Lewis Acidity of β-Heteroatom-substituted Selenophosphonium Cations: Properties of Reaction Products from Trialkylphosphine Selenides and Dihalogens

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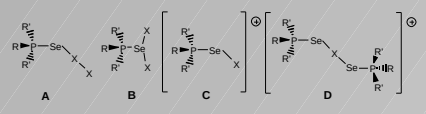
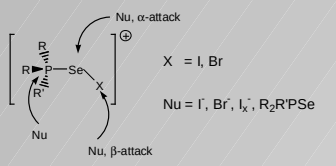
Introduction

Phosphine sulfides and selenides are known to act as donors towards dihalogen molecules X_2.[1-4] From phosphine selenides, which are stronger donors than the sulfides, a considerable number of "1:1 adducts" $R_2R'PSeX_2$ have been isolated.[5-8] *Molecular* structures have recently been determined from $R_2R'PSeI_2$ (type **A**, *Scheme 1*, R, R' = C_6H_5, NMe_2, NEt_2,[6] and R = Bu^t, R'= I [7]) and $R_2R'PSeBr_2$ (type **B**, R, R' = NMe_2, C_6H_{11} [8]). Ionic structures of solid 1:1 adducts of phosphine selenides with iodine do not involve $R_2R'PSeI^+$ cations (type **C**), as postulated earlier,[9] but $(R_2R'PSe)_2I^+$ cations and I_3^- anions (type **D**).[9, 10]



Scheme 1. Structure alternatives of phosphine selenide halogen adducts.

^{31}P- and ^{77}Se-NMR spectra, however, suggest that in solutions of 1:1 adducts equilibrium mixtures of several species are present.[5,9,10] To elucidate the role of solvents, of the size of alkyl substituents attached to phosphorus and to evaluate the role of the acceptor atoms (I, Br) coordinated by selenium, the course of stepwise halogenation of the phosphine selenides were followed by heteroatom NMR spectroscopy.[10] Formally, we regard the reaction products as being derived from hypothetic $[R_2R'P\text{-}Se\text{-}X]^+$ cations by their interactions with soft nucleophiles (Br^-, I^-, I_x^- or $R_2R'PSe$). Soft nucleophiles can approach Se-X bonds by "n→σ*-attack" at two different *Lewis*-acidic sites: Se atoms, in *α-position*, or X atoms, in *β-position* from the phosphonium center.[11]



Scheme 2. Sites of possible attack on $R_2R'PSeX^+$ cations.

Formation of "1:1 adducts"

Adding Br_2 or I_2 stepwise to solutions of phosphine selenides $R_2R'PSe$ (**1a**: R, R' = Bu^t ; **1b**: R, R' = Pr^i; **1c**: R = Bu^t, R' = Pr^i) allows to observe in all ^{31}P-NMR spectra of such solutions only one averaged ^{31}P-NMR signal with a pair of ^{77}Se satellites (*Table 1* and *Table 2*). Crystallisation of products from **1** with Br_2 provides pure solids $R_2R'PSeBr_2$ (**2a-c**; **2b**: *Figure 1*). In each of these compounds, bromine is oxidatively added to selenium, which becomes "hypervalent" (structure type **B**, 10-Se-3).[11]

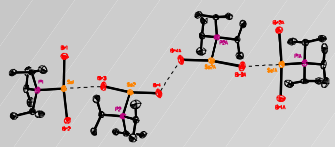


Figure 1. Structure of **2b** $Pr^i_3PSeBr_2$ (H atoms omitted for clarity).

Concerning "1:1 adducts" $R_2R'PSeI_2$, two different types of structures appear to exist in equilibria. From Bu^t_3PSe (**1a**), a crystalline 1:1 product **3a** was isolated, that contains the molecular (**A**) and ionic (**D**) species within the same crystal. From less crowded **1b, c** the ionic compounds **3b, c** (**3b**: *Figure 2*) were isolated as solid products.[11]

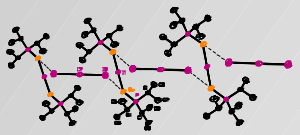


Figure 2. Structure of **3b** $(Pr^i_3PSe)_2I^+$ I_3^- (H atoms omitted for clarity).

Reactions with excess halogen

Starting with ionic **3b** and **3c**, addition of excess iodine led to colored solutions, that exhibited ^{31}P-NMR singlet signals with further decreased NMR coupling constants $^1J(^{77}Se, ^{31}P)$ which are similar to those of the type **B** molecular adducts $R_2R'PSeBr_2$. Crystallisation allowed to isolate solid products $R_2R'PSeI_7$ **7b** and **7c**. **7a** and **7c** are not higher polyiodides of $(R_2R'PSe)_2I^+$ cations, but represent rare examples of $[R_2R'PSeI]^+$ cations (type **C**; **7c**: *Figure 3*).[3,10]

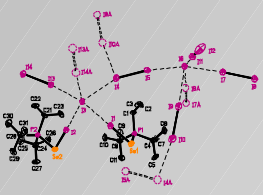


Figure 3. Structure of **7c** $Bu^t_2Pr^iPSeI_7$ (H atoms omitted for clarity).

The high iodine content of $R_2R'PSeI_7$ leads to improved separation of the $[R_2R'P\text{-}Se\text{-}I]^+$ cations of **7b** and **7c** from the anionic polyiodide networks. Addition of molecular bromine to the "1,1 dibromides" **2b, c** led to their complete consumption in favour of unselective formation of new species.

Spectroscopic investigations

Trialkylphosphine selenides ($R_2R'PSe$), like their parent trialkylphosphines ($R_2R'P$), exhibit increasing ^{31}P downfield shift with increasing α-branching of the alkyl groups. As expected, the ^{31}P signal of mixed-substituted new compound **1c** (85.8 ppm) appears downfield from **1b** (72.2 ppm) but upfield from **1a** (94.7 ppm). Stepwise addition of iodine to **1a-c** does not lead to new ^{31}P NMR signals of the reaction products, but the singlet signal is continuously shifted (depending on the amount of iodine) to lower frequencies (*upfield*, up to about 10 ppm, compared with **1a-c**, *Table 1*). After addition of one equivalent of bromine to **1a-c**, however, the position of the ^{31}P NMR singlet stays nearly constant (*Table 2*).

1a: Bu^t_3PSe **1b**: Pr^i_3PSe **1c**: $Bu^t_2Pr^iPSe$	δ ^{31}P [ppm], $^1J(^{77}Se, ^{31}P)$ [Hz] (CH_2Cl_2-C_6D_6, $^*C_6D_6$)	δ ^{31}P [ppm], $^1J(^{77}Se, ^{31}P)$ [Hz] (Toluene-C_6D_6, $^*C_6D_6$)
1a	(99.0, 711)*	(99.0, 711)*
1a + I_2	83.0, 599	-
1a + 1.5 I_2	83.0, 526	-
1b	70.6, 690	69.7, 716
1b + 0.5 I_2	67.2, 616	67.2, 663
1b + 0.75 I_2	66.3, 597	66.8, 659
1b + I_2	65.1, 557	65.3, 619
1b + 2 I_2	66.1, 529	64.6, 585
1b + 3.5 I_2	66.5, 518	-
1b + 5 I_2	67.2, -	65.2, -
1c	83.8, 692	-
1c + 0.5 I_2	80.2, 707	-
1c + I_2	76.8, 547	-
1c + 2 I_2	76.1, 544	-
1c + 3.5 I_2	76.5, 528	-

Table 1. ^{31}P NMR data for reactions of phosphine selenides **1a-c** with I_2.

More indicative for the reaction course of phosphine selenides with electrophiles are coupling constants $^1J(^{77}Se, ^{31}P)$ that can be determined from satellite doublets in the ^{31}P NMR spectra. With increasing amount of the added electrophile they decrease continuously from about 700 ± 15 Hz (in the starting materials) to about *minus 15 – 20%* (solvent-dependent) in the 1:1 products with iodine **3a-c**, and to about *minus 25%* in the 1:1 products with bromine and in the products with large excess of iodine (**7b, c**). Concerning ^{77}Se NMR spectra, a straightforward correlation (like that of δ ^{31}P) between chemical shifts of $R_2R'PSe$ and increasing α-branching of the alkyl groups does not exist.

1a: Bu^t_3PSe **1b**: Pr^i_3PSe **1c**: $Bu^t_2Pr^iPSe$	δ ^{31}P [ppm], $^1J(^{77}Se, ^{31}P)$ [Hz] (CD_2Cl_2, $^*C_6D_6$)	δ ^{77}Se [ppm], $^1J(^{77}Se, ^{31}P)$ [Hz] (CD_2Cl_2, $^*CD_3CN$)
1a	(99.0, 711)*	(-420.8, 490)†
1a + Br_2	83.0, 513	-
1b	70.6, 690	-485.2, 690
1b + Br_2	69.8, 521	-409.0, 521
1b + 5 Br_2	72.7, 499	-
1c	83.8, 692	-399, 692
1c + 0.05 Br_2	83.7, 687	-381, 689
1c + 0.10 Br_2	83.6, 682	-358, - (b, ~700±40)
1c + Br_2	82.9, 520	-

Table 2. ^{31}P and ^{77}Se NMR data for reactions of **1a-c** with Br_2.

Exchanging two Pr^i groups of **1b** against two Bu^t groups (in **1c**), does, however, not lead to a further monochronous increase of δ ^{77}Se. This holds as well for adducts of **1a-c** with electrophiles (for example with bromine: *Table 2*). To approach an understanding of influences on the unexpected variation of magnitudes of δ ^{77}Se in these sterically crowded phosphine chalcogenides, *ab initio* calculations on various conformers of the phosphine selenides **1a, b, c** and **d** were carried out with help from GIAO-SCF/641(d) calculations.[12] Qualitatively, the experimentally observed range of ^{77}Se-NMR shieldings (**1c** < **1a** << **1b** < **1d**) reflects fairly well the calculated shift values of their energetically most favourable rotamers (**1c-1** < **1a** << **1b-1** < **1d-1**; *Figure 4*). **1c**, showing the "abnormally deshielded" ^{77}Se signal (compared with naive expectations from linear interpolation between **1a** and **1b**) is apparently the only compound among the Pr^i derivatives, in which no rotamer with *anti* arrangement of the SePCH moiety (which would be **1c-3**) contributes to the rotamer population averaged ^{77}Se-NMR shift.

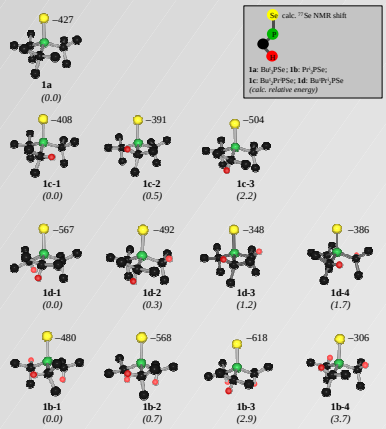


Figure 4. Calculated ^{77}Se NMR shifts for different rotamers of **1a-d**.

On addition of less than 5 mol% of I_2 as electrophile to **1c**, the ^{77}Se NMR doublet broadens and shifts slightly to lower field (from 399 to 397 ppm) and the coupling constant is now about 663 Hz. With 10 mol% of I_2, severe broadening makes the ^{77}Se NMR doublet nearly unresolvable, and with more iodine any ^{77}Se signal cannot be resolved. Similary, with very small amounts of bromine, a ^{77}Se NMR signal can still be resolved at 358 ppm, but due to broadening, the coupling constant cannot be determined accurately. This can be explained by rapid halogen exchange reactions (*^{77}Se NMR time scale*) that do involve Se-X (X = I, Br) bond breaking, but do not involve P-Se bond breaking, because $^1J(^{77}Se, ^{31}P)$ can be observed at all times.[11]

Summary

While ^{31}P NMR shifts of the phosphine selenides **1a-d** can be correlated with α-branching of the alkyl groups at the phosphorous center, there is no such easy relationship concerning the ^{77}Se NMR shifts. The $^{31}P/^{77}Se$ coupling constants of the reaction products/mixtures from this phosphine selenides with electrophiles seem to depend on the type of electrophile and polarity of the solvent. Isolated products from these reactions suggest that $R_2R'PSeI^+$ cations favour to be attacked at β-position leading to (stable) molecular or ionic structures (type **A** and **D**), whereas for $R_2R'PSeBr^-$ only species which have evolved from α-attack at selenium where observed.

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