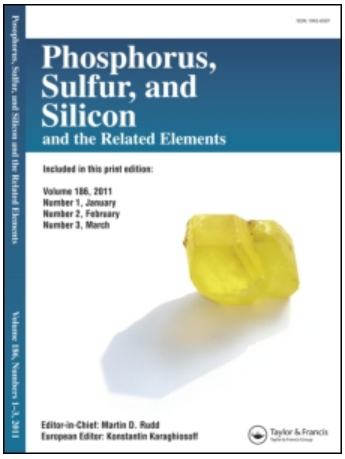

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

1,2-ADDITIONS OF PHENYLSELENENYL HALIDES TO PHOSPHAALKYNES

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To cite this Article Francis, Matthew D. , Jones, Cameron , Junk, Peter C. and Roberts, John L.(1997) '1,2-ADDITIONS OF PHENYLSELENENYL HALIDES TO PHOSPHAALKYNES', Phosphorus, Sulfur, and Silicon and the Related Elements, 130: 1, 23 — 34
To link to this Article: DOI: 10.1080/10426509708033693
URL: http://dx.doi.org/10.1080/10426509708033693

Phosphorus, Sulphur, and Silicon, 1997, Vol. 130, pp. 23–34
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1,2-ADDITIONS OF PHENYLSELENENYL HALIDES TO PHOSPHAALKYNES

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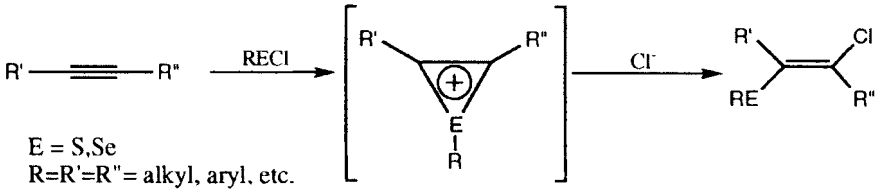
(Received 22 April 1997)

The preparation of a variety of selenophosphaalkenes by addition of phenylseleneyl halides to phosphaalkynes is described. The process is stereoselective and largely regioselective. The stereoselectivity is explained by postulating the presence of a cyclic selenophosphirenylium cation. The reaction of one of the prepared selenophosphaalkenes with ^{t}BuLi is discussed.

Keywords: phosphaalkyne; phenylselenenyl halide; selenophosphirenylium cation; selenophosphaalkene; crystal structure

The last fifteen years have seen considerable interest in the chemistry of phosphaalkynes, P≡CR. The coordination and organic chemistry of these species has been intensely researched and subject to several recent reviews.[1–4] Despite this, 1,2 additions to phosphaalkynes are comparatively rare and can be confined to a handful of examples.[5,6] In response to this relatively unexplored area of phosphaalkyne chemistry we have decided to examine the preparation of selenophosphaalkenes by the addition of phenylselenenyl halides, PhSeX, to phosphaalkynes, since the addition of such agents to carbon-carbon multiple bonds has been of considerable interest in synthetic organic chemistry.[7,8] To the best of our knowledge, only one report of two selenophosphaalkenes, $[\{(\eta^5-C_5H_5)(CO)_3\}WSeP=C(SiMe_3)(R)]$, $R=C_6H_5$ or $SiMe_3$, has appeared,[9] though neither compound was structurally characterised.

*Corresponding author.



SCHEME 1

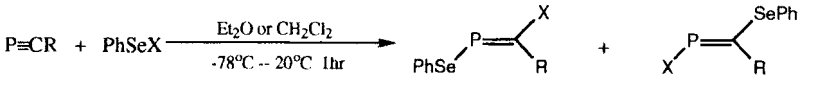
The addition of sulfur and selenium electrophiles to alkynes has been studied in detail.[10] The addition of sulfenyl halides is stereoselective (trans addition is seen) but not regioselective, the regiochemistry being dependent upon both the solvent and the alkynic substituents. For terminal alkynes predominantly anti-Markownikoff addition occurs, implying the alkyl group has a significant steric influence on the product determining step of the reaction. Similar behaviour is observed for the addition of selenium electrophiles. A mechanism has been proposed to include either cyclic thiirenium or selenirenium ions as intermediates (Scheme 1).[11,12] These cyclic species show stability in solution at low temperatures and have been examined spectroscopically.[13,14] Indeed, theoretical studies on the simplest thiirenium ion (R = R′ = R″ = H) have shown it to be 14 kcal/mol more stable than its open chain analogue.[15]

In this paper we report studies of the addition of phenylselenenyl halides to two phosphaalkynes, P≡CBu^t and P≡CAd (Ad = 1-adamantyl), and show that the reaction is completely stereoselective and largely regioselective. We explain these observations by suggesting a mechanism which proceeds *via.* a three membered cyclic intermediate. The reaction of one of the products with ^{t}BuLi is discussed. We also report the first structural characterisations of selenophosphaalkenes.

RESULTS AND DISCUSSION

Addition of PhSeX (X = Cl,Br) to P≡CR (R = ^{t}Bu, 1-Adamantyl) at −78°C in Et_2O or CH_2Cl_2 followed by slow warming to ambient temperature leads to loss of colour of the phenylselenenyl halide and formation of the selenophosphaalkenes **1–3** in moderate to high yields (Scheme 2). In each reaction a small amount of the P-halogenated phosphaalkenes **4** (8%), **5** (2%) and **6** (12%) were formed by reverse addition. The major product in each case was characterised by ^{31}P, ^1H, ^{77}Se, ^{13}C NMR spectroscopy and EI/CI mass spectrometry.

The single bond selenium-phosphorus connectivities in the major products are evidenced by the large coupling constants between the two nuclei ($^1J_{P\text{-}Se}$ ranging



Scheme 2

R=^{t}Bu	X=Cl	**1** (92%)		R=^{t}Bu	X=Cl	**4** (8%)
R=^{t}Bu	X=Br	**2** (98%)		R=^{t}Bu	X=Br	**5** (2%)
R=Ad	X=Cl	**3** (88%)		R=Ad	X=Cl	**6** (12%)

SCHEME 2

between 275 and 285 Hz), identifiable from the ^{77}Se satellites in their ^{31}P NMR spectra. These couplings are in the range normally seen in similar systems.[9,16] The ^{31}P NMR chemical shifts of **1–3** are typical of those seen for phosphaalkenes[17] while those of **5–6**, are shifted by ca. 130ppm to lower field in the region typical of P-halogenated phosphaalkenes.[18] The ^{77}Se satellites on the ^{31}P NMR resonances of **4**, **5** and **6** were not resolved but doublets in their ^{77}Se NMR spectra, with $^2J_{P\text{-}Se}$ couplings between 50 and 98 Hz were observed. The ^{31}P NMR data are collected in Table I. Evidence of the trans arrangement between the PhSe and X groups in **1–3** is obtained from the two bond coupling constant between the phosphorus and the quaternary carbon of the alkyl substituent. In phosphaalkenes such couplings lie in the region of 12–17 Hz when the carbon is trans to the phosphorus lone pair.[19,20] In **1–3** the couplings at 14, 15.1 and 13.7 Hz respectively point to the fact that the alkyl group and phosphorus lone pair, and consequently the PhSe and X groups, are indeed trans to each other.

Whereas the mixtures of (**1** and **4**) and (**2** and **5**) are mobile oils at room temperature, both compounds **3** and **6** are crystalline solids that cannot be separated by fractional crystallisation. However, a crystal suitable for X-ray diffraction studies was selected from this mixture and subsequently found to be the P-chlorinated isomer, **6**. The molecular structure of **6** (Figure 1) represents the first of any selenyl substituted phosphaalkene and shows that the PhSe group is trans to the Cl substituent as was predicted from the NMR data for the major isomer, **3**. The geometry about C(1) is distorted trigonal planar (Σ angles = 359.8°) and the P=C [1.664(9) Å] and P-Cl [2.104(5) Å] bond lengths are close to those in the only other example of a structurally characterised P-chlorinated

TABLE I ^{31}P NMR data for compounds **1** to **6**

	Compound					
	1	*2*	*3*	*4*	*5*	*6*
δ/ppm	180.5	186.0	177.6	303.0	308.8	309.1
$J_{P\text{-}Se}$/Hz	275	285	276	98	59	49

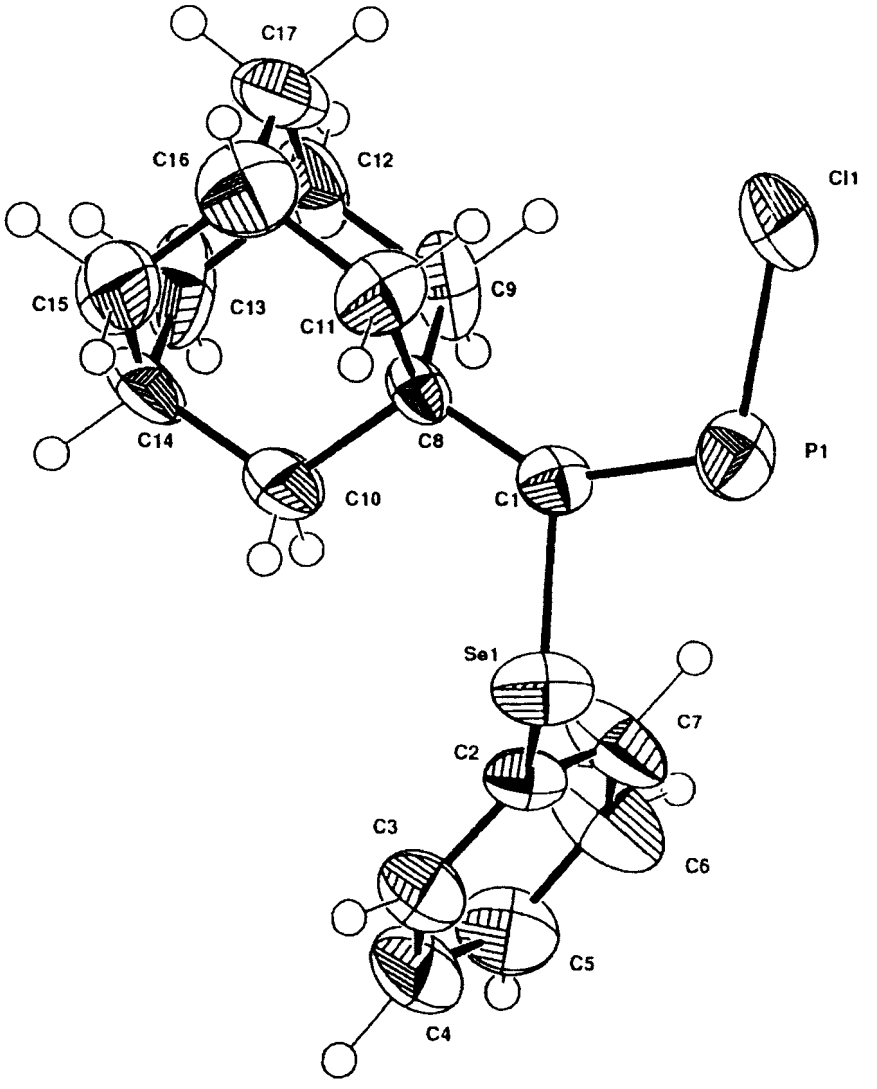
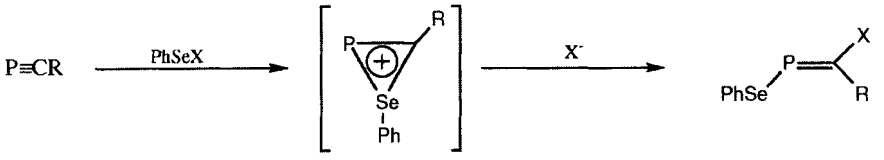


FIGURE 1 Molecular structure of **6**. Selected bond lengths (Å) and angles (°): P(1)-C(1) 1.664(9), P(1)-Cl(1) 2.104(5), C(1)-Se(1) 1.945(9), C(2)-Se(1) 1.935(9), C(1)-C(8) 1.51(1), C(1)-P(1)-Cl(1) 107.9(4), P(1)-C(1)-Se(1) 99.1(5), P(1)-C(1)-C(8) 138.9(6), C(1)-Se(1)-C(2) 101.5(3).

λ^3-phosphaalkene, $[Rh\{(Cl)P{=}C(SiMe_3)_2\}(PPh_3)_2Cl]$, (1.644 and 2.086 Å respectively).[21] However, in this case the phosphaalkene is coordinated to a rhodium fragment through its P-lone pair.

We suggest the observed trans stereochemistry maybe explainable by invoking a mechanism which proceeds *via.* an intermediate selenophosphirenylium cation



SCHEME 3

(Scheme 3), analogous to the aforementioned thiirenium and selenirenium ions. At first sight the regiochemistry seems to contradict the expectations based on both electronic and steric considerations. If, as may be expected, the phosphorus centre is the more electrophilic region then we would expect to see **4**, **5** and **6**, as the major products rather than **1**, **2**, and **3**. This also seems to be the most obvious outcome from a steric point of view. Clearly the selenium centre must be having a significant influence which is thwarting what would appear to be the most electronically and sterically favourable outcome. We are currently conducting theoretical studies to investigate the electronic balance in selenophosphirenylium cations in an attempt to explain this phenomenon.

In light of the proposed mechanism we attempted to utilise bulky non coordinating counteranions other than Cl^- (eg. $CF_3SO_3^-$ and $[B(Ph\text{-}3,5\text{-}(CF_3)_2)_4]^-$) in an effort to stabilise the putative cyclic intermediate. When $P \equiv CBu^t$ is treated with a solution of $PhSeSO_3CF_3$ in CH_2Cl_2 at low temperature followed by warming to ambient temperature, a visible reaction occurs leading to a golden yellow solution. Analysis of the solution by ^{31}P NMR spectroscopy shows a single resonance at 350 ppm ($^1J_{P\text{-}Se}$ = 315 Hz) which is consistent with the chemical shift (309.7 ppm) observed for the only known uncoordinated phosphirenylium cation $(C_6H_5CPCBu^t)^+$.[22] The $^1J_{P\text{-}Se}$ value of 315 Hz in the present system is larger than the equivalent $^1J_{P\text{-}Se}$ couplings seen in the selenophosphaalkenes **1–3** and may indicate a marginal increase in bond order between the phosphorus and selenium centres as a result of delocalisation within the selenophosphirenylium cation. Unfortunately attempts to isolate the species from solution leads to complete degradation to a multiplicity of phosphorus containing products.

C-halogenated phosphaalkenes have been shown to have considerable synthetic potential.[23] Substitution at the carbon centre has been the subject of much work by Bickelhaupt *et al.*.[24] To investigate the possibility of substitution at the alkene carbon in **1**, we have examined its reaction with ^{t}BuLi. The result, whilst unusual, is not completely unprecedented. The reaction leads to a solid compound **7**, isolated in moderate yield (17.5%), which was purified by column chromatography. The ^{77}Se NMR spectrum shows a doublet at 345ppm ($^2J_{P\text{-}Se}$ = 15 Hz) although broadness at the base of the signal in the ^{31}P NMR spectrum

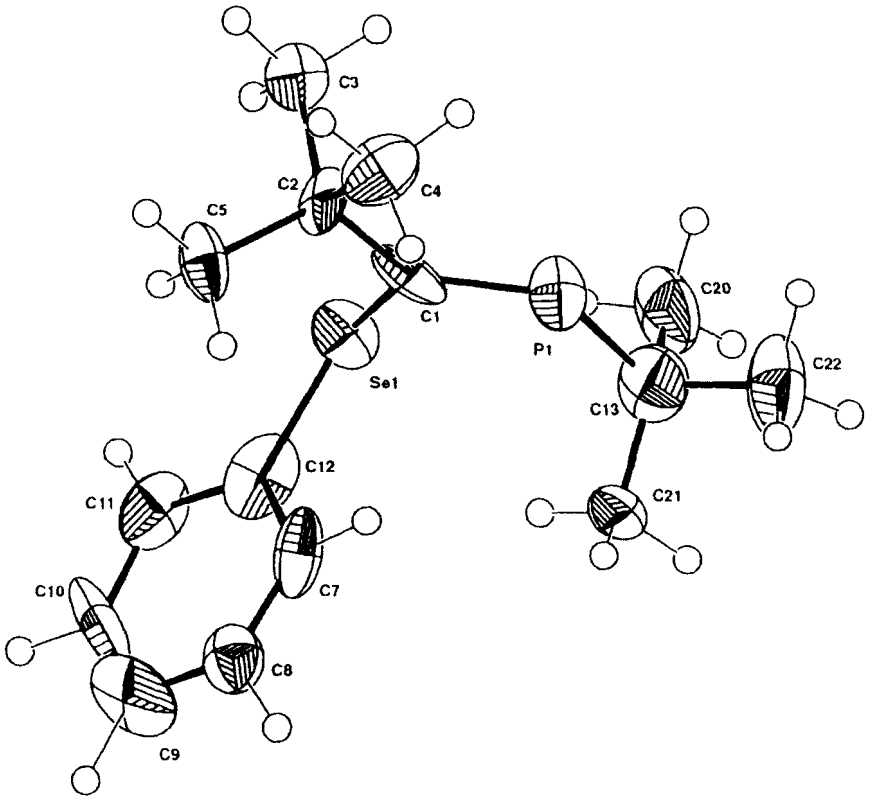
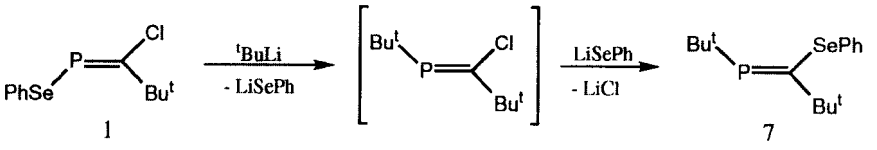


FIGURE 2 Molecular structure of **7**. Selected bond lengths (Å) and angles (°): P(1)-C(1) 1.70(2), P(1)-C(13) 1.88(2), C(1)-C(2) 1.51(3), C(1)-Se(1) 1.93(2), Se(1)-C(12) 1.88(2), C(13)-P(1)-C(1) 114.6(9), P(1)-C(1)-C(2) 120(1), P(1)-C(1)-Se(1) 123(1), C(1)-Se(1)-C(12) 102.9(8).

(δ = 360.5 ppm) precludes the precise resolution of selenium satellites. The $^2J_{P\text{-}C}$ coupling between the phosphorus centre and the quaternary carbon of the ^{t}Bu group (18Hz) lies between the two regions normally seen for tertiary butyl groups cis or trans to P-lone pairs in phosphaalkenes.[17] Therefore it cannot be sure if the two tertiary butyl substituents on **7** are cis or trans to each other. For this reason an X-ray crystal structure determination of this compound was carried out. The molecular structure of **7** (Figure 2) confirmed the trans arrangement of the tertiary butyl groups. The geometry about C(1) is trigonal planar (Σ angles = 360°) and the P=C bond length [1.70(2) Å, *cf.* 1.664(9) Å in **6**] is in the normal range for those in phosphaalkenes.[17]

With regards to a mechanism for the formation of **7**, it seems likely that the ^{t}BuLi initially cleaves the PhSe-C bond to liberate the $PhSe^-$ anion which then acts as a nucleophile to cleave the C-Cl bond, giving the appearance of a mi-



1 7

SCHEME 4

gration of the PhSe group (Scheme 4). Similar substitutions of halogens in vinyl halides by sulphur and selenium nucleophiles are well known.[25,26] In principle, **7** could result from direct cleavage of the P-Cl bond in **4** by ^{t}BuLi. However, the amount of product far exceeds the amount of **4** formed initially, so that the route, *via.* reaction with **1** is the most likely one, although the conversion of **4** to **7** by direct reaction with ^{t}BuLi cannot be ruled out as a contribution to the formation of **7**.

If this mechanism is to be reasonable then the attack of $PhSe^-$ on the intermediate species in (Scheme 4) must occur so that the configuration about the phosphaalkene carbon is retained. This is indeed the case for vinyl halides in which the substitution occurs with complete retention of stereochemistry.[25,26]

Experimental Section

All reactions were carried out under an atmosphere of high purity argon in flame dried glassware, using conventional Schlenk procedures. Solvents were predried over sodium wire (hexane, diethyl ether) or CaH_2 (CH_2Cl_2) and were distilled from NaK alloy (hexane, diethyl ether) or CaH_2 (CH_2Cl_2) under an argon atmosphere. Melting points (uncorrected): Electrothermal digital melting point apparatus. I.R.: Perkin Elmer 1725-X FT-IR spectrometer. Mass Spec.: VG 12–250 EI/CI automated mass spectrometer. NMR: ^{13}C on Bruker AC 400 (100.6 MHz, referred to residual solvent peaks). ^1H on Bruker AC 400 (400 MHz) or Bruker WM 250 (250 MHz) referred to residual solvent peaks. ^{31}P on Bruker WM 250 (101.2 MHz) 85% H_3PO_4 as external standard. ^{77}Se on Bruker WM 250 (47.73 MHz) with Me_2Se as external standard. Microanalyses were conducted at the University of Wales, Cardiff. PhSeCl and PhSeBr were purchased from Lancaster Chemicals, ^{t}BuLi was purchased as a 1.7M solution in ether from Aldrich, P≡CAd was prepared by a published method,[27] P≡CBu^t was prepared by a modification of the literature synthesis.[28]

E-phenylselenenyl-(3-chloro-2,2-dimethylpropylidene)phosphane (1)

To a stirred solution of P≡CBu^t (197mg, 1.98 mmoles) in diethyl ether(5 ml) at −78°C was added a solution of PhSeCl (315mg, 1.64 mmoles) in diethyl ether (10 ml). After complete addition (ca. 5 mins) the solution was warmed to room temperature and allowed to stir for one hour. The solvent and excess phosphaalkyne were then removed *in vacuo* to afford a mixture of **1**(92%) and **4**(8%) as a pale yellow oil, (450mg, 94.5%). Spectroscopic data for **1**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ = 180.5 (s, $^1J_{P\text{-}Se}$ = 275 Hz)—^1H NMR (C_6D_6) δ = 1.25 (s, 9H, ^{t}Bu), 6.8–7.7 (m, 5H, Ar-H)—^{77}Se NMR (C_6D_6) δ = 317 (d, $^1J_{Se\text{-}P}$ = 275 Hz)—^{13}C NMR (C_6D_6) δ = 30.0 (d, $^3J_{P\text{-}C}$ = 4.6 Hz, P=C-C($\underline{C}H_3)_3$), 44.9 (d, $^2J_{P\text{-}C}$ = 14 Hz, P=C-$\underline{C}(CH_3)_3$), 127.9, 129.5, 130.2 (s, Ar-H), 132.6 (d, $^2J_{P\text{-}C}$ = 10.7 Hz, P-Se-$\underline{C}$), 192.6 (d, $^1J_{P\text{-}C}$ = 94.3 Hz, P=$\underline{C}$).- Mass Spec. (EI/CI); m/z (%): 292 (8) [M^+], 257(12) [M^+-Cl], 187(5) [PhSeP$^+$], 157(15) [PhSe$^+$], 77(45) [$C_6H_5^+$], 57(100) [^{t}Bu$^+$] - IR (nujol) cm^{-1}: 1724 (m), 1578 (s).

E-phenylselenenyl-(3-bromo-2,2-dimethylpropylidene)phosphane (2)

To a stirred solution of ^{t}BuC≡P (99mg, 0.99 mmoles) in diethyl ether(10 ml) at −78°C was added a solution of PhSeBr (193mg, 0.82 mmoles) in diethyl ether (10 ml). After complete addition (ca. 5 mins) the solution was warmed to room temperature and allowed to stir for one hour. The solvent and excess phosphaalkyne were then removed *in vacuo* to afford a mixture of **2**(98%) and **5**(2%) as a pale yellow oil, (273mg, 98%). Spectroscopic data for **2**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ = 186 (s, $^1J_{P\text{-}Se}$ = 285 Hz)—^1H NMR (C_6D_6) δ = 1.30 (s, 9H, ^{t}Bu), 6.8–7.3 (m, 5H, Ar-H)—^{77}Se NMR (C_6D_6) δ = 338 (d, $^1J_{Se\text{-}P}$ = 282 Hz)—^{13}C NMR (C_6D_6) δ = 192.0 (d, $^1J_{P\text{-}C}$ = 106.7Hz P=$\underline{C}$), 132.2 (d, $^2J_{P\text{-}C}$ = 10.7Hz C=P-Se-$\underline{C}$), 129.7, 129.3, 127.9 (s, Ar), 45.2 (d, $^2J_{P\text{-}C}$ = 15.1Hz $\underline{C}(CH_3)_3$), 30.5 (s, -C($\underline{C}H_3)_3$)—Mass Spec. (EI/CI); m/z (%): 336(10)[M^+], 257(60) [M^+ − Br], 187(10) [PhSeP$^+$], 149(100) [^{t}BuCBr$^+$], 69(63) [^{t}BuC$^+$], 57(87) [^{t}Bu$^+$]—IR (nujol) cm^{-1}: 1578 (m), 740 (s), 691 (s).

E-phenylselenenyl-(1-adamantyl-chloromethylidene)phosphane (3)

To a stirred solution of P≡CAd (150mg, 0.845 mmoles) in diethyl ether(10 ml) at −78°C was added a solution of PhSeCl (162mg, 0.845 mmoles) in diethyl ether (10 ml). After complete addition (ca. 5 mins) the solution was warmed to room temperature and allowed to stir for one hour. The solvent was then removed *in vacuo* to afford a mixture of **3**(88%) and **6**(12%) as a pale yellow solid. Recrystallisation from diethyl ether yielded pale yellow crystals (120mg,

38%), mp: 100–106°C. Spectroscopic data for **3**: $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ = 177.6 (s, $^{1}J_{P\text{-}Se}$ = 276 Hz)—^{1}H NMR (C_6D_6) δ = 1.2–2.0 (m, 15H, Ad-H), 6.6–7.4 (m, 5H, Ar-H)- ^{77}Se NMR (C_6D_6) δ = 293 (d, $^{1}J_{Se\text{-}P}$ = 275 Hz) - ^{13}C NMR (C_6D_6) δ = 192.0 (d, $^{1}J_{P\text{-}C}$ = 96Hz P=$\underline{C}$), 133 (s, C=P-Se-$\underline{C}$ $^{2}J_{P\text{-}C}$ = 10.6 Hz), 129.2, 129.0, 128.3 (s, Ar), 39.9 (d, $^{2}J_{P\text{-}C}$ = 13.7Hz P=C-$\underline{C}$), 38.7 (s, Ad-$\underline{C}H_2$), 36.2 (d, $^{3}J_{P\text{-}C}$ = 9.2 Hz, Ad-$\underline{C}H_2$), 28.2 (s, Ad-$\underline{C}$H)—Mass Spec. (EI/CI); m/z (%): 369(5) [M^+], 334(5) [M^+-Cl], 234(5) [M^+ − Ad], 135(90) [Ad^+], 77(100) [$C_6H_5^+$]—IR (nujol) cm^{-1}: 1788(w), 1718(s), 1579(m). Calculated: C (55.22 %), H (5.45 %) Found: C (55.34 %), H (5.59 %)

Z-t-butyl-(3-phenylselenenyl-2,2-dimethylpropylidene)phosphane (7)

To a solution of **1** (478mg, 1.64mmoles) in diethyl ether (8 ml) at −78°C was added ^{t}BuLi (0.98 ml of 1.7M solution, 1.67 mmoles) over 5 minutes. A black suspension immediately formed which was allowed to warm to room temperature and was stirred for 16 hours. Volatiles were then removed *in vacuo* and the residue extracted with hexane (30 ml) and filtered to give a pale yellow solution. Volatiles were removed from the filtrate and the residue chromatographed (kieselgel, hexane) to give **7** as a pale yellow solid which was recrystallised from hexane at −30°C (90mg, 17.5%) mp: 48–52°C. Spectroscopic data for **7**: $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ = 360.5 (s)—^{1}H NMR (C_6D_6) δ = 1.32 (d, 9H, $^{3}J_{P\text{-}H}$ = 11.4Hz, ^{t}Bu), 1.38 (d, 9H, $^{4}J_{P\text{-}H}$ = 1.9Hz, ^{t}Bu), 6.8–7.3 (m, 5H, Ar-H)—^{77}Se NMR (C_6D_6) δ = 345 (d, $^{2}J_{Se\text{-}P}$ = 15 Hz)—^{13}C NMR (C_6D_6) δ = 191.9 (d, $^{1}J_{P\text{-}C}$ = 79.3Hz P=$\underline{C}$), 136.7 (d $^{3}J_{P\text{-}C}$ = 4.6Hz, P=C-Se-$\underline{C}$;), 129.9, 128.6, 128.0 (s, Ar), 47.0 (d, $^{2}J_{P\text{-}C}$ = 18.3Hz, P=C-$\underline{C}$), 37.4 (d, $^{1}J_{P\text{-}C}$ = 44.3Hz, P-$\underline{C}$), 32.5 (d, $^{2}J_{P\text{-}C}$ = 16.8 Hz, P-C($\underline{C}H_3$)$_3$), 29.4 (d, $^{3}J_{P\text{-}C}$ = 13.7Hz P=C-C-($\underline{C}H_3$)$_3$)—Mass Spec. (EI/CI); m/z (%): 313(20) [M^+], 256(48) [M^+ − ^{t}Bu], 56(15) [M^+ − PhSe], 57(100) [^{t}Bu&rsqb—IR (nujol) cm^{-1} : 1723.7 (m), 1576.6 (m). Accurate MS/EI: M^+—calc. for $^{12}C_{15}{}^{1}H_{23}{}^{80}Se^{31}P$: 314.07026; found: 314.0703

Structure Determinations

Crystals of **6** and **7** suitable for X-ray structure determination were grown from diethyl ether and hexane respectively and mounted in Lindeman capillaries. Intensity data were measured on a CAD4 diffractometer using MoKα radiation. Both structures were solved by direct methods and refined by least squares using the Xtal 3.4 program.[29] The structures were refined on F using data I > 3σ(I). Neutral-atom complex scattering factors were employed.[30] Crystal data, details

TABLE II Crystal data for compounds **6** and **7**

	6	**7**
Chemical formula	$C_{17}H_{21}PClSe$	$C_{15}H_{23}PSe$
Fw	370.7	313.3
Space group	$P\bar{1}$	$P\,c2_{1n}$
a (Å)	9.5958(9)	5.969(3)
b (Å)	9.8336(11)	8.241(2)
c (Å)	10.1610(14)	32.703(3)
α (°)	63.867(15)	90.0
β (°)	86.393(10)	90.0
γ (°)	70.334(8)	90.0
V (Å^3)	806.4(2)	1608.5(8)
Z	2	4
T (K)	298(2)	298(2)
λ (Å)	0.71069	0.71069
ρ calcd. (gcm^{-1})	1.522	1.293
F(000)	378	648
Reflections collected	3097	1769
Observed reflections		
$I > 3\sigma(I)$	1978	707
Crystal size (mm)	0.28 × 0.24 × 0.18	0.32 × 0.22 × 0.20
2θ max(°)	50	50
R	0.067	0.060
wR'	0.078	0.057

of data collections and refinement are given in Table II. Molecular structures are shown in Figures 1 and 2. Anisotropic thermal parameters were refined for all non hydrogen atoms. The hydrogen atoms in both structures were included in calculated positions. Atom coordinates, thermal parameters, hydrogen atom parameters and full lists of bond lengths and angles have been deposited as

TABLE III Fractional atomic coordinates and equivalent isotropic thermal parameters for compound **6**.

	x	y	z	Ueq
Se(1)	0.5676(3)	0.78306	0.60026(5)	0.0517(6)
P(1)	0.3397(9)	0.8894(8)	0.6846(2)	0.055(2)
C(1)	0.384(3)	0.923(3)	0.6338(6)	0.054(8)
C(2)	0.293(3)	1.074(2)	0.6135(5)	0.044(7)
C(3)	0.494(3)	1.188(2)	0.6041(5)	0.048(7)
C(4)	0.131(3)	1.163(3)	0.6418(6)	0.063(9)
C(5)	0.175(3)	1.038(3)	0.5745(5)	0.053(8)
C(7)	0.146(3)	0.612(2)	0.5880(5)	0.057(8)
C(8)	0.010(3)	0.511(3)	0.5649(5)	0.051(8)
C(9)	0.059(3)	0.458(3)	0.5269(6)	0.082(9)
C(10)	0.250(4)	0.503(3)	0.5120(5)	0.08(1)
C(11)	0.409(3)	0.606(2)	0.5309(5)	0.059(8)
C(12)	0.354(3)	0.659(2)	0.5717(6)	0.062(9)
C(13)	0.475(3)	0.701(3)	0.7053(6)	0.069(9)
C(20)	0.737(4)	0.721(2)	0.7037(6)	0.081(1)
C(21)	0.400(3)	0.544(2)	0.6876(5)	0.063(8)
C(22)	0.401(4)	0.706(3)	0.7501(6)	0.09(1)

TABLE IV Fractional atomic coordinates and equivalent isotropic thermal parameters for compound **7**.

	x	*y*	*z*	*Ueq*
Se(1)	0.8591(1)	1.0414(1)	0.1681(1)	0.0579(5)
P(1)	1.1176(3)	0.7818(3)	0.2315(3)	0.060(1)
Cl(1)	1.2359(3)	0.5547(3)	0.2396(3)	0.079(2)
C(1)	0.9370(9)	0.8161(9)	0.2063(8)	0.040(4)
C(2)	0.781(1)	1.0253(9)	0.3526(9)	0.045(4)
C(3)	0.643(1)	1.135(1)	0.3452(9)	0.055(5)
C(4)	0.590(1)	1.135(1)	0.476(1)	0.065(5)
C(5)	0.671(1)	1.026(1)	0.607(1)	0.067(5)
C(6)	0.805(1)	0.919(1)	0.612(1)	0.085(6)
C(7)	0.860(1)	0.918(1)	0.484(1)	0.073(5)
C(8)	0.8373(8)	0.7302(9)	0.1961(8)	0.037(4)
C(9)	0.879(1)	0.560(1)	0.322(1)	0.063(5)
C(10)	0.672(1)	0.817(1)	0.199(1)	0.075(7)
C(11)	0.856(1)	0.721(1)	0.0495(9)	0.059(5)
C(12)	0.782(1)	0.473(1)	0.304(1)	0.068(5)
C(13)	0.622(1)	0.563(1)	0.307(1)	0.075(7)
C(14)	0.575(1)	0.731(1)	0.177(1)	0.074(6)
C(15)	0.604(1)	0.717(1)	0.035(1)	0.076(6)
C(16)	0.762(1)	0.625(1)	0.037(1)	0.076(6)
C(17)	0.806(1)	0.461(1)	0.165(1)	0.075(6)

supplementary material. Further details of the crystal structure investigations are available on request from the director of the Cambridge Crystallographic Data Centre.

Acknowledgements

We gratefully acknowledge the University of Wales for financial support (MDF).

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