



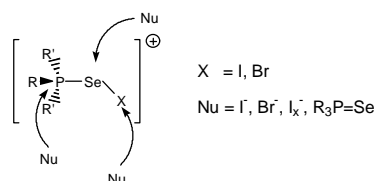
X-Ray Crystallographic and Solution NMR Studies on Selenophosphorane-Halogen Complexes: Molecular and Ionic Structure Alternatives

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Introduction

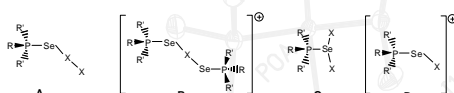
Phosphine selenides $R_2R'P=Se$ are known to act as donors towards dihalogen molecules, providing 1:1 adducts $R_2R'PSeX_2$ [1-7]. The formation of a hypothetical $[R_2R'PSeX^+ X^-]$ [6] in the reaction mixture would provide an "multifunctional" electrophile with three closed-shell centers (Se, X or P) for attack by nucleophiles (Scheme 1). The intensity and the site of this attack may differ for the chosen halogen and type of phosphane selenide, leading to interesting solid state and solution properties of the product(s). Thus suitable experiments were carried out to study the system $R_2R'P=Se/X_2$ in detail.



Scheme 1. Possible centers for a nucleophilic attack.

Solid state & Solution

Molecular structures have been determined for $R_2R'PSeI_2$ (type A, Scheme 2; $R, R' = C_6H_5, NMe_2, NEt_2$ [3] and $R = Bu^t, R' = I$ [4]) and $R_2R'PSeBr_2$ (type C; $R, R' = NMe_2, C_6H_5$ [5] and $R = Bu^t, R' = Pr^i, R, R' = Pr^i$, Figure 2 [2,7]). Bromo- and iodoselenophosphonium ions (type D) have been postulated, but have never been structurally characterised [6]. The first X-ray crystallographically characterised purely ionic solid 1:1 adduct is $(R_2R'PSe)_2I^+ I_3^-$ (type B; $R, R' = Pr^i$, Figure 1, $R = Bu^t, R' = Pr^i$) [7]. NMR spectra, however, suggest that in solutions of such 1:1 adducts equilibrium mixtures of several species are present [2,6,7]. Such an equilibrium is "frozen" in solid $Bu^t_2Pr^iPSeI_2$ [consisting of molecular $Bu^t_2Pr^iPSe-I$ and ionic $(Bu^t_2Pr^iPSe)_2I^+ I_3^-$] [2,7].



Scheme 2. Structural alternatives of phosphane selenide halogen adducts.

NMR Studies

Solutions prepared from $R_2R'P=Se$ ($R, R' = Pr^i; R = Bu^t, R' = Pr^i; R, R' = Bu^t$) and various amounts of dihalogen X_2 ($X = I, Br$) always exhibit only one averaged ^{31}P -NMR line accompanied by satellites arising from $^1J(^{77}Se, ^{31}P)$. The magnitude of this coupling decreases with increasing amounts of halogen.

Solution (CDCl ₃)	$\delta(^{31}P)$ [ppm]	$^1J(^{77}Se, ^{31}P)$ [Hz]	$\delta(^{77}Se)$ [ppm]	$^1J(^{77}Se, ^{31}P)$ [Hz]
$Pr^i_2P=Se$	70.6, 690	-	-485.2, 690	-
$Pr^i_2P=Se + Br_2$	69.8, 521	-	409.0, 521	-
$Pr^i_2P=Se + 5 Br_2$	72.7, 499	-	-	-
$Bu^t_2Pr^iP=Se$	83.8, 692	-	-399, 692	-
$Bu^t_2Pr^iP=Se + 0.05 Br_2$	83.7, 687	-	-381, 689	-
$Bu^t_2Pr^iP=Se + 0.10 Br_2$	83.6, 682	-	-358, - (broad, ~700±40)	-
$Bu^t_2Pr^iP=Se + Br_2$	82.9, 520	-	-	-

Table 1. NMR studies on $R_2R'P=Se$ with different amounts of bromine.

Addition of less than 5% of X_2 to $R_2R'P=Se$ leads to severe broadening and a slight downfield shift of the ^{77}Se -NMR doublet. With larger amounts of X_2 , as in the pure "1:1 adducts", in most cases the ^{77}Se resonances become too broad to be detected (Table 1). This indicates kinetic lability of $R_2R'P=Se/X_2$ systems and equilibration by exchange reactions that are fast on the ^{31}P - and 1H -NMR time scales [7].

X-Ray determinations

The transition from the molecular adduct $R_2R'PSeI_2$ and cationic form $(R_2R'PSe)_2I^+$ to a more or less "free" ion of type D can be achieved by use of an excess of iodine on $R_2R'P=Se$. In contrast to $[I(py)_2]^+ [I_3]^-$ [8], $R_2R'P=Se$ do not form higher polyiodides like $[I(py)_2]^+ [I_4]^-$, but instead provide compounds of the composition $R_2R'PSeI_3$ ($R = Bu^t, R' = Pr^i$, Figure 3, $R, R' = Pr^i$, Figure 4), which represent the first examples of $[R_2R'PSeI]^+$ cations.

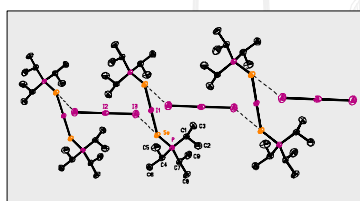


Figure 1. Structure of $(Pr^i_2PSe)_2I^+ I_3^-$ (H atoms omitted for clarity); selected bond lengths (pm) and angles($^\circ$): P-Se 219.05(10), Se-I 277.71(5), Se-I 386.4, I2-I3 290.38(4), P-Se-I 103.52(3).

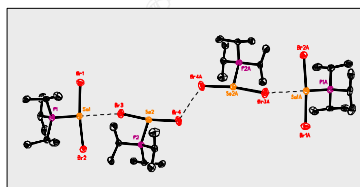


Figure 2. Structure of $Pr^i_2PSeBr_2$ (H atoms omitted for clarity); selected bond lengths (pm) and angles($^\circ$): P-Se 273.2(2)/227.1(2), Se-Br 257.6(9)/260.2(9)/260.6(9)/254.2(9), Br-Br 361.2, Se-Br 346.2, Br-Se-Br 169.19(3)/168.17(3).

^{31}P -NMR spectra of these compounds exhibit further decreased coupling constants $^1J(^{77}Se, ^{31}P)$, which are now similar to that of the type B molecular adduct $Pr^i_2PSeBr_2$ (Table 1), which contains a P-Se single bond. These can be described as salts $[(R_2R'PSeI)_2(I_2)]_n$, containing $[R_2R'P=Se-I]^+$ cations surrounded by weakly donating polyiodide networks [9].

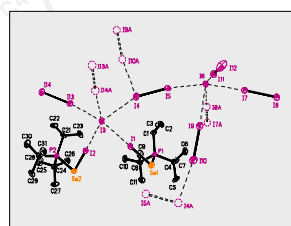


Figure 3. Structure of $Bu^t_2Pr^iPSeI_3$ (H atoms omitted); selected bond lengths (pm) and angles ($^\circ$): I1-Se1 256.4(6), P1-Se1 223.5(1), I1-I3 330.2(4), I2-Se2 256.7(6), P2-Se2 223.7(1), I2-I3 324.8(5), P1-Se1-I1 102.1(3), P2-Se2-I2 101.6(4).

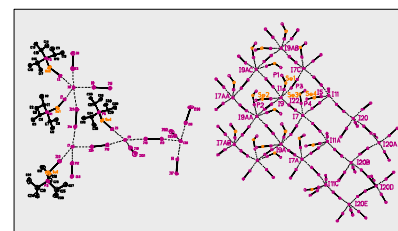


Figure 4. Structure (H atoms omitted) and packing diagram of $Pr^i_2PSeI_3$ (Pr^i -groups omitted); selected bond lengths (pm) and angles ($^\circ$): I1-Se1 256.3(2), P1-Se1 222.6(4), I1-I9 326.7(2), I4-Se2 256.4(2), P2-Se2 222.8(4), I4-I9 328.6(1), I22-Se3 257.1(2), P3-Se3 220.7(5), I22-I7 330.9(2), I5-Se4 257.8(2), P4-Se4 222.1(4), I5-I11 328.5(2), P1-Se1-I1 99.9(1), P2-Se2-I4 99.9(1), P3-Se3-I22 100.3(3), P4-Se4-I5 99.2(1).

In spite of the fact that $Pr^i_2PSeI_3$ and $Bu^t_2Pr^iPSeI_3$ display analogous stoichiometries the slight steric difference between the alkyl groups of the corresponding cations lead to a quite different long-range order of their polyiodide anion structures. In solid $Pr^i_2PSeI_3$, one I^- is surrounded by two cations and four I_2 molecules performing a distorted octahedral coordination sphere, two I^- (five-coordinated, nearly quadratic-planar) are in contact with one cation and four I_2 molecules, the fourth I^- is surrounded by five I_2 molecules with a similar coordination pattern. In solid $Bu^t_2Pr^iPSeI_3$, one iodide anion bridges two of the $Bu^t_2Pr^iPSeI^+$ cations and is in further contact with three I_2 molecules, one of which contacts the other I^- anion. This is in contact with five I_2 molecules, thus in this structure only a coordination number of five is reached for the anions.

Summary

NMR studies on the system $R_2R'P=Se/X_2$ clearly indicate kinetic lability of the corresponding "contact pairs" (Scheme 1). Regarding the solid state structures, only bromide ions are observed to attack at the selenium center leading to T-shaped adducts for $R_2R'P=Se/Br_2$ (Figure 2). In the $R_2R'P=Se/I_2$ systems the present nucleophiles I^- and $R_2R'P=Se$ prefer to attack at the iodine atom adjacent to selenium. We expect that the use of counter anions of a lower nucleophilicity than the presented polyiodide networks will permit syntheses and studies of the properties of a larger number of stable (halogenoseleno)phosphonium ions of type D.

Acknowledgements

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