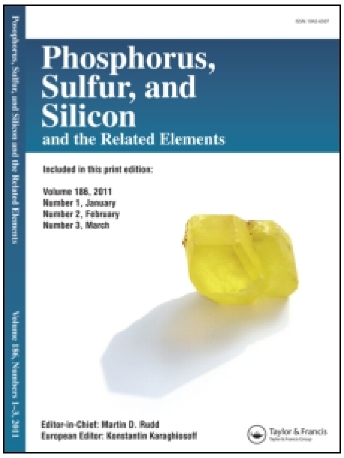

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# ORGANOPHOSPHORUS COMPOUNDS WITH TERTIARY ALKYL SUBSTITUENTS. VII[1]: 1-ADAMANTYLPHOSPHONOSELENOIC DICHLORIDE. THE FIRST EXAMPLE OF A STRUCTURALLY CHARACTERIZED PHOSPHONOSELENOIC DIHALIDE

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# ORGANOPHOSPHORUS COMPOUNDS WITH TERTIARY ALKYL SUBSTITUENTS. VII[1]: 1-ADAMANTYLPHOSPHONOSELENOIC DICHLORIDE. THE FIRST EXAMPLE OF A STRUCTURALLY CHARACTERIZED PHOSPHONOSELENOIC DIHALIDE

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1-Adamantylphosphonoselenoic dichloride **1** was formed in the reaction of the corresponding dichlorophosphine with grey selenium in 42% yield. Compared to other compounds with a P=Se double bond **1** exhibits a strong downfield shift of the $^{77}$Se NMR resonance. The X-ray structure determination reveals a molecule with mirror symmetry and a P=Se bond length of 206.8(2) pm.

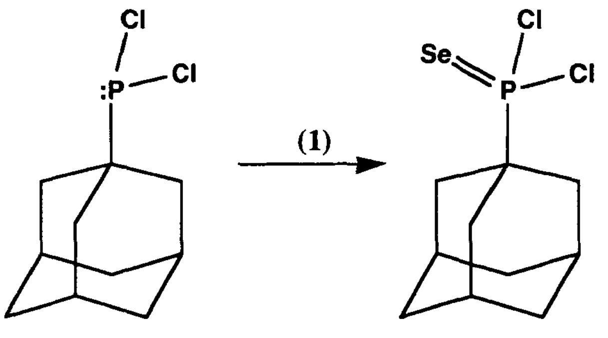
*Key words:* 1-Adamantyl phosphorus compounds, $^{77}$Se NMR, X-ray crystal structure.

## INTRODUCTION

We have been interested in organophosphorus halides for many years and have studied the structure of various compounds involving $\lambda^3$P(III), $\lambda^4$P(V), and $\lambda^5$P(V), e.g. $^t$BuPF$_2$,[2] ($^t$Bu)$_2$PF,[2] (AntPF$_2$)$_2$[3] (Ant = 9-anthracenyl), TrtPCl$_2$[4] (Trt = triphenylmethyl), TrtP(H)Cl,[5] TrtP(:O)F$_2$,[6] TrtP(:S)F$_2$,[4] (1-Ad)$_2$P(:O)Cl[7] (1-Ad = 1-adamantyl), MePF$_4$,[8] Me$_2$PF$_3$,[9] Me$_3$PF$_2$,[9] Ph$_2$[C(:O)Ph]PF$_2$,[10] Trt($^t$Bu)PF$_3$[11] and Trt(Ph)PF$_3$.[11] Here we wish to report the X-ray crystal structure and $^{77}$Se NMR data of 1-AdP(:Se)Cl$_2$ **1**.

## SYNTHESIS AND NMR SPECTROSCOPIC DATA

1-Adamantylphosphonoselenoic dichloride **1** was synthesized as previously described[12] according to Equation (1) by treatment of 1-adamantyldichlorophosphine with an excess of elemental selenium in the presence of tin tetrachloride as a Lewis-acid catalyst:



1

(1)

(1): Se, $SnCl_4$, $CH_2Cl_2$

Both $\delta$(P) and $^1J$(PSe) for **1** (105.5 ppm and 910 Hz, respectively) are in the range expected for a phosphine selenide.[13–15] Presumably as a consequence of the steric demand of the 1-adamantyl group at phosphorus, a downfield shift compared to phosphonoselenoic dichlorides bearing less bulky alkyl or aryl substituents at phosphorus was observed for **1** (R = Me: 55.1 ppm,[13] Et: 73.3 ppm,[13] Ph: 56.8 ppm[13,16]). As a consequence of the electronegativity of the chlorine atoms attached to phosphorus, $^1J$(PSe) is large[15,17,18] (The largest $^1J$(PSe) value, 1200 Hz, was reported for $ClP(:Se)F_2$[19]). Its magnitude indicates the presence of a P═Se bond with only a small contribution for ylidic bonding of the type $R^1R^2{}_2P^+\text{-}Se^-$($R^1$ = 1-Ad, $R^2$ = Cl).[15] This is supported by the fact that **1** shows $\delta$(Se) at 60.65 ppm (cf. $PhP(:Se)Cl_2$: $\delta$(Se) 149 ppm[16]), a considerable downfield shift compared to $\delta$(Se) of other compounds with the P═Se group.[20,21]

## STRUCTURE OF 1-ADAMANTYLPHOSPHONOSELENOIC DICHLORIDE 1

The molecular structure of 1-adamantylphosphonoselenoic dichloride **1** is depicted in Figure 1; selected bond lengths and angles are given in Table I. The molecule possesses crystallographic mirror symmetry, the mirror plane passing through the atoms P, Se, C1, C2, C3 and C7. The phosphorus atom, as expected, displays somewhat distorted tetrahedral coordination geometry, with the largest deviations from ideality for the angle between the 1-adamantyl group and the selenium atom, C1—P—Se [115.4(2)°]. The smallest angle is subtended by the two chlorine atoms with 103.13(13)°. The P═Se double bond [206.8(2)pm] is 2.5 pm longer than the P═Se standard bond length.[22] The P—C1 [184.2(7) pm] and the P—Cl [204.8(2) pm] bond lengths are similar to those in di-1-adamantylphosphinic chloride [P—C1: 185.0(3), P—C1′: 184.0(3), P—Cl: 204.84(12) pm].[7] The C5—C7 bond [148.6(10) pm) is shorter than the other C—C bonds [C3—C4 151.9(11) pm to 154.6(12) pm] of the 1-adamantyl group. However, these values may be affected by the high displacement parameters (even at low temperature) of the 1-adamantyl group.

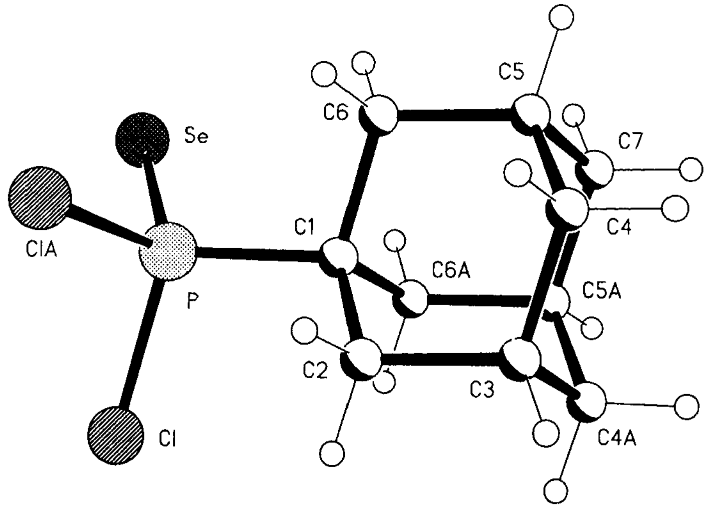


FIGURE 1 The molecule of 1-adamantylphosphonoselenoic dichloride **1** in the crystal. Atom names with "A" indicate symmetry equivalent atoms. Atomic radii are arbitrary. Symmetry transformation used to generate equivalent atoms: #1 x, −y + 1/2, z.

TABLE I

Selected bond lengths and angles for **1**

| | | | |
|---|---|---|---|
| P-C(1) | 184.2(7) | P-Cl | 204.8(2) |
| P-Se | 206.8(2) | C(1)-C(6) | 152.1(7) |
| C(1)-C(2) | 153.3(10) | C(2)-C(3) | 154.6(12) |
| C(3)-C(4) | 151.9(11) | C(4)-C(5) | 152.4(11) |
| C(5)-C(7) | 148.6(10) | C(5)-C(6) | 154.6(8) |
| | | | |
| C(1)-P-Cl | 107.29(14) | Cl-P-Cl#1 | 103.13(13) |
| C(1)-P-Se | 115.4(2) | Cl-P-Se | 111.45(8) |
| C(6)-C(1)-C(6)#1 | 108.8(7) | C(6)-C(1)-C(2) | 110.9(5) |
| C(6)-C(1)-P | 107.3(4) | C(2)-C(1)-P | 111.7(5) |
| C(1)-C(2)-C(3) | 108.0(7) | C(4)-C(3)-C(4)#1 | 109.0(9) |
| C(4)-C(3)-C(2) | 109.5(5) | C(3)-C(4)-C(5) | 109.6(6) |
| C(7)-C(5)-C(4) | 110.1(7) | C(7)-C(5)-C(6) | 109.5(7) |
| C(4)-C(5)-C(6) | 109.3(6) | C(1)-C(6)-C(5) | 108.2(5) |
| C(5)-C(7)-C(5)#1 | 110.4(8) | | |

## EXPERIMENTAL

The working conditions were described elsewhere.[4]

### *Preparation of 1-Adamantylphosphonoselenoic Dichloride* 1

To a solution of 1.72 g (7.3 mmol) of 1-adamantyldichlorophosphine in 30 ml of dichloromethane were added at r.t. 0.91 g (11.5 mmol) of grey selenium and 1 ml of tin tetrachloride as a catalyst. The mixture was stirred for 10 d at r.t. Subsequently excess selenium was filtered off and the volume of the filtrate was reduced in vacuo (0.1 mm Hg) to ca. 10 ml. Storage at −18°C gave after 10 d yellow crystals of **1**, suitable for the X-ray crystal structure determination. Yield: 0.98 g (42.5%); mp.: 117–118°C (lit.[12]: 119°C).

TABLE II

Atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P | 4699(3) | 2500 | 6848(2) | 20.4(5) |
| Se | 7386.0(12) | 2500 | 6795.7(12) | 40.0(4) |
| Cl | 4246(2) | 4054.3(15) | 8183(2) | 34.8(4) |
| C(1) | 2830(10) | 2500 | 4742(9) | 17.7(14) |
| C(2) | 893(11) | 2500 | 4909(12) | 48(3) |
| C(3) | -579(12) | 2500 | 3089(12) | 53(3) |
| C(4) | -326(10) | 1302(8) | 2132(10) | 56(2) |
| C(5) | 1607(10) | 1318(8) | 1982(8) | 51(2) |
| C(6) | 3101(9) | 1302(6) | 3790(8) | 41(2) |
| C(7) | 1839(16) | 2500 | 1057(12) | 60(3) |

### *X-Ray Structure Determination of* **1**

*Crystal data*: $C_{10}H_{15}Cl_2PSe$, M = 316.05, monoclinic, space group $P2_1/m$, a = 763.8(2), b = 1032.2(3), c = 833.2(3) pm, $\beta$ = 110.11(3)°, U = 0.6168(3) nm$^3$, Z = 2, $D_x$ = 1.702 Mg m$^{-3}$, $\lambda(MoK_\alpha)$ = 71.073 pm, $\mu$ = 3.567 mm$^{-1}$, F(000) = 316, T = −130°C.

*Data collection and reduction*: A yellow prism 0.80 × 0.70 × 0.40 mm was mounted on a glass fibre in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with Siemens LT-2 low temperature attachment). Of the 1768 intensities registered in the 2Θ-range 6–50°, 1151 were unique ($R_{int}$ = 0.035). The cell constants were refined from $\pm\omega$ angles of 52 reflections in the 2Θ range 20–23°. The atom coordinates are given in Table II.

*Structure solution and refinement*: The structure was solved by direct methods and refined anisotropically on $F^2$ (program system: SHELXL-93, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model. The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$. The final R(F) value was 0.0595, with $wR(F^2)$ = 0.1855 for all reflexions. S = 1.1; max $\Delta/\sigma$ = 0.001; max $\Delta_\rho$ = 1426 e nm$^{-3}$.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. This material may be obtained on quoting the full literature citation and the reference number CSD 404613.

## ACKNOWLEDGEMENTS

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