe(R)]^+$ behave kinetically labile with respect of R_3PSe ligand exchange.

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