Chlorination of Phosphane Selenides

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Dedicated to Professor Martin Jansen on the Occasion of His 70th Birthday

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Abstract. Chlorination of the phosphane selenide $iPrtBu_2PSe$ with PhICl₂ leads to the compound $iPrtBu_2PSe_2Cl_2$, which contains a P–Se–SeCl₂ moiety and is formally a phosphane selenide complex of selenium dichloride. Two polymorphs of the product were identified

Introduction

Phosphane chalcogenides $R_3P=E$ (E = S, Se) are known to form adducts with dihalogen molecules.^[1,2] [N.B. For brevity we denote phosphanes by the general formula R_3P , even if the R groups are not identical]. A considerable number of 1:1 adducts of phosphane selenides have been isolated because of their stronger donor abilities. These adducts can have various forms (Scheme 1), such as a molecular (**A** and **B**) or an ionic form (**C** and **D**).^[3] For phosphane sulfides only a few examples of adducts with iodine exist in the literature (form **A**).^[1,4]



Scheme 1. Various forms of halogen adducts of phosphane selenides. $(X = Br \text{ or } I; I_x^- = various polyiodides).^{[5]}$

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by X-ray structure analysis. The analogous reaction with tBu_3PSe gave an oil, presumably $tBu_3PSe_2Cl_2$, from which small quantities of $tBu_3PSe_3Cl_2$ were obtained and characterized by X-ray structure analysis.

Although we have not investigated phosphane tellurides here, it should also be pointed out that halogen adducts of triethylphosphane telluride, Et_3PTeX_2 , have been isolated and structurally characterized for X = Cl, Br, and I; they exhibit the structure type **B** and are linked into dimers by Te···X contacts.^[6]

Recently we reported the first synthesis of R_3PEX^+ cations (E = S, Se; X = Cl, Br) as their Au X_4^- salts, through oxidation of the corresponding gold(I) complexes with iodobenzene dichloride or elemental bromine.^[7] The chlorine derivatives represent the first examples of compounds with a stable P–*E*–Cl unit. As a logical consequence of this work we have now focussed on the direct chlorination of phosphane chalcogenides to form chlorine adducts.

Results and Discussion

Reacting iodobenzene dichloride with phosphane sulfides in a 1:1 ratio leads to decomposition of the starting material and the formation of R_3PCl_2 and separation of elemental sulfur; the ³¹P NMR spectra show only the signal for R_3 PCl₂,^[8] between δ = 120 and 130 ppm for the bulky aliphatic R groups employed herein.^[9] Even with three sterically demanding tert-butyl groups the decomposition upon chlorination is rapid. This shows the strong tendency of chlorine to attack directly at the more electropositive phosphorus atom. In case of the selenides a second product 1, R₃PSe-SeCl₂, is formed (Scheme 2), whose stability depends on the nature of the R groups at the phosphorus atom. For 1a the starting material decomposes upon chlorination and the ³¹P NMR spectrum shows only a singlet at $\delta = 65.9$ ppm for Ph₃PCl₂. Compound **1b** decomposes slowly in solution and upon crystallization, but its ³¹P NMR signal at $\delta = 86.5$ ppm can be observed. In case of 1c the compound is stable and can be crystallized from dichloromethane/pentane. The product 1d is also stable, but is formed as orange oil. After a few weeks red single crystals of com-

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pound 2 (R_3 PSe–Se–SeCl₂, see below) formed in the oil and their crystal structure was determined. However, dissolving the crystals for ³¹P NMR investigations led to decomposition.

$$2 \operatorname{R}' \xrightarrow{P} \operatorname{Se} \frac{2 \operatorname{PhlCl}_2}{\operatorname{CH}_2 \operatorname{Cl}_2} \xrightarrow{R' \xrightarrow{P} \operatorname{Se} \cdot \operatorname{Se} \cdot \operatorname{I}} \xrightarrow{R' \xrightarrow{P} \operatorname{Se} \cdot \operatorname{Se} \cdot \operatorname{I}} \xrightarrow{R' \xrightarrow{P} \operatorname{Cl}} \xrightarrow{R' \xrightarrow{P} \operatorname{Cl}} \xrightarrow{R' \xrightarrow{P} \operatorname{Se} \cdot \operatorname{Se} \cdot \operatorname{I}} \xrightarrow{R' \xrightarrow{P} \operatorname{Cl}} \xrightarrow{Ia \cdot d} \xrightarrow{Ia \cdot d} \xrightarrow{Ia \cdot R} \xrightarrow{Ia$$

Scheme 2. Chlorination of phosphane selenides.

The products 1 are to the best of our knowledge the first neutral molecules containing the linkage -Se-SeCl₂ and may be regarded as adducts LSeCl₂ between SeCl₂ and phosphane selenide ligands L. Such compounds are already known for L = tetramethylthiourea,^[10] for which LSeCl₂ was synthesized directly from $SeCl_2$, and for L = dimethylsulfide^[11] or various N-heterocyclic carbenes,^[12] for which the adducts were synthesized via reductive processes from SeCl₄. We tried to reproduce the synthesis of 1c using two different approaches. In the first, we treated elemental selenium with PhICl₂ and then added *i*PrtBu₂PSe. The mixture was stirred for 10 min, but the ³¹P NMR spectrum showed mostly a signal for the decomposition product and only traces of **1c**. In the second approach^[10] we used in situ generated SeCl₂ and added the phosphane selenide. Soon after adding the phosphane selenide, the formation of red selenium was observed and the ³¹P NMR spectrum showed only the signal for R_3PCl_2 .

Two polymorphs of **1c** were obtained. The first crystallizes in the triclinic space group $P\overline{1}$ with two molecules in the asymmetric unit (Figure 1). The second polymorph (**1c**') crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 2). In both cases the arrangement around the selenium atom bonded directly to the phosphorus atom is bent, with an approximately tetrahedral angle, and at



Figure 1. Asymmetric unit of **1c** (hydrogen atoms omitted). Ellipsoids in all diagrams correspond to 50% probability levels. Selected molecular dimensions /Å,°: Se2–P1 2.2563(6), Se2–Se1 2.3257(3), Se1–Cl1 2.4695(7), Se1–Cl2 2.4002(7), Se4–P2 2.2616(6), Se4–Se3 2.3207(3), Se3–Cl3 2.4569(6), Se3–Cl4 2.4254(6); Cl1–Se1–Cl2 169.01(2), Cl3–Se3–Cl4 167.00(2), P1–Se2–Se1–Cl1 –78.04(2), P1–Se2–Se1–Cl2 105.14(2), P2–Se4–Se3–Cl3 93.99(2), P1–Se4–Se3–Cl4 –91.31(2).



the second selenium atom T-shaped. The associated bond lengths and angles (see Figure captions) may be regarded as "normal", although Se-Se and Se-Cl bond lengths are very variable depending on coordination number and the formation of short contacts leading to polymeric materials.^[13] The P-Se bonds, 2.25-2.26 Å, are appreciably lengthened in comparison to isolated phosphane selenides (database average value 2.110 Å) and may be compared with 2.27–2.28 Å in a cationic P⁺–Se–Se–P⁺ system^[14] and 2.25 Å in cations R₃PSeCl⁺.^[7b] The three molecules of 1c/1c' are similar except for some differences in Se-Cl bond lengths and, particularly, the P-Se-Se-Cl torsion angles for 1c, which differ by ca. 15°. The alkyl groups are arranged such that the *iso* propyl groups make an absolute C-P-Se-Se torsion angle of ca. 50°, whereas one tertbutyl group is antiperiplanar across the same bond. A leastsquares fit for the two molecules of 1c gives a root-meansquare deviation of 0.13 Å omitting the chlorine atoms, while a similar fit of 1c' to molecule 2 of 1c gives an r.m.s.d. of 0.20 Å including the chlorine atoms.



Figure 2. Asymmetric unit of **1c**' (hydrogen atoms omitted). Selected molecular dimensions /Å,°: Se2–P1 2.2607(3), Se2–Se1 2.32079(16), Se1–Cl1 2.4494(3), Se1–Cl2 2.4297(3); Cl1–Se1–Cl2 164.990(12), P1–Se2–Se1–Cl1 –86.01(1), P1–Se2–Se1–Cl2 95.68(1).

The SeCl₂ adducts of tetramethylthiourea^[10] and dimethyl sulfide^[11] display packing patterns that are characterized by short Se···Cl contacts of 3.276 Å, forming dimers, and 3.085 Å, forming chains, respectively. All contacts between the heavier atoms of **1c** and **1c**' are appreciably longer than this; there are also a considerable number of H···X contacts (X = Cl, Se), the shortest being around 2.8 Å, that might be regarded as "weak" hydrogen bonds. The packing of **1c** shows contacts between two selenium atoms (molecule 1), which leads in both cases to the formation of dimers (Figure 3, Figure 4). In the packing of **1c**' the molecules form chains through one selenium-chlorine contact and one H···Cl hydrogen bond (Figure 5).

The crystal structure of **2** reveals the newly formed PSeSe-SeCl₂ unit, which must have arisen following a slow decomposition of **1d**. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 6). The arrangement at the two two-coordinate selenium atoms is bent and at the third selenium atom T-shaped. Bond lengths and angles are broadly similar to those of **1c/1c'**; the



Figure 3. Dimers in 1c, molecule 1 (hydrogen atoms omitted). Selected contact distances /Å and angles /°: Se2···Se2A 3.5470(4), Se2···Se1A 3.8740(3); P1–Se2···Se2A 150.00(2), Se1–Se2···Se2A (76.82(1).



Figure 4. Dimers in 1c, molecule 2 (hydrogen atoms omitted). Selected contact distances /Å and angles /°: Se4---Se4A 3.5470(4), Se4---Cl3A 3.6184(6); Se4A---Se4---Cl3A 58.57(1).



Figure 5. Chains in **1c**' (hydrogen atoms omitted). Selected contact distances /Å and angle /°: Se2···Cl1 3.6102(3), H31A···Cl2 2.78; C31–H31A···Cl2 175.9.



Figure 6. Crystal structure of **2** (hydrogen atoms omitted). Selected molecular dimensions /Å,°: Se3–P1 2.2453(6), Se3–Se2 2.3581(3), Se2–Se1 2.3132(3), Se1–Cl1 2.4708(6), Se1–Cl2 2.4168(6); Cl1–Se1–Cl2 174.29(2), P1–Se3–Se2–Se1 114.24(2), Se3–Se2–Se1–Cl1 59.39(2), Se3–Se2–Se1–Cl2 –118.19(1).

(P)Se–Se bond is significantly longer than Se–Se(Cl). The packing involves the formation of dimers via a selenium-chlorine contact (Figure 7).



Figure 7. Dimers in **2** (hydrogen atoms omitted). Selected contact distance /Å and angle /°: Se2···Cl2A 3.3451(6); Se1–Se2···Cl2A 116.58(1).

Conclusions

Direct halogenation of phosphane sulfides with the chlorinating agent PhICl₂ is not possible because of the strong tendency of chlorine to attack at the electropositive phosphorus atom. However, in the case of the selenides some unexpected adducts $R_3PSe_nCl_2$ (n = 2, 3) are formed.

Experimental Section

Materials and Measurements: All chemical reagents were commercially available. Solvents were dried and distilled in a nitrogen atmosphere prior to use: dichloromethane (P₄O₁₀), pentane and diethyl ether (SPS-Machine from MBraun). CHN elemental analyses were carried out with an Elementar Vario MICRO (Germany) elemental analyzer. ¹H NMR and ³¹P NMR spectra were recorded at room temperature with a Bruker DPX-200 spectrometer.

General Procedure: All reactions were carried out at room temperature in a nitrogen atmosphere. To a solution of the phosphane chalcogenide in dichloromethane, PhICl₂ was added in a 1:1 ratio and the mixture was stirred for 30 min at room temperature. The solvent was evaporated in vacuo and the residue analysed by ³¹P NMR spectroscopy. A signal for the R₃PCl₂ usually appeared between 120– 130 ppm (in the case of the triphenyl derivative at $\delta = 65.9$ ppm). Unfortunately only the product **1c** was stable enough to be reproducibly synthesized, whereas **2** was only obtained once as a few single crystals, resulting from decomposition of **1d**.

Synthesis of 1c: To a solution of *i*PrrBu₂PSe (230 mg, 0.9 mmol) in dichloromethane (20 mL), PhICl₂ (237 mg, 0.9 mmol) was added and the reaction mixture was stirred for 30 min. The solvent was evaporated in vacuo and the yellow oily crude product was washed several times with diethyl ether (4×5 mL). 1c was re-crystallized from dichloromethane and pentane, giving a yellow powder (yield: 168 mg, 48%; max. 50% yield is possible because of the stoichiometric P:Se imbalance between starting materials and product). Diffusion of pentane into a dichloromethane solution gave yellow single crystals. ¹H NMR (200 MHz, CDCl₃): $\delta = 4.10-3.86$ (m, 1 H, CHCH₃), 1.71 (d, $J_{PH} = 16.9$ Hz, 18 H, CCH₃), 1.70–1.53 (m, 6 H, CHCH₃). The signal of the

Table 1. Crysta	ıl data and	structure	refinement	for	1c,	1c',	and	2.
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	1c	1c'	2	
Formula	C ₁₁ H ₂₅ Cl ₂ PSe ₂	$C_{11}H_{25}Cl_2PSe_2$	C ₁₂ H ₂₇ Cl ₂ PSe ₃	
Temperature /K	100(2)	100(2)	100(2)	
Wavelength /Å	0.71073	0.71073	0.71073	
Crystal system	triclinic	monoclinic	monoclinic	
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	
Unit cell dimensions				
a /Å	9.4388(3)	8.0234(2)	14.3170(4)	
b /Å	12.7374(4)	16.1806(3)	8.8361(2)	
c /Å	13.9910(5)	12.9830(2)	15.7361(5)	
a /°	81.746(3)	90	90	
β /°	86.117(4)	93.578(2)	107.982(3)	
γ /°	84.547(2)	90	90	
$V/Å^3$	1654.63(9)	1682.23(6)	1893.50(9)	
Z	4	4	4	
Density (calcd.) /Mg·m ⁻³	1.674	1.647	1.789	
Absorption coeff. /mm ⁻¹	4.9	4.8	6.2	
<i>F</i> (000)	832	832	1000	
Crystal size /mm ³	$0.2 \times 0.08 \times 0.02$	$0.18 \times 0.12 \times 0.09$	$0.20 \times 0.18 \times 0.05$	
Theta range /°	2.34 to 30.03	2.52 to 30.90	2.67 to 30.90	
Index range	$-13 \le h \le 13,$	$-11 \le h \le 11,$	$-19 \le h \le 20,$	
	$-17 \le k \le 17,$	$-22 \le k \le 23,$	$-12 \le k \le 12,$	
	$-19 \le l \le 19$	$-18 \le l \le 18$	$-22 \le l \le 22$	
Completeness	98.5% to 60°	96.2% to $2\theta_{\rm max}$	98.9% to 60°	
Data / parameters	9537 / 305	5118 / 153	5665 / 172	
GOOF on F^2	1.03	1.08	1.05	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0286,$	$R_1 = 0.0176,$	$R_1 = 0.0264,$	
	$wR_2 = 0.0597$	$wR_2 = 0.0356$	$wR_2 = 0.0537$	
R indices (all data)	$R_1 = 0.0389,$	$R_1 = 0.0222,$	$R_1 = 0.0375,$	
	$wR_2 = 0.0630$	$wR_2 = 0.0368$	$wR_2 = 0.0572$	
Largest diff. peak, hole /e·Å ⁻³	1.9 and -0.60	0.39 and -0.30	0.65 and -0.64	

one methine proton, split into two septets, was not entirely clear, and there was overlap in the methyl region. ³¹P NMR (81 MHz, CDCl₃): $\delta = 86.4$ (s, ${}^{1}J_{PSe} = 213.2$, ${}^{2}J_{PSe} = 168.5$ Hz). C₁₁H₂₅PSe₂Cl₂: calcd. C 31.67, H 6.04%; found: C 31.63, H 6.00%. Not enough material was obtained for ⁷⁷Se NMR studies. The second polymorph **1c**' was obtained by chance on repeating the synthesis under apparently the same conditions. No attempts were made to isolate a particular polymorph reproducibly, or to investigate thermodynamic relationships between the polymorphs; we note however that **1c**' has a significantly lower calculated density than **1c** and thus may be thermodynamically less stable.

X-ray Structure Determination: Data were collected at 100 K with an Oxford Diffraction Xcalibur E diffractometer using monochromated Mo- K_{α} radiation. Structures were refined using the program SHELXL-97.^[15] The structures were refined anisotropically using full-matrix least-squares on F^2 . Hydrogen atoms were included using idealized rigid methyl groups or a riding model for non-methyl H. Crystallographic data and structure refinement results are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1014066 (1c), CCDC-1014067 (1c'), and CCDC-1014068 (2) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): ³¹P NMR spectra and crystallographic tables.

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conditioned) and their derivatives as, for example, R_3P –E–X–X. The whole concept of double bonds involving elements of the third and higher periods is indeed the subject of much debate. See, for example M. S. Schmøkel, S. Cenedese, J. Overgaard, M. R. V. Jørgensen, Y.-S. Chen, C. Gatti, D. Stalke, B. B. Iversen, *Inorg. Chem.* **2012**, *51*, 8607–8616. We prefer to write the adduct formulae with single bonds (to indicate connectivity) and without explicit formal charges, which might imply a particular bonding pattern that may not be strictly valid.

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