ChemComm

Syntheses of the novel cage compounds $\mathrm{P_3Se_3C_3Bu^t{}_3}$ and $\mathrm{P_3Se_4C_3Bu^t{}_3}$ and an unusual insertion reaction of $\mathrm{[PtCl_2(PMe_3)]}$ into the Se–Se bond of the latter to give the six-coordinate Pt(IV) complex $\mathrm{[PtCl_2(PMe_3)P_3Se_4C_3Bu^t{}_3]}$

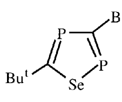
Peter B. Hitchcock, John F. Nixon* and Nurgün Sakarya

School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, Sussex, UK BN1 9QJ.
E-mail: J.Nixon@sussex.ac.uk

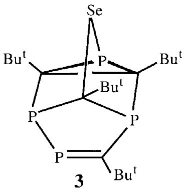
Received (in Cambridge, UK) 26th June 2000, Accepted 2nd August 2000
First published as an Advance Article on the web 29th August 2000

The novel cage compounds $\mathrm{P_3Se_3C_3Bu^t{}_3}$ and $\mathrm{P_3Se_4C_3Bu^t{}_3}$ are formed (together with the 1,2,4-selenadiphosphole $\mathrm{P_2SeC_2Bu^t{}_2}$) from the reaction of the phosphaalkyne $\mathrm{Bu^tCP}$ with selenium; the $\mathrm{[PtCl_2(PMe_3)]}$ fragment undergoes an unusual insertion reaction into the Se–Se bond of $\mathrm{P_3Se_4C_3Bu^t{}_3}$.

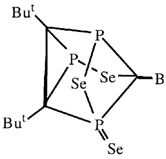
There is current interest in the chemistry of (i) low-coordinate phosphorus compounds, (ii) phospholes containing additional heteroatoms and (iii) novel phosphorus containing cage compounds.[1–14] Regitz and coworkers have recently described[15] the facile, high-yield, synthesis of the previously known[8,9] 1,2,4-selenadiphosphole $\mathrm{P_2SeC_2Bu^t{}_2}$ **1** by treatment of selenium with the phosphaalkyne $\mathrm{Bu^tCP}$ **2** in the presence of $\mathrm{NEt_3}$. The ready [2 + 2 + 2] cycloaddition reaction of **1** with two further mol of **2** to yield the tetracyclic cage compound $\mathrm{P_4SeC_4Bu^t{}_4}$ **3**, prompts us to describe the syntheses and structural characterisation of two new cages $\mathrm{P_3Se_3C_3Bu^t{}_3}$ **4** and $\mathrm{P_3Se_4C_3Bu^t{}_3}$ **5**, both also derived from **1**. We also report an unusual oxidation of a Pt(II) complex to a Pt(IV) complex *via* insertion of the Pt(II) into the Se–Se bond of **5**.



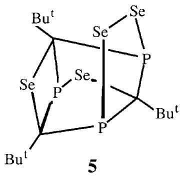
1



3



4



5

Treatment of a suspension of a slight excess of selenium in toluene with **2** for 4 days at 75 °C, afforded **1** as the expected main product, which was removed by sublimation. The residue was chromatographed (Florisil/hexane) to give colourless crystals of $\mathrm{P_3Se_3C_3Bu^t{}_3}$ **4** (5.3%) and red crystals of $\mathrm{P_3Se_4C_3Bu^t{}_3}$ **5** (7%). ^{1}H, ^{31}P and ^{77}Se NMR data for **4** and **5** were entirely consistent with the proposed structures,† which were also confirmed by single crystal X-ray diffraction studies. The molecular structures of **4**‡ and **5**‡ are shown in Fig. 1 and 2. Both cages are most likely to have been derived from a common intermediate **6**, which would be formed *via* the initial [4 + 2] cycloaddition reaction of **1** with **2**.

Thus **4** probably arises from (i) insertion of Se, still present in the reaction mixture, into the weak P–P bond (resulting from the intramolecular [2 + 2] cycloaddition cage-formation step) of the intermediate **6** and (ii) a second exocyclic Se addition to one of these phosphorus atoms. Likewise, in an analogous way, the more symmetrical cage compound **5** would result from insertion of $\mathrm{Se_2}$ into the P–P bond, as well as a separate single Se atom insertion into the C–C bond of the initially formed strained three-membered CPC ring. Compound **5** is noteworthy because

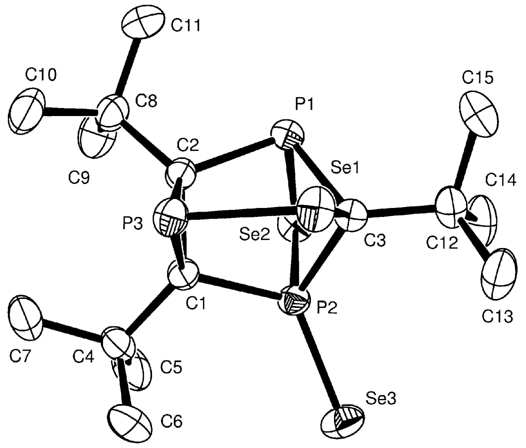


Fig. 1 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Se(1)–C(3) 1.980(2), Se(1)–P(3) 2.2392(8), Se(2)–P(2) 2.2707(7), Se(2)–P(1) 2.3023(7), Se(3)–P(2) 2.0862(7), P(1)–C(3) 1.890(3), P(1)–C(2) 1.892(3), P(2)–C(3) 1.839(3), P(2)–C(1) 1.886(3), P(3)–C(1) 1.857(2), P(3)–C(2) 1.858(3); C(3)–Se(1)–P(3) 91.61(8), P(2)–Se(2)–P(1) 70.81(2), C(3)–P(1)–C(1) 95.24(12), C(3)–P(1)–Se(2) 87.22(8), C(2)–P(1)–Se(2) 94.31(8), C(3)–P(1)–P(2) 43.96(8), C(2)–P(1)–P(2) 71.83(8), Se(2)–P(1)–P(2) 54.04(2), C(3)–P(2)–C(1) 98.22(11), C(3)–P(2)–Se(3) 20.49(9).

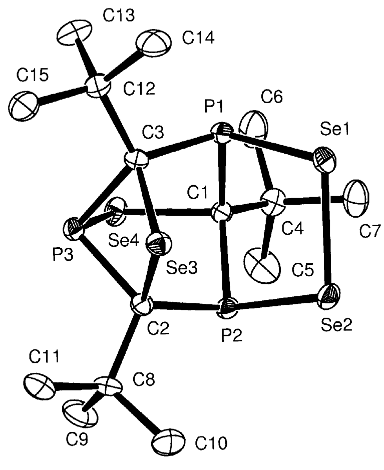
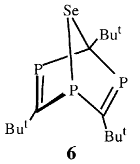


Fig. 2 Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Se(1)–P(1) 2.2260(13), Se(1)–Se(2) 2.3966(9), Se(2)–P(2) 2.2267(14), Se(4)–P(3) 2.2445(14), Se(4)–C(1) 2.016(4), Se(3)–C(2) 1.998(4), Se(3)–C(3) 1.997(4), P(1)–C(1) 1.874(4), P(1)–C(3) 1.900(4), P(2)–C(1) 1.885(4), P(2)–C(2) 1.890(4): P(3)–C(2) 1.862(4), P(3)–C(3) 1.867(4); P(1)–Se(1)–Se(2) 99.32(4), P(2)–Se(2)–Se(1) 99.16(4), C(3)–Se(3)–C(2) 79.51(17), C(1)–Se(4)–P(3) 89.22(13), C(1)–P(1)–C(3) 101.13(19), C(1)–P(1)–Se(1) 102.37(13).

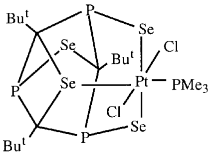
DOI: 10.1039/b005123n



6

although homonuclear S–S bonds are common in monocyclic $(RP)_xS_y$ systems, analogous Se–Se bonded compounds are rare.[16]

Interestingly, the cage compound **5** undergoes an unexpected reaction with $[PtCl_2(PMe_3)]_2$. It was anticipated that simple η^1-coordination would occur, *via* either the P or Se lone pair electrons, however the platinum(II) fragment also unexpectedly inserts into the Se(1)–Se(2) bond of **5** as well as undergoing ligation to Se(3) of the four-membered P(3)C(3)Se(3)C(2) ring, to afford the novel deep-red Pt(IV) complex $[PtCl_2(PMe_3)\text{-}P_3Se_4C_3Bu^t{}_3]$ **7** (55.8%).[§]



7

The latter was fully structurally characterised by a single crystal X-ray diffraction study[‡] and its molecular structure is shown in Fig. 3.

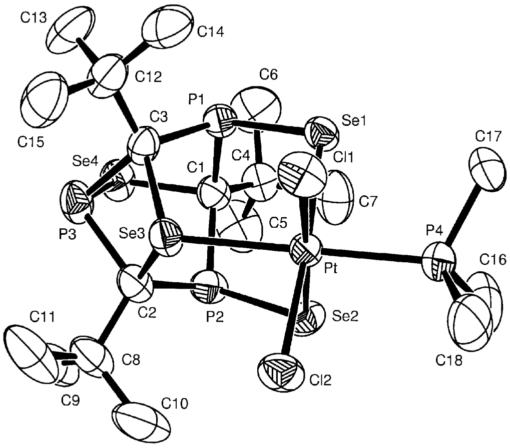


Fig. 3 Molecular structure of **7**. Selected bond lengths (Å) and angles (°): Pt–P(4) 2.3103(13), Pt–Cl(1) 2.4120(14), Pt–Cl(2) 2.4241(12), Pt–Se(2) 2.4434(6), Pt–Se(1) 2.4493(5), Pt–Se(3) 2.4679(5), Se(1)–P(1) 2.2266(13), Se(2)–P(2) 2.2175(14), Se(4)–P(3) 2.2301(16), Se(4)–C(1) 2.007(5), Se(3)–C(2) 2.026(5), Se(3)–C(3) 2.030(5), P(1)–C(1) 1.869(5), P(1)–C(3) 1.869(5), P(2)–C(1) 1.885(5), P(2)–C(2) 1.872(6): P(3)–C(2) 1.890(6), P(3)–C(3) 1.889(5); P(4)–Pt–Cl(1) 88.03(5), P(4)–Pt–Cl(2) 92.33(5), Cl(1)–Pt–Cl(2) 89.28(5), P(1)–Pt–Se(2) 93.57(4).

We thank the Turkish government for a research grant (for N. S.) and the British Council for financial support for part of this work.

Notes and references

† *NMR data*: for **4**: $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 80.7 [P(2), dd, $^2J(^{31}P^{31}P)$ 53.3, $^1J(^{31}P^{77}Se)$ 208.4, $^2J(^{31}P^{31}P)$ 53.3 Hz], 21.5 [P(3), d, $^1J(^{31}P^{77}Se)$ 170.4, $^2J(^{31}P^{31}P)$ 51.3 Hz], −54.2 [P(1), d, $^1J(^{31}P^{77}Se)$ 203.0, $^2J(^{31}P^{77}Se)$ 48.1 Hz]. For **5**: ^1H NMR (toluene-d_8): δ 0.80 (s, 18H, ^{t}Bu), 0.97 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 74.5 [P(1) and P(2), d, $^2J(^{31}P^{31}P)$ 7.2, $^1J(^{31}P^{77}Se)$ 317.4, $^2J(^{31}P^{77}Se)$ 0.4, 14.0 Hz], −36.0 [P(3), t, $^1J(^{31}P^{77}Se)$ 177.8, $^2J(^{31}P^{77}Se)$ 42.1, $^2J(^{31}P^{77}Se)$ 14.5 Hz]. $^{77}Se\{^1H\}$ NMR: δ 256.5 [Se(4), dt, $^1J(^{31}P^{77}Se)$ 177.8, $^2J(^{31}P^{77}Se)$ 23.2 Hz], 514.3 [Se(3), d, $^2J(^{31}P^{77}Se)$ 52.5], 67.6 [Se(1) and Se(2), m, $^1J(^{31}P^{77}Se)$ 317.4, $^2J(^{31}P^{77}Se)$ 40.3, $^2J(^{31}P^{77}Se)$ 15.4 Hz].

‡ *Crystal data*: **4** $C_{15}H_{27}P_3Se_3$, $M = 537.16$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.7751(3)$, $b = 16.2798(7)$, $c = 11.6992(3)$ Å, $\beta = 102.264(2)°$, $U = 2005.4(1)$ Å^3, $Z = 4$, $D_c = 1.78$ Mg m^{-3}, crystal dimensions $0.2 \times 0.1 \times 0.1$ mm, $F(000) = 1056$, $T = 293(2)$ K, Mo-Kα radiation, $\lambda = 0.71073$ Å. Data collection Kappa CCD, 16312 reflections collected, 5787 independent ($R_{int} = 0.0498$), $R1 = 0.038$, $wR2 = 0.083$ for 4569 reflections with $I > 2\sigma(I)$, $R1 = 0.055$, $wR2 = 0.090$ for all data.

5: $C_{15}H_{27}P_3Se_4$, $M = 16.12$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.902(2)$, $b = 10.340(4)$, $c = 12.760(4)$ Å, $\alpha = 69.17$, $\beta = 71.11(2)$, $\gamma = 61.57°$, $U = 1054.6(6)$ Å^3, $Z = 2$, $D_c = 1.94$ Mg m^{-3}, crystal dimensions $0.35 \times 0.20 \times 0.20$ mm, $F(000) = 596$, $T = 173(2)$ K, Mo-Kα radiation, $\lambda = 0.71073$ Å. Data collection CAD4. Of the total 5081 independent reflections measured, the final indices for 3999 reflections with $I > 2\sigma(I)$ were $R1 = 0.037$, $wR2 = 0.076$ and $R1 = 0.057$, $wR2 = 0.088$ for all data.

7: $C_{18}H_{36}Cl_2P_4PtSe_4$, $M = 958.18$, rhombohedral, space group $R\bar{3}$ (no. 148), $a = 34.5455(6)$, $c = 16.7221(2)$ Å, $U = 17282.4(5)$ Å^3, $Z = 18$, $D_c = 1.66$ Mg m^{-3}, crystal dimensions $0.2 \times 0.1 \times 0.1$ mm, $F(000) = 8136$, $T = 293(2)$ K, Mo-Kα radiation, $\lambda = 0.71073$ Å. Data collection Kappa CCD, 41518 reflections collected, 10989 independent (R_{int} 0.0553), $R1 = 0.039$, $wR2 = 0.083$ for 7872 reflections with $I > 2\sigma(I)$, $R1 = 0.069$, $wR2 = 0.095$ for all data.

CCDC 182/1736. See http://www.rsc.org/suppdata/cc/b0/b005123n/ for crystallograhic files in .cif format.

§ NMR data for **7**: $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 62.7 [P(1) and P(2), m, $^2J(^{31}P^{31}P)$ 14.9, $^1J(^{31}P^{77}Se)$ 330.5, $^2J(^{31}P^{31}P)$ 6.0 Hz]; 35.4 [P(3), m, $^2J(^{31}P^{31}P)$ 13.1, $^2J(^{31}P^{31}P)$ 6.0 Hz], −8.1 [P(4), m, $^1J(^{31}P^{195}Pt)$ 2221, $^2J(^{31}P^{31}P)$ 14.9, $^2J(^{31}P^{31}P)$ 5.9 Hz]. $^{195}Pt\{^1H\}$ NMR: δ −3630.4 [$^1J(^{31}P^{195}Pt)$ 2209 Hz].

1 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, John Wiley and Sons, Chichester, 1998, pp. 1–366 and references therein.
2 *Carbocyclic and Heterocyclic (P, As, N) Cage Compounds and their Building Blocks: Synthesis, Structure, Mechanism and Theory*, ed. K. K. Laali and B. Halton, JAI Press Inc., Stamford, CT, 1999.
3 A. Mack and M. Regitz, *Chem. Ber.*, 1997, **130**, 823.
4 V. Caliman, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1995, 1661.
5 P. B. Hitchcock, J. F. Nixon and N. Sakarya, *Chem. Commun.*, 1996, 2751.
6 V. Caliman, P. B. Hitchcock and J. F. Nixon, *J. Organomet. Chem.*, 1997, **536**, 273.
7 V. Caliman, P. B. Hitchcock, J. F. Nixon, L. Nyulászi and N. Sakarya, *Chem. Commun.*, 1997, 1305.
8 V. Caliman, P. B. Hitchcock, J. F. Nixon and N. Sakarya, *Bull. Soc. Chim. Belg.*, 1996, **105**, 675.
9 M. Regitz and S. Krill, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1996, **115**, 99.
10 V. Caliman, P. B. Hitchcock and J. F. Nixon, *Heteroatom Chem.*, 1998, **9**, 1.
11 F. G. N. Cloke, P. B. Hitchcock, P. Hunnable, J. F. Nixon, L. Nyulászi, E. Niecke and V. Thelen, *Angew. Chem., Int. Ed.*, 1998, **37**, 1083.
12 V. Caliman, P. B. Hitchcock and J. F. Nixon, *Chem. Commun.*, 1998, 1537.
13 M. D. Francis, D. E. Hibbs, P. B. Hitchcock, M. B. Hursthouse, C. Jones, T. Mackewitz, J. F. Nixon, L. Nyulászi, M. Regitz and N. Sakarya, *J. Organomet. Chem.*, 1999, **580**, 156.
14 F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, D. J. Wilson, F. Tabellion, U. Fishbeck, F. Preuss, M. Regitz and L. Nyulászi, *Chem. Commun.*, 1999, 2363.
15 S. M. F. Asmus, U. Bergstrasser and M. Regitz, *Synthesis*, 1999, 1642.
16 P. Lonnecke and R. Blachnik, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1997, **131**, 191 and references therein.