^2J(H,H) = 12.9, ^3J(H,H) = 10.1 Hz, 1H), 2.15 – 2.09 (m, 1H), 1.02 (s, 3H), 0.87 (ddd, ^2J(H,H) = 13.0, ^3J(H,H) = 4.7, ^4J(H,H) = 2.1 Hz, 1H), 0.83 (dd, ^2J(H,H) = 14.1, ^3J(H,H) = 2.4 Hz, 1H), 0.70 (s, 3H), 0.26 (dd, ^2J(H,H) = 13.9, ^3J(H,H) = 13.3 Hz, 1H), 0.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 219.5, 143.6, 138.3, 129.5, 128.6, 128.5, 128.5, 127.2, 126.9, 55.8, 55.6, 51.6, 48.3, 40.1, 35.0, 21.6, 14.4, 10.6, −0.3; IR (thin film): $\tilde{\nu}$ = 1756.8 cm^{-1}; elemental analysis calcd for $C_{25}H_{32}OSi$: C 79.71, H 8.58; found: C 79.63, H 8.57. **3a**: m.p. 80 – 81 °C; R_f = 0.50 (hexanes/EtOAc 4/1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.23 – 7.11 (m, 10H), 5.87 – 5.73 (m, 1H), 5.28 – 5.22 (m, 2H), 3.69 (d, ^3J(H,H) = 12.2 Hz, 1H), 3.25 (dd, ^3J(H,H) = 12.0, 12.0 Hz, 1H), 2.53 (dddd, ^2J(H,H) = 14.3, ^3J(H,H) = 5.6, ^4J(H,H) = 1.7, 1.7 Hz, 1H), 2.26 (dq, ^3J(H,H) = 11.7, 6.9 Hz, 1H), 2.11 (dd, ^2J(H,H) = 14.4, ^3J(H,H) = 13.9 Hz, 1H), 1.13 (d, ^3J(H,H) = 6.8 Hz, 3H), 0.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 221.5, 140.9, 137.4, 134.6, 129.4, 128.8, 128.3, 127.9, 127.0, 126.8, 119.5, 53.5, 53.4, 52.8, 50.8, 41.2, 20.6, 13.2; IR (thin film): $\tilde{\nu}$ = 1734 cm^{-1}; elemental analysis calcd for $C_{22}H_{24}O$: C 86.78, H 7.96; found: C 86.64, H 8.07. **3b**: R_f = 0.46 (hexanes/EtOAc 4/1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.28 – 7.11 (m, 10H), 5.85 – 5.70 (m, 1H), 5.30 – 5.24 (m, 2H), 4.15 (dd, ^3J(H,H) = 13.2, 8.3 Hz, 1H), 3.93 (d, ^3J(H,H) = 13.0 Hz, 1H), 2.84 (dq, ^3J(H,H) = 8.1, 8.0 Hz, 1H), 2.55 (dddd, ^2J(H,H) = 14.2, ^3J(H,H) = 5.1, ^4J(H,H) = 1.6, 1.6 Hz, 1H), 2.11 (dd, ^2J(H,H) = 14.0, ^3J(H,H) = 9.0 Hz, 1H), 0.83 (s, 3H), 0.74 (d, ^3J(H,H) = 7.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 223.3, 138.4, 137.7, 135.0, 129.2, 129.0, 128.4, 126.9, 126.5, 119.4, 54.4, 47.1, 46.6, 44.8, 40.4, 20.7, 12.0 (one carbon resonance is obscured by an overlapping resonance from **3c**). **3c**: m.p. 96 °C; R_f = 0.46 (hexanes/EtOAc 4/1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.28 – 7.11 (m, 10H), 5.51 (dddd, ^3J(H,H) = 16.8, 10.0, 7.3, 7.3 Hz, 1H), 4.97 (dddd, ^3J(H,H) = 10.0, ^2J(H,H) = 2.1, ^4J(H,H) = 1.0, 1.0 Hz, 1H), 4.86 (dddd, ^3J = 16.8, ^2J(H,H) = 2.2, ^4J(H,H) = 1.4, 1.1 Hz, 1H), 3.44 (dd, ^3J(H,H) = 11.9, 11.2 Hz, 1H), 3.43 (d, ^3J(H,H) = 11.9 Hz, 1H), 2.38 (dq, ^3J(H,H) = 11.2, 6.8 Hz, 1H), 2.13 (dd, ^2J(H,H) = 14.1, ^3J(H,H) = 7.1 Hz, 1H), 1.72 (dddd, ^2J(H,H) = 14.1, ^3J(H,H) = 7.3, ^4J(H,H) = 1.1, 1.1 Hz, 1H), 1.22 (s, 3H), 1.19 (d, ^3J(H,H) = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 220.7, 141.0, 136.7, 133.6, 129.4, 128.8, 128.3, 127.9, 127.1, 127.0, 118.2, 58.9, 53.2, 52.3, 50.4, 37.8, 22.1, 13.7; IR (thin film): $\tilde{\nu}$ = 1734.7 cm^{-1}; elemental analysis calcd for $C_{22}H_{24}O$: C 86.78, H 7.96; found: C 86.71, H 8.01.

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Reaction of [{PhP(Se)(μ-Se)}$_2$] with Dialkyl Cyanamides: X-ray Crystal Structures of the Phosphorus-Containing Triselenapentalenes [Me$_2$N–C(Se)=N]$_2$P(Se)Ph and [O(CH$_2$CH$_2$)$_2$N–C(Se)=N]$_2$P(Se)Ph**

Pravat Bhattacharyya, Alexandra M. Z. Slawin, and J. Derek Woollins*

The chemistry of phosphorus – selenium heterocycles $(RP)_xSe_y$ (R = alkyl or aryl), which are generally prepared by oxidation of the parent homocyclic polyphosphanes $(RP)_n$ with stoichiometric quantities of elemental selenium, has received scant attention.[1–7] The studies undertaken on the reactivity of these molecules have to date been directed towards the development of new selenating reagents for the transformation of carbonyl groups in organic molecules to selenocarbonyls.[1, 8] In this regard, an analogue is sought of the commercially available 2,4-bis(*p*-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide [{(*p*-MeOC$_6$H$_4$)P(S)(μ-S)}$_2$] (Lawesson's reagent), a valuable tool for the conversion of carbonyl compounds to their thiocarbonyl counterparts.[9]

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The oxidation of pentaphenylcyclopentaphosphane, $(PhP)_5$, with ten molar equivalents of selenium gives an insoluble red solid which has been characterized as 2,4-diphenyl-1,3-diselenadiphosphetane-2,4-diselenide $[\{PhP(Se)(\mu\text{-}Se)\}_2]$.[4, 5] Few investigations into the reactivity of this compound have been carried out. Hill and co-workers have reported its use, prepared in situ from $(PPh)_5$/Se, for the conversion of molybdenum and tungsten ketenyl complexes to their selenoketenyl analogues.[8] Additionally, treatment of *cis*-$[PtCl_2(PR_3)_2]$ ($R = \frac{1}{2}$dppe, PEt_3, PMe_2PH or PPh_2Me) with $[\{PhP(Se)(\mu\text{-}Se)\}_2]$ in THF leads to rupture of the four-membered $P_2(\mu\text{-}Se)_2$ ring to afford $[Pt(Se_3PPh\text{-}Se,Se')(PR_3)_2]$.[10] The facile heterocycle formation from $[\{FcP(S)(\mu\text{-}S)\}_2]$ (Fc = ferrocenyl) using dialkyl cyanamides, to give thiadiazaphosphorines,[11] led us to investigate the reactivity of cyanamides with $[\{PhP(Se)(\mu\text{-}Se)\}_2]$, the results of which we report here.

A refluxing toluene solution of $[\{PhP(Se)(\mu\text{-}Se)\}_2]$ with a ten-fold excess of R_2NCN ($R_2 = Me_2$, $-CH_2CH_2OCH_2CH_2-$, or $-(CH_2)_5-$) changes from red to lime green over 18 h, with precipitation of small quantities of elemental selenium. Following column chromatography and recrystallization from dichloromethane/*n*-hexane, the 1,6,6λ^4-triselena-3a-phospha-3,4-diazapentalenes **1**–**3** are available as air- and moisture-stable yellow solids, albeit in poor yields (about 5%), together with $R_2NC(Se)NH_2$. Compounds **1**–**3** represent the first phosphorus-containing triselenapentalenes; two of them, **1** and **2**, have been crystallographically characterized (Figures 1 and 2).[12]

$[Me_2N{-}C(Se){=}N]_2P(Se)Ph$ **1**

$[O(CH_2CH_2)_2N{-}C(Se){=}N]_2P(Se)Ph$ **2**

$[CH_2(CH_2CH_2)_2N{-}C(Se){=}N]_2P(Se)Ph$ **3**

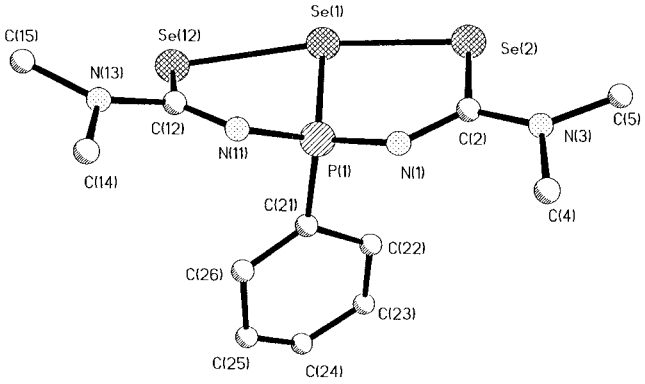

Figure 1. Molecular structure of **1** (C–H bonds omitted for clarity). Selected bond lengths [Å] and angles [°]: Se(1)-P(1) 2.229(1), Se(1)-Se(12) 2.703(1), Se(1)-Se(2) 2.578(1), P(1)-N(11) 1.620(3), P(1)-N(1) 1.609(3), N(1)-C(2) 1.308(5), N(11)-C(12) 1.318(4), C(2)-Se(2) 1.921(4), C(12)-Se(12) 1.913(4) N(3)-C(2) 1.329(5), N(13)-C(12) 1.332(5); P(1)-Se(1)-Se(12) 78.66(3), P(1)-Se(1)-Se(2) 86.25(3), Se(12)-Se(1)-Se(2) 164.27(2), N(11)-P(1)-N(1) 110.4(2), N(11)-P(1)-Se(1) 110.08(12), N(1)-P(1)-Se(1) 109.37(12), C(2)-N(1)-P(1) 124.8(3), C(12)-N(11)-P(1) 119.5(3), C(2)-Se(2)-Se(1) 93.35(12), C(12)-Se(12)-Se(1) 90.86(12).

The structures of **1** and **2** contain a central core of two fused five-membered PSe_2NC rings with the amine substituents lying in the same approximate plane as the five-membered ring with which they are associated, with the phenyl substituent on the central phosphorus approximately orthogonal to the central core. In contrast to triselenapentalenes with carbon- and nitrogen-containing backbones,[13–15] the tetrahedral geometry at P(1) in **1** and **2** imparts substantial nonplanarity to the pentalene ring system in these compounds. For **2**, the mean deviations of the P(1)-Se(1)-C(2)-N(1)-Se(2) and P(1)-Se(1)-C(12)-N(11)-Se(12) planes are 0.19 Å and 0.18 Å, respectively, while in **1** these values are 0.09 Å and 0.26 Å. The Se(2)-Se(1)-Se(12) angles are similar in each structure (164.27(2)° for **1**, 165.21(3)° for **2**); the Se–Se distances in **2** are approximately equal (Se(1)–Se(12) 2.621(1), Se(1)–Se(2) 2.648(1) Å), although there is a pronounced asymmetry in the corresponding bond length values for **1** (Se(1)–Se(12) 2.703(1) Å, Se(1)–Se(2) 2.578(1) Å).

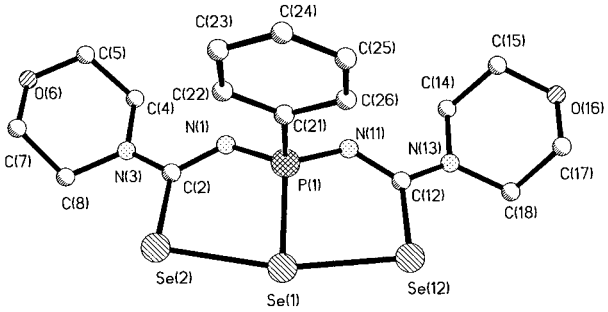

Figure 2. Molecular structure of **2** (C–H bonds omitted for clarity). Selected bond lengths [Å] and angles [°]: Se(1)-P(1) 2.224(2), Se(1)-Se(12) 2.621(1), Se(1)-Se(2) 2.648(1), P(1)-N(11) 1.605(5), P(1)-N(1) 1.608(5), N(1)-C(2) 1.320(8), N(11)-C(12) 1.315(8), C(2)-Se(2) 1.913(6), C(12)-Se(12) 1.925(6), N(3)-C(2) 1.332(9), N(13)-C(12) 1.328(8); P(1)-Se(1)-Se(12) 83.37(5), P(1)-Se(1)-Se(2) 82.31(5), Se(12)-Se(1)-Se(2) 165.21(3), N(11)-P(1)-N(1) 109.3(3), N(11)-P(1)-Se(1) 109.7(2), N(1)-P(1)-Se(1) 110.3(2), C(2)-N(1)-P(1) 122.5(5), C(12)-N(11)-P(1) 123.3(4), C(2)-Se(2)-Se(1) 92.5(2), C(12)-Se(12)-Se(1) 92.2(2).

In **1**, a short intermolecular distance between Se(12) and a phenyl ring hydrogen atom in an adjacent molecule (Se(12)···H(22a′) 3.08 Å) may make a small contribution to lengthening of the Se(1)–Se(12) vector compared with that in **2**, however, the absence of any other significant intermolecular contacts such as π-stacking of the phenyl rings or Se···Se interactions in either structure makes the disparate Se–Se lengths in **1** more perplexing. The P(1)–Se(1) distances in **1** and **2** (2.229(1) and 2.224(2) Å, respectively) are substantially longer than the more typical lengths of 2.08–2.12 Å for selenides containing P^V=Se bonds,[4, 16] but still about 0.06 Å shorter than reported for heterocycles containing P^V–Se single bonds.[1, 2, 4] In conjunction with the short P–N bond lengths (1.605(5)–1.620(3) Å), this indicates extensive electron delocalization within the pentalene framework. The remaining bonding parameters in **1** and **2** are in good agreement with each other and to related triselenapentalene structures.[13–15]

The weakness of the P(1)–Se(1) bond in the molecular structures of **1** and **2** is highlighted by the abnormally low ^1J(P-Se) couplings observed in the $^{31}P\{^1H\}$ NMR spectra of **1**–**3** (317–324 Hz), values more comparable with the ^1J(P-Se) couplings in the triphospholane $(PhP)_3Se_2$ (260–305 Hz) which contains P^{III}–Se single bonds.[5] No ^2J(P-Se) couplings

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are resolved for **1**–**3**. The results described here suggest that there is a potentially large and interesting cycloaddition chemistry associated with phosphorus–selenium heterocycles.

Experimental Section

General procedure for **1**–**3**: A toluene solution (10 mL) of [{PhP(Se)-(μ-Se)}$_2$] (0.15 mmol) and R_2N–CN (1.5 mmol) was heated at reflux for 18 h during which time the solution changed color from red to lime green, with the precipitation of a small quantity of selenium. Upon cooling to room temperature, the solvent was removed in vacuo and the products extracted into dichloromethane (2 mL). Column chromatography using silica (dichloromethane eluant) gave **1**–**3** as yellow solids. Yellow crystals of **1** and **2** were isolated upon layering of a dichloromethane (1 mL) solution of each compound with *n*-hexane at room temperature.

IR: KBr disk; $^{31}P\{^1H\}$ NMR: $CDCl_3$ solvent, 121.5 MHz; MS: FAB^+, 3-nitrobenzyl alcohol (3-NOBA) matrix.

1: IR: $\tilde{\nu}$ = 1528 s (ν_{CN}), 1109 s (ν_{PC}), 990 s (ν_{PN}), 524 m cm^{-1} (ν_{PSe}); MS: 486 [M^+]; $^{31}P\{^1H\}$ NMR: δ = 82.7 (^1J(P,Se) = 317 Hz).

2: IR: $\tilde{\nu}$ = 1502 s (ν_{CN}), 1112 s (ν_{PC}), 997 s (ν_{PN}), 521 s cm^{-1} (ν_{PSe}); MS: 570 [M^+]; $^{31}P\{^1H\}$ NMR: δ = 83.9 (^1J(P,Se) = 324 Hz).

3: IR: $\tilde{\nu}$ = 1500 s (ν_{CN}), 1109 m (ν_{PC}), 984 s (ν_{PN}), 512 m cm^{-1} (ν_{PSe}); MS: 566 [M^+]; $^{31}P\{^1H\}$ NMR: δ = 81.7 (^1J(P,Se) = 318 Hz).

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[12] X-ray diffraction studies on crystals of **1** and **2**, grown from dichloromethane/*n*-hexane, were performed using a Bruker SMART diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by direct methods, the non-hydrogen atoms were refined[17] with anisotropic displacement parameters, hydrogen atoms bound to carbon were idealized and fixed (C–H 0.95 Å). Structural refinements were performed with the full-matrix least-squares method on F^2 using the program SHELXTL-PC.[17] Crystal data for **1**: $C_{12}H_{17}N_4PSe_3$, yellow needles, 0.3 × 0.2 × 0.2 mm^3, M_r = 485.15, monoclinic, a = 9.537(1), b = 12.523(1), c = 14.178(2) Å, β = 95.049(2)°, $F(000)$ = 936, V = 1687.5(3) Å^3, T = 298 K, space group $P2_1/n$, Z = 4, $\mu(Mo_{K\alpha})$ = 6.629 mm^{-1}, $2\theta_{max}$ = 46°. Of 7191 measured data 2409 were unique reflections (R_{int} 0.0300) to give $R1$ [$I > 2\sigma(I)$] = 0.0265 and $wR2$ = 0.0568. Crystal data for **2**: $C_{16}H_{21}N_4O_2PSe_3$, yellow needles, 0.2 × 0.1 × 0.1 mm^3, M_r = 569.22, monoclinic, a = 6.807(1), b = 16.023(1), c = 18.983(1) Å, β = 94.787(1)°, $F(000)$ = 1112, V = 2063.28(7) Å^3, T = 293 K, space group $P2_1/c$, Z = 4, $\mu(Mo_{K\alpha})$ = 5.444 mm^{-1}, $2\theta_{max}$ = 46°. Of 10306 measured data 2970 were unique reflections (R_{int} 0.2251) to give $R1$ [$I > 2\sigma(I)$] = 0.0618 and $wR2$ = 0.1017. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138177 for **1** and -138178 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Highly Regioselective Allylic Alkylation of Dienyl Acetates and Enynyl Acetates Catalyzed by an Iridium Complex**

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Allylic substitution catalyzed by transition metal complexes that proceed via a π-allylmetal complex is one of the most efficient reactions for selective carbon–carbon and carbon–heteroatom bond formation.[1] The substituent on the π-allyl ligand has a considerable effect on the reactivity and the selectivity. Alkenyl and alkynyl groups are particularly important as substituents on the π-allyl ligand. 1-(1-Alkenyl)-π-allylmetal intermediate **1** isomerizes to 1-alkyl-3-vinyl-π-allylmetal intermediate **2** through a σ-π-σ interconversion.[2] Similarly, 1-(1-alkynyl)-π-allylmetal intermediate **3** isomerizes to the 1-alkyl-3-vinyl-σ-allenylmetal intermediate **4** (Scheme 1).[3] Selective reaction of these intermediates with a nucleophile increases the importance of this type of transformation in organic synthesis. We first reported that an iridium complex was a new and efficient catalyst for allylic alkylation, and showed a different regio- and stereoselectivity compared to those of π-allylpalladium chemistry.[4] We describe here the allylic alkylation of dienyl acetates and enynyl acetates catalyzed by an iridium complex [Eq. (1) and (2)].[5]

The results of the allylic alkylation of **5** and **6** are summarized in Table 1. Acetate **5a** reacted with two equivalents of **7a**–**c** in the presence of a catalytic amount of

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