

## A NEW STABLE TRICOORDINATE PHOSPHORUS(V) COMPOUND: *P*-2,6-DIMETHYLPHENYL-*C,C*-DIPHENYLSELENOPHOSPHENE

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### Summary

Reaction of 2,6-dimethylphenyl(diphenylmethylene)phosphine (**1**) with selenium in benzene leads to the compound *P*-2,6-dimethylphenyl-*C,C*-diphenylselenophosphene (**2c**). Compound **2c** is stable at room temperature, but decomposes on heating with partial regeneration of the starting materials. Ethanol adds to the P=C bond of **2c** to give the selenophosphinate **3c**. No reaction was observed between **1** and tellurium.

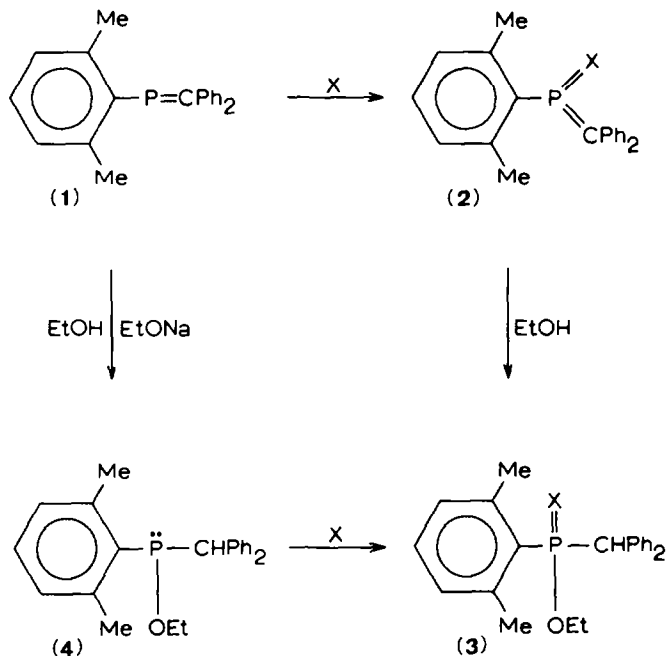
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In the course of a systematic investigation of the chemical reactivity of phosphathenes, we studied the reaction of 2,6-dimethylphenyl(diphenylmethylene)phosphine (**1**) [1] with, inter alia, oxygen and sulfur [2]. We were able to show that an important primary step in these reactions is the oxidation of **1** to the phosphene **2a** or thiophosphene **2b** analogous to the corresponding reactions of tertiary phosphines. However, **2a** and **2b** were too reactive to survive under the reaction conditions. In the absence of suitable reaction partners, they polymerized but they could be intercepted, e.g. with ethanol to furnish **3a** or **3b**, respectively (Scheme 1).

However, the analogous reaction with grey selenium in benzene at 80°C led to selenophosphene [3] **2c**, which was stable enough to survive the conditions used. After heating for 16 h with 1.4 equivalents of Se, 75% of **2c** was formed while 25% of **1** remained. Prolonged heating with an excess of Se did not yield more **2c**, as decomposition occurred. Although **2c** was stable at ambient temperatures, its purification was thwarted by its partial decomposition to **1** and red Se on sublimation. Selenium was also formed on exposure of **2c** to air and it could not be completely removed by crystallization. Therefore, **2c** was characterized by NMR spectroscopy and by its reaction with ethanol to give **3c**.

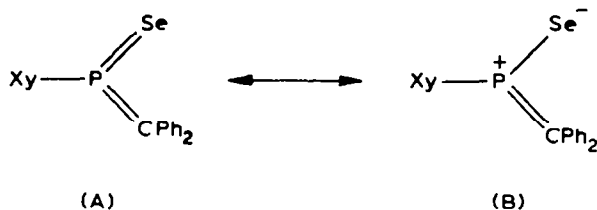
All the NMR data are consistent with the structure assigned to **2c** (see Experimental); the following are characteristic. In the <sup>13</sup>C NMR spectrum, a doublet is found at δ 152.8 ppm (<sup>1</sup>J(PC) 114 Hz) which is assigned to the carbon atom of the P=C bond. The coupling constant is typical, though large, for a methylene-

## SCHEME 1



(a : X = O ; b : X = S ; c : X = Se)

phosphorane; the chemical shift is about 40 ppm downfield from that of the aminoselenoxophosphorane (Me<sub>3</sub>Si)<sub>2</sub>N-P(=Se)=CSiMe<sub>3</sub> ( $\delta$  110.7 ppm,  $^1J(\text{PC})$  70.4 Hz) [5]. Both effects may be explained in terms of a relatively large contribution of resonance structure B [6].



(2c; Xy = 2,6-dimethylphenyl)

Also of interest is the rather large  $^{31}\text{P}$ - $^{77}\text{Se}$  coupling constant of 890 Hz (cf. Ph<sub>3</sub>P=Se:  $^1J(\text{PSe})$  736 Hz; Me<sub>2</sub>PhP=Se:  $^1J(\text{PSe})$  710 Hz [6]). It implies high *s*-character in the P-Se bond, as expected for *sp*<sup>2</sup>-type hybridization of phosphorus. A similarly high coupling constant was found for RR'N-P(=Se)=NR ( $\delta(^{31}\text{P})$  118.75 ppm,  $^1J(\text{PSe})$  960 Hz; R = *t*-Bu, R' = SiMe<sub>3</sub>) [7].

The structure of 2c was confirmed by its reaction with ethanol to give the expected [2] addition product 3c. The structure of 3c was verified by independent synthesis: base-catalysed addition of ethanol to 1 gave 4 [2,8], which was then oxidized with selenium to 3c.

When the reaction of **1** with selenium was performed in boiling ethanol, it was complete within 3 h; **3c**, formed via **2c**, was the only product. The reverse sequence of events, i.e. addition of ethanol to **1** to form **4** followed by selenium-oxidation to **3c**, can be excluded, as ethanol does not add to **1** without acid or base catalysis [2,8]. The formation of **3c** under these conditions is therefore evidence for the interception of **2c** by ethanol; this behaviour parallels that of **2a** [2,4] and **2b** [2]. The enhanced rate in ethanol compared with that in benzene deserves some comment. While solubility effects cannot be excluded, we feel that the rapid and complete reaction in ethanol is largely due to the irreversible shift of a thermal equilibrium by ethanol (Scheme 2); the dissociation of **2c** on heating and the incomplete reaction in benzene point in the same direction.

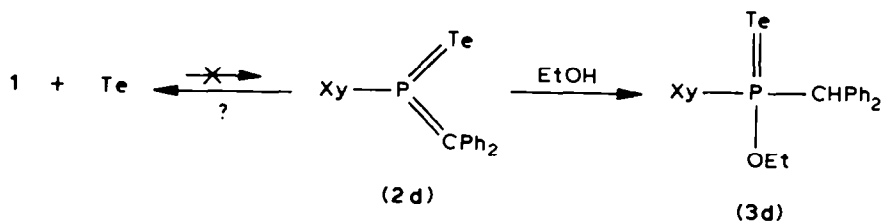
SCHEME 2



On attempted reaction with tellurium, **1** was recovered unchanged, even after prolonged heating in toluene (110°C). This is not surprising in view of the results of Zingaro et al. on the formation of tellurides from tertiary phosphines and tellurium [9]. Triphenylphosphine did not react at all; with two phenyl groups on phosphorus, an equilibrium was established (analogous to that postulated between **1** and Se, (Scheme 2)); only with one or no phenyl groups on phosphorus were stable tellurides isolated.

In **1**, the nucleophilicity of the lone pair is reduced because of its high *s*-character [10,11] but steric hindrance by the two *ortho*-methyl groups and the diphenylmethyl substituent may also be important. The extreme lack of reactivity is particularly evident in boiling ethanol which, by an interception reaction analogous to that of Scheme 2, would have irreversibly converted traces of **2d** into **3d** (Scheme 3); **3d** was not observed, and **1** was recovered unchanged.

SCHEME 3



## Experimental

Reactions were performed under argon or nitrogen. NMR spectra were recorded on a Bruker WH 90 or a Bruker WM 250. Low field NMR signals have a positive sign; references are Me<sub>4</sub>Si (<sup>1</sup>H), 85% H<sub>3</sub>PO<sub>4</sub> (external, <sup>31</sup>P), CDCl<sub>3</sub> (<sup>13</sup>C) and Ph<sub>3</sub>PSe (external, δ 263.2 ppm relative to (CH<sub>3</sub>)<sub>2</sub><sup>77</sup>Se, δ 0 ppm). Mass spectra were recorded on a Varian CH5DF. Melting points are uncorrected.

*2,6-Dimethylphenyl-C,C-diphenylselenophosphene (2c)*

Compound **1** (147 mg, 0.49 mmol) was dissolved in benzene (5 ml) and grey selenium (110 mg, 0.69 mmol) was added. The mixture was heated under reflux for 16 h; it turned orange/red. After filtration and evaporation NMR spectra were recorded in CDCl<sub>3</sub>; signals of unreacted **1** (25%) are omitted. <sup>1</sup>H NMR: δ 2.62 (d, <sup>4</sup>J(PH) 2 Hz, 6H, *o*-CH<sub>3</sub>) 6.71–8.00 ppm (m, 13H, aryl H). <sup>13</sup>C NMR: δ 22.6 (d, <sup>3</sup>J(PC) 6 Hz, *o*-CH<sub>3</sub>) 126.6–140.7 (m, aryl C) 152.8 ppm (d, <sup>1</sup>J(PC) 114 Hz, P=C). <sup>31</sup>P NMR: δ 125.7 (s) (satellite: d, <sup>1</sup>J(<sup>77</sup>Se<sup>31</sup>P) 890 Hz). <sup>77</sup>Se NMR: δ –182 ppm (d, <sup>1</sup>J(<sup>77</sup>Se<sup>31</sup>P) 890 Hz).

*o-Ethyl 2,6-dimethylphenyl(diphenylmethyl)selenophosphinate (3c)*

(a) *From ethyl 2,6-dimethylphenyl(diphenylmethyl)phosphinite (4) with selenium.* Compound **1** (191 mg, 0.63 mmol) was dissolved in ethanol (10 ml) and a trace of sodium was added. After 1.5 h of heating under reflux the typical yellow colour of **1** had disappeared. To the solution of **4** thus obtained [2,8] grey selenium (150 mg, 1.9 mmol) was added, and the mixture was heated under reflux for another 2 h. The excess of selenium was filtered off, the solution was boiled with decolourising carbon, filtered again and evaporated, yielding **3c** as a light yellow viscous oil (220 mg, 82%). Crystallisation from ethanol gave colourless crystals, m.p. 92–93.5°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.11 (t, <sup>3</sup>J(HH) 7 Hz, CH<sub>2</sub>CH<sub>3</sub>) 3.33–4.22 (m, 2H, CH<sub>2</sub>) 5.06 (d, <sup>2</sup>J(PH) 10 Hz, 1H, CHPh<sub>2</sub>) 6.67–7.61 ppm (m, 13H, aryl H). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 94.26 (s) (satellite d, <sup>1</sup>J(<sup>31</sup>P<sup>77</sup>Se) 782 Hz). <sup>77</sup>Se NMR (CDCl<sub>3</sub>): δ –191.6 ppm (d, <sup>1</sup>J(<sup>77</sup>Se<sup>31</sup>P) 782 Hz). Mass spectrum *m/z* (relative intensity): 428 (21) [*M*<sup>+</sup>(<sup>80</sup>Se)] 426 (11) [*M*<sup>+</sup>(<sup>78</sup>Se)] 348 (19) [*M*<sup>+</sup> – Se] 261 (87) [*M*<sup>+</sup> – Ph<sub>2</sub>CH(<sup>80</sup>Se)] 259 (40) [*M*<sup>+</sup> – Ph<sub>2</sub>CH(<sup>78</sup>Se)] 181 (30) [C<sub>10</sub>H<sub>14</sub>OP<sup>+</sup>] 167 (100) [Ph<sub>2</sub>CH<sup>+</sup>]. Found C, 64.65; H, 6.03; P, 7.48. C<sub>23</sub>H<sub>24</sub>OPSe calcd.: C, 64.64; H, 5.90; P, 7.25%.

(b) *From 2c with ethanol.* Compound **1** (75 mg, 0.248 mmol) was dissolved in benzene (5 ml) and grey selenium (34 mg, 0.43 mmol) was added. After 3 h heating under reflux the solution had become orange. After filtration and evaporation 86 mg of a mixture of **1** and **2c** (ca. 1/1; <sup>1</sup>H NMR spectrum) remained as an orange oil. Ethanol (2.5 ml) was added and the mixture was stirred at room temperature until the orange oil had dissolved. Some traces of residual black selenium were filtered off and the solution was evaporated to dryness. The <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra indicated the presence of approximately equal amounts of **1** and **3c**.

(c) *From 1 with selenium in the presence of ethanol.* Compound **1** (150 mg, 0.5 mmol) was dissolved in ethanol (10 ml) and grey selenium (54 mg, 0.68 mmol) was added. After another 1.75 h heating under reflux the typical yellow colour of **1** had disappeared. After 1.25 h of heating, followed by filtration and evaporation, almost pure **3c** remained (202 mg, 95%) according to the <sup>1</sup>H and <sup>31</sup>P NMR spectrum. After one crystallisation from ethanol pure product of m.p. 92–93.5°C was obtained.

## References

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- 3 For simplicity, we use the "phosphene" nomenclature for **2c**; alternative names are 2,6-dimethylphenyl(diphenylmethylene)phosphine selenide or 2,6-dimethylphenyl(diphenylmethylene)selenoxophosphorane; cf. ref. [4] for the nomenclature of the oxo-analogues such as **2a**.

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