New pathways in the reaction between the 1,2,4-triphosphole $P_3C_2Bu^t_2CH(SiMe_3)_2$ and selenium: Crystal and molecular structures of three new cage compounds, $P_3Se_4C_2Bu^t_2CH(SiMe_3)_2$, $P_3Se_3C_2Bu^t_2 H_2CH(SiMe_3)_2$ and $P_5Se_2C_4Bu^t_4(CHSiMe_3Bu^t)$

Sevim Bilgiç [a], Nurgün S. Büyükkıdan [b], Bülent Büyükkıdan [b],
Peter B. Hitchcock [c], John F. Nixon [c,*]

[a] *Department of Chemistry, Arts and Science Faculty, Osmangazi University, Eskihehir, Turkey*
[b] *Department of Chemistry, Arts and Science Faculty, Dumlupınar University, Kütahya, Turkey*
[c] *Department of Chemistry, School of Life Sciences, University of Sussex, Brighton, Sussex BN1 9QJ, UK*

Abstract

Three new, fully structurally characterised cage compounds $P_3Se_4C_2Bu^t_2CH(SiMe_3)$, $P_3Se_3C_2Bu^t_2H_2CH(SiMe_3)_2$ and $P_5Se_2C_4Bu^t_4$ $(CHSiMe_3Bu^t)$, are formed (together with the previously reported 1,2,4-selenadiphosphole, $P_2SeC_2Bu^t_2$) from the reaction of the 1,2, 4-triphosphole $P_3C_2Bu^t_2CH(SiMe_3)_2$, with elemental selenium. Possible mechanistic aspects concerning this and related reactions are discussed.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Phosphorus cages; Selenium; Triphosphole

1. Introduction

There is a considerable interest in the chemistry of phosphole and heterophosphole ring systems and organo-phosphorus cage compounds [1–8]. Regitz and coworkers have described [4 + 2] cycloaddition reactions of both the 1,2,4-thiadiphosphole, $P_2C_2Bu^t_2S$ [9], and the corresponding 1,2,4-oxadiphosphole $P_2C_2Bu^t_2O$ [10] with alkynes R′CCR′. In each case the initial reaction is followed by a further retro Diels–Alder reaction involving the loss of the phospha-alkyne to afford the 1,2-thiaphosphole and 1,2-oxaphosphole, respectively (see Scheme 1). In the case of the 1,2,4-thiadiphosphole a [4 + 2] cycloaddition reaction with the phospha-alkyne, PCBu^t, gives a product which can undergo further a [2 + 2 + 2] cycloaddition with alkynes R′CCR′ to give the novel cage compound shown in Scheme 1 [9].

Likewise, as shown in Scheme 2, phospha-alkynes act as dienophiles in [4 + 2] cycloaddition reactions with the 1,2,4-oxadiphosphole [10] 1,2,4-thiadiphosphole [9,11] and the 1,2,4-selenadiphosphole [12,13]. In these systems the initially formed [4 + 2] cyclo-adduct rapidly undergoes a homo Diels–Alder reaction with a second phospha-alkyne to afford the tetra-phospha cage compounds.

In the case of the 1,2,4-thiadiphosphole [9,11], the homo Diels–Alder reaction of the intermediate bicyclodiene with the phospha-alkyne occurs regiospecifically, but reactions involving either the 1,2,4-selenadiphosphole [12,13] or the 1,2,4-oxadiphosphole [10] afford both regioisomers, which have been fully structurally characterised. The intermediates in these reactions could not be detected even by ^{31}P NMR spectroscopy.

* Corresponding author.
*E-mail address:* J.Nixon@sussex.ac.uk (J.F. Nixon).
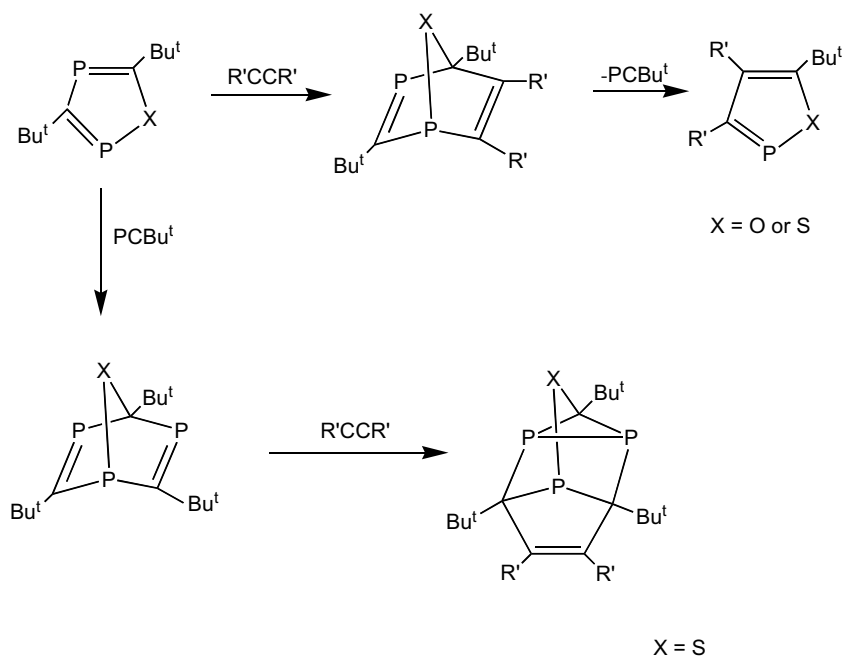
Scheme 1.

2. Results and discussion

Regitz and coworker reported [12,14] the high yield synthesis of the 1,2,4-selenadiphosphole $P_2C_2Bu_2^tSe$ (5) by treatment of selenium with the phospha-alkyne, Bu^tCP, in the presence of NEt_3 and subsequently its structure was established by single crystal X-ray studies on sigma bonded metal pentacarbonyl complexes [15].

We later showed that novel cage compounds $P_3C_3Bu_3^t$ Se_3 and $P_3C_3Bu_3^tSe_4$ (in addition to 5) could also be formed by this route [16]. We also reported the unexpected synthesis of 5 via the reaction between elemental selenium and the 1,2,4-triphosphole [17], $P_3C_2Bu_2^tCH(SiMe_3)_2$ 1 [18].

We now describe further studies involving the reaction of selenium with the 1,2,4-triphosphole ring system 1.

1
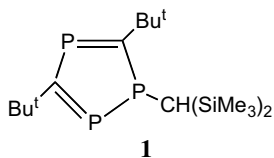
Depending on the reaction time and conditions detailed in the experimental section, the triphosphole P_3C_2Bu-$Bu_2^tCH(SiMe_3)_2$ 1 reacts with selenium in benzene in the presence of NEt_3 to give either $P_3C_2Bu_2^tCH(SiMe_3)_2Se_4$ 2, $P_3C_2Bu_2^tH_2CH(SiMe_3)_2Se_3$ 3, and $P_5C_4Bu_4^t(CHSiMe_3$ $Bu^t)Se_2$ 4, together with the previously reported 1,2,4-selenadiphosphole $P_2C_2Bu_2^tSe$ 5 which is always the major product.

R * = $(Me_3Si)_2CH-$

R** = $(Me_3Si)Bu^tCH-$
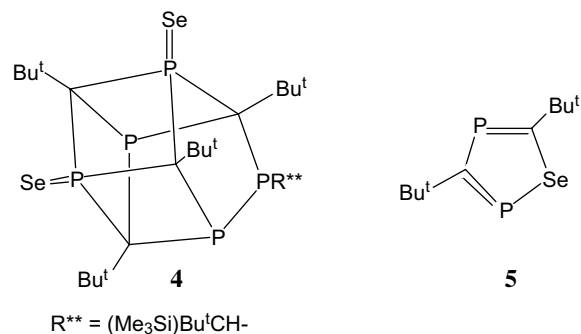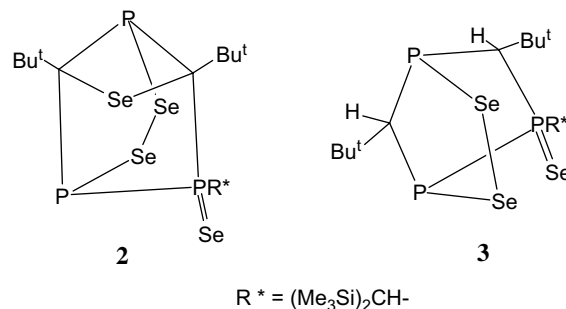
The new compounds 2–4 were identified my mass spectroscopy, elemental analysis and/or multinuclear NMR spectroscopy and confirmed by single crystal X-ray diffraction studies. The peak in the mass spectrum at $m/e = 708$ for 2 showed that the compound contained four more Se atoms than the parent 1,2,4- triphosphole 1, establishing its formula as $P_3C_2Bu_2^tCH(SiMe_3)_2Se_4$.
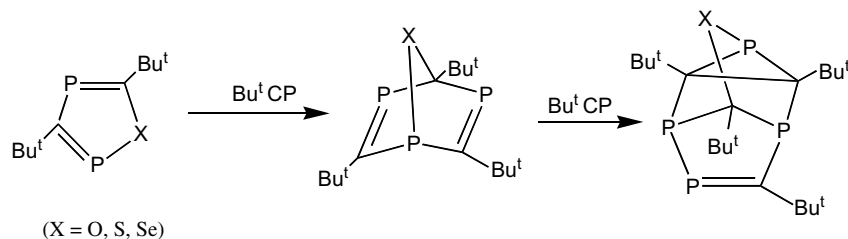
Scheme 2.

The $^{31}P\{^1H\}$ NMR spectrum showed three sharp doublet of doublet resonances at δ 73.0, 87.6 and 105.0, each exhibiting ^{77}Se satellites. The very large one-bond coupling (728 Hz) to ^{77}Se for the resonance at δ 73.0 established it as being pentavalent. The other two resonances also exhibited $^1J(PSe)$ couplings of 344 and 273 Hz, respectively, which are consistent with their assignment as trivalent phosphorus centres. The observation of a large J(PP) coupling constant (269.2 Hz), suggested the presence of a P(III)–P(V) bond. The $^{77}Se\{^1H\}$ NMR spectrum of **2** showed four resonances; three of them exhibiting doublets arising from one bond coupling to phosphorus, while the fourth selenium clearly is bridged between two carbon atoms. (Quoted $^1J(PSe)$ values are taken from the $^{77}Se\{^1H\}$ NMR spectrum.)

The proposed structure based on the spectroscopic data was confirmed by a single crystal X-ray diffraction study. The diffraction was very weak but the structure determina-

tion is sufficient to confirm the overall nature of the compound. There are three, essentially identical, independent molecules in the asymmetric unit, and one of these is illustrated in Fig. 1.

The mass spectrum of **3** showed a parent ion at m/z 630 corresponding to the species $P_3C_2Bu^t_2$ $H_2CH(SiMe_3)_2Se_3$ indicating that it contained one Se less than compound **2** and two H atoms more. Although the $^{31}P\{^1H\}$ NMR spectrum of **3** showed an [ABX] pattern; (A = P(3), B = P(2), X = P(1)); with the expected large $^1J(P(2)P(3))$ coupling (296.2 Hz), both the P(3) and P(1) resonances were very broad and exhibited no further resolvable fine structure. The $^{77}Se\{^1H\}$ NMR spectrum exhibited three distinct doublet resonances. The molecular structure of **3** was confirmed by a single crystal X-ray diffraction study and is shown in Fig. 2.

The likely mechanism of formation of compounds **2**, **3** and **5** can be most easily discussed by consideration of the reaction sequences summarised in Fig. 3.
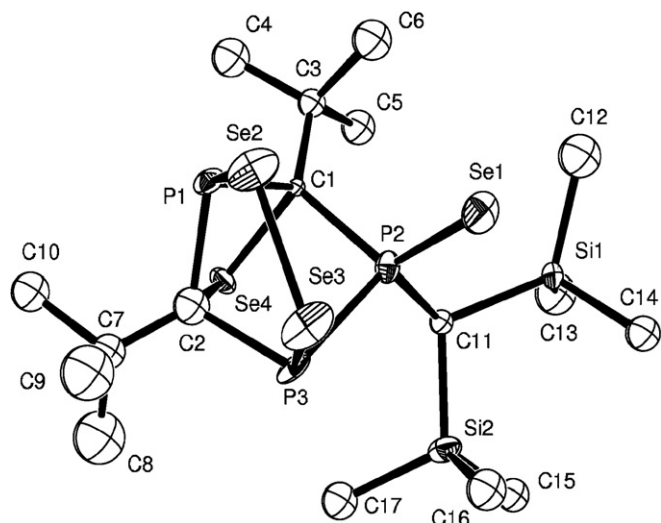

Fig. 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Se(1)–P(2) 2.113(8), Se(2)–P(1) 2.234(8), Se(3)–P(3) 2.217(8), Se(2)–Se(3) 2.398(5), Se(4)–C(2) 2.050(3), Se(4)–C(1) 2.030(2), Se(4)–P(1) 2.671(8), P(1)–C(1) 1.880(2), P(1)–C(2) 1.880(3), P(2)–C(11) 1.820(3), P(2)–C(1) 1.930(2), P(2)–P(3) 2.289(11), P(3)–C(2) 1.880(3), P(1)–Se(2)–Se(3) 98.7(2), P(3)–Se(3)–Se(2) 97.4(3), C(2)–Se(4)–C(1) 79.8(11), C(2)–Se(4)–P(1) 44.5(9), C(1)–Se(4)–P(1) 44.7(7), C(2)–P(1)–C(1) 88.1(13), C(2)–P(1)–Se(2) 104.0(9), C(1)–P(1)–Se(2) 116.4(8), C(2)–P(1)–Se(4) 49.9(9), C(1)–P(1)–Se(4) 49.2(7), Se(2)–P(1)–Se(4) 143.5(4), C(11)–P(2)–C(1) 112.3(11), C(11)–P(2)–Se(1) 110.8(8), C(1)–P(2)–Se(1) 116.9(8), C(11)–P(2)–P(3) 109.1(9), C(1)–P(2)–P(3) 94.4(8), Se(1)–P(2)–P(3) 112.1(4), C(2)–P(3)–Se(3) 102.5(10), C(2)–P(3)–P(2) 95.3(11), Se(3)–P(3)–P(2) 99.4(4).
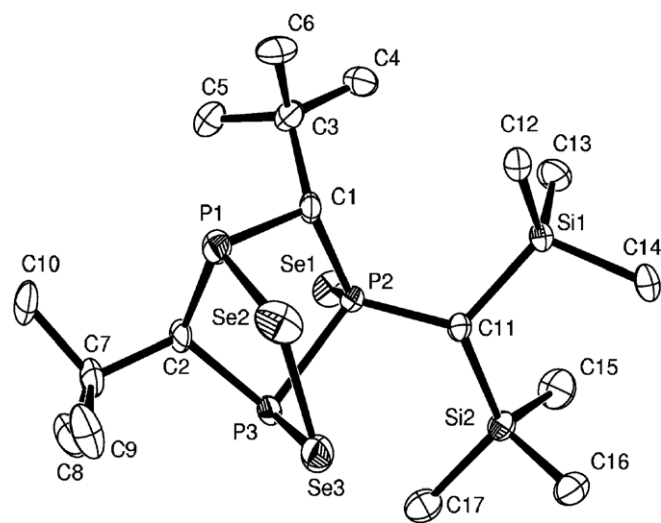

Fig. 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Se(1)–P(2) 2.123(2), Se(2)–P(1) 2.226(2), Se(3)–P(3) 2.228(2), Se(2)–Se(3) 2.384(1), P(1)–C(1) 1.883(6), P(1)–C(2) 1.863(5), P(2)–C(11) 1.825(5), P(2)–C(1) 1.889(5), P(2)–P(3) 2.227(2), P(3)–C(2) 1.856(6), P(1)–Se(2)–Se(3) 99.50(5), P(3)–Se(3)–Se(2) 97.60(5), C(2)–P(1)–C(1) 98.7, C(1)–P(1)–Se(2) 102.8(2), C(2)–P(1)–Se(2) 102.8(2), C(11)–P(2)–C(1) 110.5(2), C(11)–P(2)–Se(1) 115.5(2), C(1)–P(2)–Se(1) 116.9(2), C(11)–P(2)–P(3) 107.5(2), C(1)–P(2)–P(3) 102.5(2), Se(1)–P(2)–P(3) 102.18(7), C(2)–P(3)–P(2) 91.6(2), P(3)–C(2)–P(1) 110.0(3), P(1)–C(1)–P(2) 110.1(3), C(7)–C(2)–P(3) 117.7(4), C(7)–C(2)–P(1) 118.0(4).
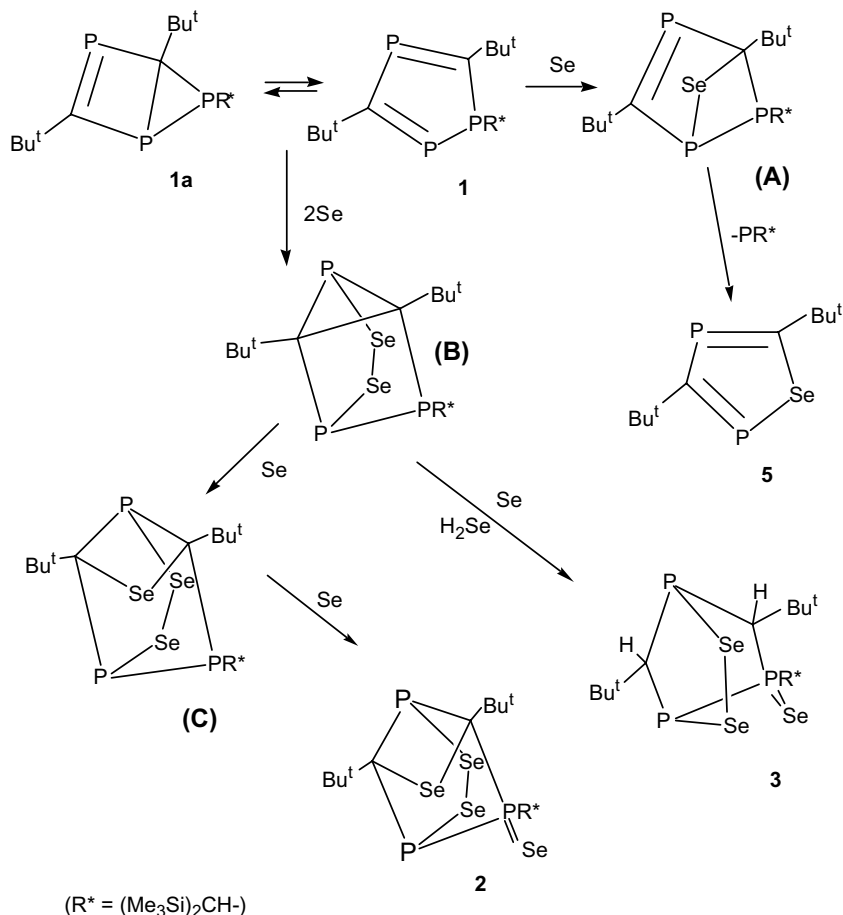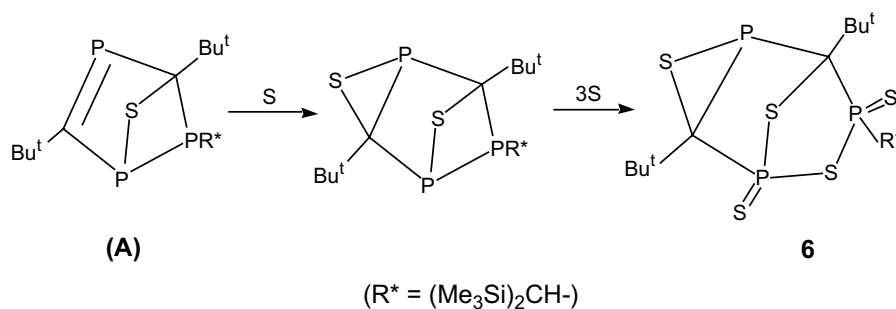
Fig. 3.

Fig. 4.

We showed previously [19] that the 1,2,4-triphosphole **1** can readily undergo an electrocyclic process to afford **1a** in the presence of sunlight. Either species **1** or **1a** could then react further with selenium to afford the intermediate compounds (A) or (B) shown in Fig. 3. Subsequent elimination of the phosphinidine fragment PR* (R* = –CH(SiMe$_3$)$_2$) from (A) would give rise to the aromatic selenadiphosphole **5**. Likewise further addition of Se to (B) would produce the cage compound **2** (*via* cage (C)) and addition of H$_2$Se (possibly generated by hydrolysis of the phosphinidine selenide, Se = PR*) would afford the cage compound **3**. Strong sup-

port for the involvement of the postulated intermediate (A), containing a bridging Se, comes from our previously reported [18] isolation and full structural characterisation of the pentasulphide P$_3$S$_5$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$, **6**, which was *exclusively* formed in the analogous reaction of the 1,2,4-triphosphole **1** with elemental sulphur.

Fig. 4 shows the likely stepwise formation of the pentasulphide which contains two pentavalent and one trivalent phosphorus centre.

The third product **4** from the reaction of 1,2,4-triphosphole **1** with selenium clearly results from a different path-
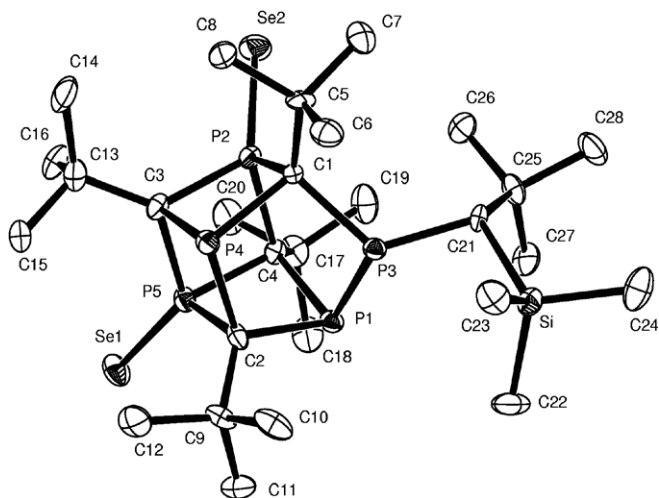
Fig. 5. Molecular structure of **4** selected bond lengths (Å) and angles (°): Se(1)–P(5) 2.085(2), Se(2)–P(2) 2.091(2), P(1)–C(2) 1.890(6), P(1)–C(4) 1.910(6), P(1)–P(3) 2.159(2), P(2)–C(1) 1.880(6), P(2)–C(3) 1.885(6), P(2)–C(4) 1.897(7), P(3)–C(21) 1.870(6), P(3)–C(1) 1.875(6), P(4)–C(1) 1.914(6), P(4)–C(3) 1.925(6), P(4)–C(2) 1.923(7), P(5)–C(2) 1.844(6), P(5)–C(3) 1.845(6), P(5)–C(4) 1.871(6), C(2)–P(1)–C(4) 85.1(3), C(2)–P(1)–P(3) 89.9(2), C(4)–P(1)–P(3) 106.1(2), C(1)–P(2)–C(3) 91.1(3), C(1)–P(2)–C(4) 102.5(3), C(3)–P(2)–C(4) 87.9(3), C(1)–P(2)–Se(2) 121.5(2), C(3)–P(2)–Se(2) 123.9(2), C(4)–P(2)–Se(2) 121.8(2), C(21)–P(3)–P(1) 115.8(2), C(1)–P(3)–P(1) 94.0(2), C(1)–P(4)–C(3) 88.9(3), C(1)–P(4)–C(2) 99.5(3), C(3)–P(4)–C(2) 86.4(3), C(2)–P(5)–C(3) 91.1(3), C(2)–P(5)–C(4) 87.5(3), C(3)–P(5)–C(4) 89.9(3), C(2)–P(5)–Se(1) 123.6(2), C(3)–P(5)–Se(1) 127.8(2), C(4)–P(5)–Se(1) 125.3(2).

way to those described above. The cage compound **4** exhibited a parent ion in the mass spectrum at $m/z = 734$ corresponding to the compound $P_5C_4Bu_4^t(CHSiMe_3Bu^t)Se_2$. The $^{31}P\{^1H\}$ NMR spectrum of **4** consists of five distinct resonances whose chemical shifts are all typical for the presence of saturated phosphorus atoms lying within a cage structure. Of special structural significance are the signals at δ 67.9 P(5) and 99.4 P(2), which both show large one bond P–Se couplings (804 Hz and 824 Hz, respectively), which can be easily assigned to pentavalent phosphorus atoms doubly bonded to Se. The signals at δ 14.4 for P(3), δ 33.5 for P(4), and δ 50.3 for P(1) are all typical for saturated trivalent phosphorus centres and exhibit multiple fine structure. One very large doublet coupling ($^1J(P(1)P(3))$ 327.8 Hz) arises from the two directly bonded phosphorus atoms. As expected the ^{77}Se NMR spectrum showed two doublets from coupling to the pentavalent P = Se atoms. The molecular structure of **4** was confirmed by a single crystal X-ray diffraction study and is shown in Fig. 5.

Interestingly, the cage compound **4** structurally resembles the well known tetraphosphacubane, $P_4C_4Bu_4^t$, first reported by Regitz and coworkers from cyclotetamerisation of the phospha-alkyne PCBu^t, into which a phosphinidene fragment PR has been inserted into one of the cube edges.

In view of the established cyclodimerisation mechanism involving the intermediate 1,3-diphosphacyclobutadiene ring to afford the tetraphosphacubane, we tentatively propose a mechanism involving this intermediate as shown in Fig. 6. The [2 + 2] cycloaddition of the 1,2,4-triphosphole with the 1,3-diphosphacyclobutadiene would afford a compound of type (D) (following oxidation of two of the cage phosphorus centres by Se).

However, unexpectedly, the actual isolated compound **4** has a slightly different composition to (D), because the organic substituent R of the phosphinidene fragment, PR, is found to be –CH(SiMe$_3$)Bu^t and not the expected –CH(SiMe$_3$)$_2$. We suggest that this may be the result of a light induced radical reaction, since we and others [20], have previously noticed that in alkylation reactions of the $P_3C_2Bu_2^t$ anion with BrCH(SiMe$_3$)$_2$ which afford mainly the expected 1,2,4 triphosphole $P_3C_2Bu_2^t$ CH(SiMe$_3$)$_2$ **1**, on occasions also gave two isomeric organophosphorus cage compounds, $P_6C_4Bu_4^t$CHSiMe$_3$ (albeit in rather low yield) with partial elimination of the –CH(SiMe$_3$) side-chain.

In support of this proposal, we subsequently found that the reaction between **1** and the stable organometallic radical cobaltocene, [Co(η^5-C$_5$H$_5$)$_2$], readily afforded the two novel cage compounds [Co(η^5-C$_5$H$_5$)(η^4-C$_4$H$_4$CHCHP$_6$-C$_4$Bu$_4^t$)] and $P_6C_4Bu_4^t$CH(SiMe$_3$) shown below in Fig. 7 [21].

Also noteworthy in this context, are our recently described [8i], structurally related series of cages containing an additional heteroatom, $P_6C_4Bu_4^tE$ (**1**) (E = S, Se, Te).

These chalcogen containing compounds were obtained by an unprecedented reaction involving the facile specific insertion reaction into a P–P bond of the hexaphosphaprismane, $P_6C_4Bu_4^t$.

3. Experimental

All manipulations (unless otherwise stated) were conducted in an inert atmosphere of argon or dinitrogen using a dual vacuum/argon (or dinitrogen) line, employing conventional Schlenk line techniques. All solvents were predried by distillation under dinitrogen over the appropriate drying agent and subsequently degassed and stored in glass ampoules under argon in the presence of a sodium (or potassium) mirror. All glassware, cannulae and Celite were stored in an oven (>373 K) and glassware and Celite were flame-dried *in vacuo* immediately prior to use. Solution NMR spectra were recorded on Brüker ACP250, WM360, DMX300, DMX400 or AMX500 instruments at ambient temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on a Kratos MS80RF instrument in the School of Chemistry at the University of Sussex by Dr. A. Abdul-Sada. Microanalyses were performed by Medac Ltd. (UK).

4. Experiment 1

The triphosphole **1** and selenium were heated at 80 °C for 2 h and the solution filtered to separate the excess of selenium and the solvent removed *in vacuo*. The residue was chromatographed (Florosil/p.e. 60–80 °C) to give **5**
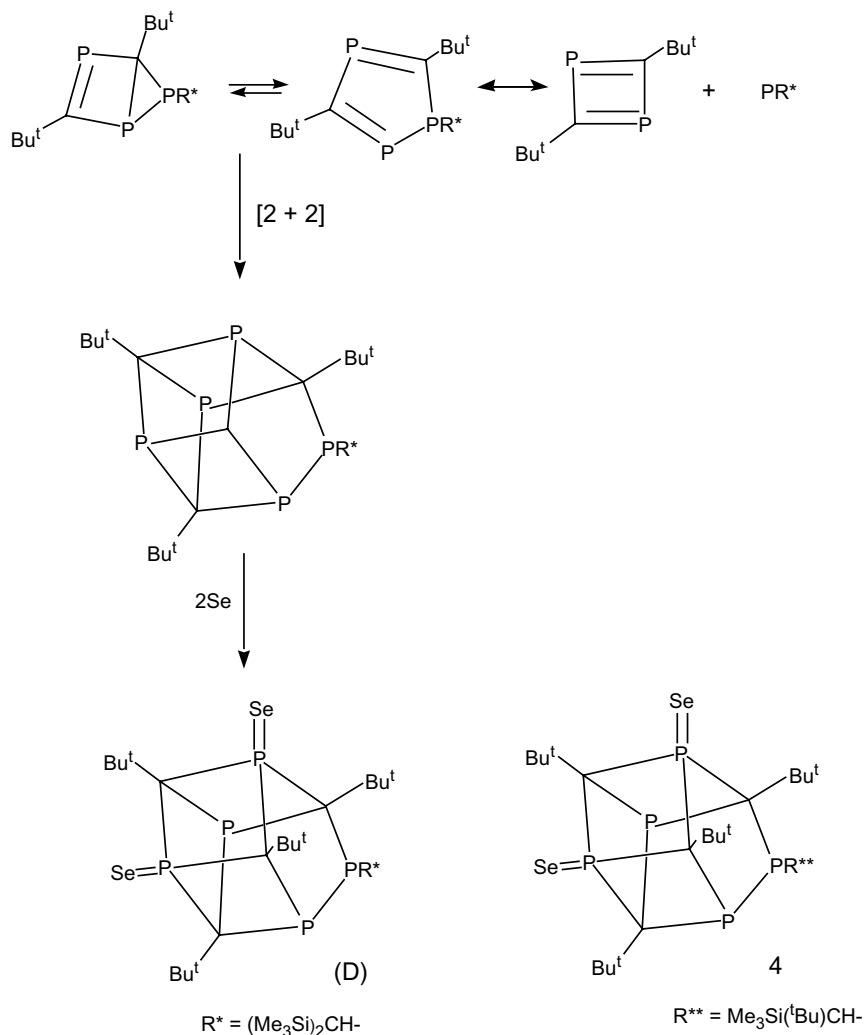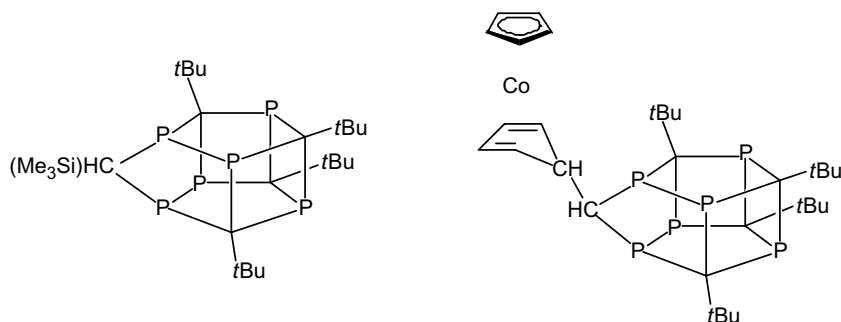
Fig. 6.

Fig. 7.

as the expected main product and two new compounds $P_3C_2Bu^t_2$ CH(SiMe$_3$)$_2$Se$_4$ **2** as orange–red crystals (6.2 %) and $P_3C_2Bu^t_2$ H$_2$CH(SiMe$_3$)$_2$Se$_3$ **3** as red crystals (5.3%).

For **2**: ^{31}P{^{1}H} NMR (121.49 MHz, C$_6$D$_6$) (for numbering scheme see crystal structure): δ 105.0 P(3), dd, ^1J(P(3)P(2)) 269.2, ^1J(PSe) 728, ^2J(P(3)P(1)) 7.2 Hz; δ 87.6 P(1), dd, ^2J(P(1)P(3)) 22.5, ^2J(P(1)P(2)) 7.2 Hz; δ 73.0 P(3), dd, ^1J(^{31}P^{31}P) 269.2, ^2J(^{31}P^{31}P) 22.6 Hz.

^{77}Se{^{1}H} NMR (95.4 MHz, CDCl$_3$): δ 731 Se(3), d, ^1J(PSe) 344, δ 590 Se(2), dt, ^1J(PSe) 275, ^2J(PSe) 53 Hz; δ 299.0 Se(4), ddd, ^2J(PSe) 52.9, ^2J(PSe) 22, ^2J(PSe) 6 Hz; δ 74.6 Se(1), d, ^1J(PSe) 728 Hz.

^{1}H NMR (300.1 MHz, C$_6$D$_6$)δ 1.61 [CH], d, ^2J(HP) 15.3 Hz; δ 1.05 [CBu^t], s, δ 0.34 [Si(CH$_3$)$_3$], s, δ 0.22 [Si(CH$_3$)$_3$], s. EI-MS: m/z 708 [P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$Se$_4$]$^+$, 630 [P$_3$C$_2$Bu$^t_2$-CH(SiMe$_3$)$_2$Se$_3$]$^+$, 390[P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$]$^+$.

Crystal data for **2**: $C_{17}H_{39}P_3$ Se_4Si_2, $M = 706.4$, monoclinic, space group $P2_1/c$ (no. 14), $a = 30.004(11)$, $b = 14.794(3)$, $c = 18.700(7)$ Å, $\beta = 99.43(3)°$, $V = 8188(5)$ Å^3, $T = 173(2)$ K, $Z = 12$, $D_c = 1.72$ Mg m^{-3}, $\mu = 5.64$ mm^{-1}, $\lambda = 0.71073$ Å, crystal size $0.40 \times 0.05 \times 0.02$ mm^3, 11 362 measured reflections, 11 362 independent reflections, 4618 reflections with $I > 2\sigma(I)$, Final indices $R_1 = 0.105$, $wR_2 = 0.200$ for $I > 2\sigma(I)$, $R_1 = 0.259$, $wR_2 = 0.295$ for all data. Data collection: Enraf Nonius CAD4. Structure solution SHELXS-86. Refinement using SHELXL-93. Diffraction was very weak. C atoms were left isotropic. P, Se and Si were anisotropic, except for one P atom which otherwise went non-positive-definite.

For **3**: $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6) (numbering scheme as in crystal structure): [ABX] see text; δ 97.4 P(1), vbr s; δ 72.4 P(3), v br, $^1J(P(3)P(2))$ 296.2 Hz, δ 65.0 P(2), $^1J(P(2)P(3))$ 296.2, $^2J(P(2)P(1))$ 27.9 Hz, $^{77}Se\{^1H\}$ NMR (95.4 MHz, CDCl$_3$): δ 413, Se(2), d, $^1J(PSe)$ 242 Hz; δ 320 Se(3), d, $^1J(PSe)$ 181 Hz; δ −125 Se(1), d, $^1J(PSe)$ 681 Hz.

EI-MS: m/z 630 $[P_3C_2Bu_2^tH_2CH(SiMe_3)_2Se_3]^+$, 552 $[P_3C_2Bu_2^tH_2CH(SiMe_3)_2Se_2]^+$.

Crystal data for **3**: $C_{17}H_{39}P_3$ Se_3Si_2, $M = 629.5$, monoclinic, space group $P2_1/c$ (no. 14), $a = 7.433(2)$, $b = 17.365(11)$, $c = 21.100(6)$ Å, $\beta = 98.54(2)°$, $V = 2693(2)$ Å^3, $T = 173(2)$ K, $Z = 4$, $D_c = 1.55$ Mgm^{-3}, $\mu = 4.37$ mm^{-1}, $\lambda = 0.71073$ Å, crystal size $0.25 \times 0.20 \times 0.10$ mm^3, 3732 measured reflections, 3732 independent reflections, 2829 reflections with $I > 2\sigma$ (I), final indices $R_1 = 0.041$, $wR_2 = 0.088$ for $I > 2\sigma(I)$, $R_1 = 0.067$, $wR_2 = 0.099$ for all data. Data collection: Enraf Nonius CAD4. Structure solution SHELXS-86. Refinement using SHELXL-93.

5. Experiment 2

In a similar way selenium was treated with **1** in benzene for 1 h at 80 °C to give **5** as the expected main product together with colourless crystals of $P_5C_4Bu_4^t(CHSiMe_3Bu^t)Se_2$ **4** (2.6 %). Elemental analysis: Found C: 46.2, H: 7.6; $C_{28}H_{55}P_5Se_2Si$ requires C: 45.9, H: 7.6%. EI-MS: m/z 734 $[P_5C_4Bu_4^t(CHSiMe_3Bu^t)Se_2]^+$, 654 $[P_5C_4Bu_4^t-(CHSiMe_3Bu^t)Se]^+$, 73 $[SiMe_3]^+$.

For **4** $^{31}P\{^1H\}$ NMR (121.49 MHz, CDCl$_3$) (numbering scheme as in crystal structure): δ 99.4 P(2), m, $^1J(P(2)Se(2))$ 824, $^2J(P(2)P(3))$ 30.5, $^2J(P(2)P(5))$ 14.2, $^2J(P(2)P(4))$ 4.2 Hz; δ 67.9 P(5), m, $^1J(P(5)Se(1))$ 804, $^2J(P(5)P(1))$ 70.6, $^2J(P(5)P(3))$ 23.0 Hz; δ 50.3 P(1), dddd, $^1J(P(1)P(3))$ 327.8, $^2J(P(1)P(4))$ 121.3, $^2J(P(1)P(5))$ 70.6, $^2J(P(1)P(2))$ 14.2 Hz; δ 33.5 P(4), m, $^2J(P(4)P(1))$ 121.3, $^2J(P(4)P(2))$ 4.2 Hz; δ 14.4 P(3), ddd, $^1J(P(3)P(1))$ 327.8, $^2J(P(3)P(2))$ 30.5, $^2J(P(3)P(5))$ 23.0 Hz.

$^{77}Se\{^1H\}$ NMR (95.4 MHz, CDCl$_3$): δ 181 Se(1), d, $^1J(PSe)$ 804 Hz; δ 101.4 Se(2), d, $^1J(PSe)$ 824 Hz.

Crystal data: for **4**: $C_{28}H_{55}P_5Se_2Si$, $M = 732.6$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.240(2)$, $b = 16.618(4)$, $c = 16.923(3)$ Å, $\beta = 97.660(10)°$, $V = 3411.5$ (12) Å^3, $T = 173(2)$ K, $Z = 4$, $D_c = 1.43$ Mg m^{-3}, $\mu =$ 2.45 mm^{-1}, $\lambda = 0.71073$ Å, crystal size $0.25 \times 0.20 \times 0.15$ mm^3, 8572 measured reflections, 8213 independent reflections ($R_{int} = 0.0595$), 4272 reflections with $I > 2\sigma(I)$, Final indices $R_1 = 0.070$, $wR_2 = 0.109$ for $I > 2\sigma(I)$, $R_1 = 0.169$, $wR_2 = 0.144$ for all data. Data collection: Enraf Nonius CAD4. Structure solution SHELXS-86. Refinement using SHELXL-93.

References

[1] R. Streubel, Angew. Chem., Int. Ed. Eng. 3 (1995) 436, and references therein.
[2] A. Mack, M. Regitz, in: K.K. Laali (Ed.), Carbocyclic and Heterocyclic Cage Compounds and Their Building Blocks, J.A.I. Press, Stamford, CT, USA, 1999, p. 199.
[3] J.F. Nixon, in: K.K. Laali (Ed.), Carbocyclic and Heterocyclic Cage Compounds and Their Building Blocks, J.A.I. Press, Stamford, CT, USA, 1999, p. 257.
[4] L. Weber, Adv. Organomet. Chem. 41 (1997) 1.
[5] K. B. Dillon, F. Mathey, J. F. Nixon, Chapter 4, in Phosphorus: The Carbon Copy, J. Wiley, Chichester, 1998.
[6] A. Schmidpeter, Chapter 4 in: F. Mathey (Ed.), Phosphorus–Carbon Heterocyclic Chemistry the Rise of a New Domain, Pergamon 2001, and references therein.
[7] M. Regitz, A. Hoffmann, U. Bergsträsser, in: P.J. Stang, F. Diederich (Eds.), Modern Acetylene Chemistry, VCH Weinheim, 1995.
[8] (a) B. Geissler, S. Barth, U. Bergsträsser, M. Slany, J. Durkin, P.B. Hitchcock, M. Hofmann, P. Binger, J.F. Nixon, P.vonR. Schleyer, M. Regitz, Angew. Chem., Int. Ed. Engl. 34 (1995) 484;
(b) V. Caliman, P.B. Hitchcock, J.F. Nixon, M. Hofmann, P.vonR. Schleyer, Angew. Chem., Int. Ed. Engl. 33 (1994) 2202;
(c) B. Geissler, T. Wettling, S. Barth, P. Binger, M. Regitz, Synthesis (1994) 1337;
(d) F. Tabellion, A. Nachbauer, S. Leininger, C. Peters, F. Preuss, M. Regitz, Angew. Chem., Int. Ed. Engl. 37 (1998) 1233;
(e) T. Wettling, J. Schneider, O. Wagner, C.G. Kreiter, M. Regitz, Angew. Chem., Int. Ed. Engl. 28 (1989) 1013;
(f) R. Bartsch, P.B. Hitchcock, J.F. Nixon, J. Organomet. Chem. 375 (1989) C31–C34;
(g) M.M. Al-Ktaifani, W. Bauer, U. Bergsträsser, B. Breit, M.D. Francis, F.W. Heinemann, P.B. Hitchcock, A. Mack, J.F. Nixon, H. Pritzkow, M. Regitz, M. Zeller, U. Zenneck, Chem. Eur. J. 8 (2002) 2622;
(h) A.G. Avent, F.G.N. Cloke, M.D. Francis, P.B. Hitchcock, J.F. Nixon, J.C.S. Chem. Commun. (2000) 879;
(i) M.M. Al-Ktaifani, D.P. Chapman, M.D. Francis, P.B. Hitchcock, J.F. Nixon, L. Nyulászi, Angew. Chem., Int. Ed. Engl. 40 (2001) 3474;
(j) M.M. Al- Ktaifani, P.B. Hitchcock, J.F. Nixon, Inorg. Chim. Acta 356 (2003) 103.
[9] J. Dietz, T. Schmidt, J. Renner, U. Bergsträsser, F. Tabellion, F. Preuss, P. Binger, H. Heydt, M. Regitz, Eur. J. Org. Chem. (2002) 1664.
[10] A. Mack, U. Bergsträsser, G.J. Reiss, M. Regitz, Eur. J. Org. Chem. (1999) 587.
[11] S.E. d'Arbeloff-Wilson, P.B. Hitchcock, J.F. Nixon, L. Nyulaszi, J. Organomet. Chem. 655 (2002) 7.

[12] S.M.F. Asmus, U. Bergsträsser, M. Regitz, Synthesis (1999) 1642.
[13] S.M.F. Asmus, G. Seeber, U. Bergsträsser, M. Regitz, Heteroatom Chem. 12 (2001) 406.
[14] M. Regitz, S. Krill, Phosphorus, Sulfur, Silicon Related Elements 115 (1996) 99.
[15] M.D. Francis, D.E. Hibbs, P.B. Hitchcock, M.B. Hursthouse, C. Jones, T. Mackewitz, J.F. Nixon, L. Nyulászi, M. Regitz, N. Sakarya, J. Organomet. Chem. 580 (1999) 156.
[16] P.B. Hitchcock, J.F. Nixon, N. Sakarya, J.C.S. Chem. Commun. (2000) 1745.
[17] V. Caliman, P.B. Hitchcock, J.F. Nixon, J.C.S. Chem. Commun. (1995) 1661.
[18] V. Caliman, P.B. Hitchcock, J.F. Nixon, N. Sakarya, Bull. Soc. Chim. Belg. 105 (1996) 675.
[19] S.M. Bachrach, V. Caliman, J.F. Nixon, J.C.S. Chem. Commun. (1995) 2395.
[20] M.H. Araujo, V. Caliman, E.E. Castellano, A.C. Doriguetto, J. Ellena, P.B. Hitchcock, D.A. Rajão, J. Brazilian Chem. 13 (2002) 555.
[21] P.B. Hitchcock, J.F. Nixon, N. Sakarya Buyukkidan, J.C.S. Chem. Commun. (2001) 2720.