

Experimental Section

Unless otherwise stated, all reactions were carried out under an oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work up procedures were performed in air. Solvents were dried, purified, and stored according to common procedures.

^1H (270 Hz), ^{13}C (67.9 Hz), ^{31}P - $\{^1\text{H}\}$ (109 Hz) and ^{77}Se - $\{^1\text{H}\}$ (51.4 Hz referenced to external Me_2Se) NMR spectra were recorded in CDCl_3 at 25 °C (unless stated otherwise) on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000 - 250 cm^{-1} on a Perkin-Elmer 2000 FTIR/Raman spectrometer. Microanalysis was performed by the University of St Andrews microanalysis service. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St Andrews Mass Spectrometry Service.

Reaction of WR with 1,4-diphenylbutadiyne — synthesis of 3,5-diphenyl-4-(phenylethynyl)-3*H*-1,2,3-diselenaphosphole-3-selenide (1) and 3,3',4,4'-tetraphenyl-3*H*,3'*H*-5,5'-bi-1,2,3-diselenaphosphole-3,3'-diselenide (2a,b): A mixture of WR (1.07 g, 2 mmol) and 1,4-diphenylbutadiyne (0.20 g, 1 mmol) in toluene (10 ml) in a sealed tube was refluxed over 10 h, giving a deep red solution. Upon cooling to room temperature the solution was column chromatographed by silica gel (toluene as eluant) to give a red fraction of **1** (109 mg, 19%) followed by the other red fraction of **2a,b**. Layering a chloroform solution of **2a,b** with hexane gave brown crystals of **2a** (196 mg, 22%) and pale brown powder **2b** (84 mg, 10%).

Compound 1: Elemental analysis: calcd for $\text{C}_{22}\text{H}_{15}\text{PSe}_3$ (%): C, 53.9, H, 3.1; found (%): C, 53.8, H, 3.3; Selected IR data (KBr) ν/cm^{-1} : 2145 (m, $\nu_{\text{C}\equiv\text{C}}$), 536 (s, $\nu_{\text{P}=\text{Se}}$); δ_{H} = 7.24-7.28 (m, 13H, Ph) ppm, 8.04-8.10 (m, 2H, Ph) ppm; δ_{C} = 140.6, 139.6, 134.7, 134.0, 132.9, 132.6, 132.4, 32.2, 131.9, 129.8, 129.7, 129.3, 129.1, 128.7, 128.5, 128.3 ppm; δ_{P} = 67.7 (s, $^1J(\text{P},\text{Se}) = 359$ Hz, $^1J(\text{P},\text{Se}) = 784$ Hz) ppm; δ_{Se} = 543.1 (d, $^2J(\text{P},\text{Se}) = 10$ Hz) ppm, 394.9 (d, $^1J(\text{P},\text{Se}) = 358$ Hz) ppm, -34.1 (d, $^1J(\text{P},\text{Se}) = 784$ Hz) ppm; MS (CI, m/z): 548 $[\text{M}+\text{H}]^+$.

Compound 2a: Elemental analysis: calcd for $C_{28}H_{20}P_2Se_6 \cdot CHCl_3$ (%): C, 37.7, H, 2.3; found (%): C, 37.5, H, 2.4; Selected IR data (KBr) ν/cm^{-1} : $\nu = 514$ (s, $\nu_{P=Se}$); $\delta_H = 6.84$ – 7.61 (m, 20H, Ph) ppm; $\delta_C = 134.7, 132.6, 132.3, 132.1, 131.9, 131.7, 131.2, 131.0, 130.6, 130.4, 129.9, 129.6, 129.0, 128.6, 128.4, 128.3, 128.1$ ppm; $\delta_P = 72.7$ (s, $^1J(P,Se) = 362$ Hz, $^1J(P,Se) = 798$ Hz) ppm; $\delta_{Se} = 536.2$ (d, $^2J(P,Se) = 7$ Hz) ppm; 409.1 (d, $^1J(P,Se) = 360$ Hz) ppm; -41.9 (d, $^1J(P,Se) = 797$ Hz) ppm; MS (Cl, m/z): 893 $[M+H]^+$.

Compound 2b: Elemental analysis: calcd for $C_{28}H_{20}P_2Se_6$ (%): C, 37.7, H, 2.3; found (%): C, 37.3, H, 2.5; selected IR data (KBr) ν/cm^{-1} : $\nu = 519$ (s, $\nu_{P=Se}$); $\delta_H = 6.94$ – 7.71 (m, 20H, Ph) ppm; $\delta_C = 134.9, 132.6, 132.4, 132.3, 132.1, 132.0, 131.8, 131.2, 131.0, 130.6, 130.4, 129.9, 129.0, 128.6, 128.4, 128.2, 127.8$ ppm; $\delta_P = 71.2$ (s, $^1J(P,Se) = 362$ Hz, $^1J(P,Se) = 790$ Hz) ppm; $\delta_{Se} = 534.3$ (d, $^2J(P,Se) = 7$ Hz) ppm; 395.8 (d, $^1J(P,Se) = 360$ Hz) ppm; -43.3 (d, $^1J(P,Se) = 787$ Hz) ppm; MS (Cl, m/z): 893 $[M+H]^+$.

Reaction of WR with 1,4-bis(trimethylsilyl)-1,3-butadiyne — synthesis of 3-phenyl-4-(trimethylsilyl)-5-[(trimethylsilyl)ethynyl]-3H-1,2,3-diselenaphosphole-3-selenide (3) and 3,3'-diphenyl-4,4'-bis(trimethylsilyl)-3H,3'H-5,5'-bi-1,2,3-diselenaphosphole-3,3'-diselenide (4a,b): A mixture of WR (1.07g, 2mmol) and 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.17g, 1mmol) in 10 ml toluene was heated at reflux for 10 h, giving a red solution. After cooling down the purification by column chromatography (silica gel, toluene) gave a brown fraction **3** (127 mg, 23.5%) followed by a yellow fraction **4a,b**. Layering a dichloromethane solution of **4a,b** with hexane afforded pale yellow needles of **4a** (150 mg, 17%). Compound **4b** could not be completely freed from traces of **4a**, precluding full characterisation.

Compound 3: Elemental analysis: calcd for $C_{16}H_{23}PSe_3Si_2$ (%): C, 35.6, H, 4.3; found (%): C, 35.8, H, 4.1; selected IR data (KBr) ν/cm^{-1} : 2067 (s, $\nu_{C\equiv C}$), 554 (s, $\nu_{P=Se}$); $\delta_H = 8.10$ (m, 2H, Ph) ppm, 7.50 (m, 2H, Ph) ppm, 7.20 (m, 1H, Ph) ppm, 0.16 (s, 9H, CH_3) ppm; $\delta_C = 140.7, 98.6, 132.7, 132.6, 128.6, 128.4, 88.1, 85.9, -0.4, -0.7$ ppm; $\delta_P = 87.7$ (s, $^1J(P,Se) = 329$ Hz, $^1J(P,Se) = 767$ Hz) ppm; $\delta_{Se} = 680.9$ (d, $^2J(P,Se) = 12$ Hz) ppm, 438.9 (d, $^1J(P,Se) = 334$ Hz) ppm, 34.1 (d, $^1J(P,Se) = 770$ Hz) ppm; MS (ES^+ , m/z): 562 $[M+Na]^+$.

Compound 4a: Elemental analysis: calcd for $C_{22}H_{28}P_2Se_6Si_2$ (%): C, 29.88, H, 3.19; found (%): C, 29.78, H, 3.11; δ_H = 8.01-8.10 (m, 4H, Ph) ppm, 7.32-7.50 (m, 6H, Ph) ppm, 0.11 (s, 9H, CH_3) ppm; δ_C = 132.8, 132.6, 128.6, 128.4, 88.0, 86.0, -0.4 ppm; δ_P = 87.5 (s, $^1J(P,Se)$ = 333 Hz, $^1J(P,Se)$ = 770 Hz) ppm; δ_{Se} = 681.0 (d, $^2J(P,Se)$ = 12 Hz) ppm, 438.8 (d, $^1J(P,Se)$ = 334 Hz) ppm, 34.8 (d, $^1J(P,Se)$ = 770 Hz) ppm; MS (ES^+ , m/z): 907 $[M+Na]^+$.

Reaction of WR with 2,2,7,7-tetramethyl-3,5-octadiynebutadiyne — synthesis of 3-tert-butyl-4-(3,3-dimethylbut-1-yn-1-yl)-2-phenyl-2H-1,2-selenaphosphete-2-elenide (5) and 3,6-di-tert-butyl-2,5-diphenyl-2,5-dihydro[1,2]selenaphospholo[5,4-d][1,2]selenaphosphole-2,5-diselenide (6a,b): A solution of WR (1.07g, 2mmol) and 2,2,7,7-tetramethyl-3,5-octadiynebutadiyne (0.16 g, 1mmol) in toluene (10ml) in a sealed tube was heated at 130 °C for 10 h, affording a red solution. Upon cooling to room temperature, the toluene solution was purified by column chromatography (silica gel). Elution with toluene gave a brown band **5** (71 mg, 18%) followed by a red fraction of **6a,b**. Compounds **6a,b** were inseparable from each other either chromatographically or by layering experiments. However, 50 mg of red crystals of **6a** were collected from a dichloromethane/hexane solution of **6a,b**, which was evaporated to almost dryness over three weeks at room temperature.

Compound 5: Elemental analysis: calcd for $C_{18}H_{23}PSe_2$ (%): C, 50.5, H, 5.4; found (%): C, 50.3, H, 5.5; selected IR data (KBr) ν/cm^{-1} : 2144 (m, $\nu_{C\equiv C}$), 561 (s, $\nu_{P=Se}$); δ_H = 8.15-8.23 (m, 2H, Ph) ppm, 7.47-7.50 (m, 3H, Ph) ppm, 1.22 (s, 9H, CH_3) ppm, 1.29 (s, 9H, CH_3) ppm; δ_C = 134.8, 131.9, 131.7, 128.9, 128.7, 50.5, 40.4, 30.2, , 29.0 ppm; δ_P = 12.6 (s, $^1J(P,Se)$ = 106 Hz, $^1J(P,Se)$ = 805 Hz) ppm; δ_{Se} = 768.4 (d, $^1J(P,Se)$ = 107 Hz) ppm, -161.4 (d, $^1J(P,Se)$ = 801 Hz) ppm; MS (Cl, m/z): 429 $[M+H]^+$.

Compound 6a: Elemental analysis: calcd for $C_{24}H_{28}P_2Se_4$ (%): C, 41.44, H, 4.06; found (%): C, 41.42, H, 4.11; selected IR data (KBr) ν/cm^{-1} : 537 (s, $\nu_{P=Se}$); δ_H = 8.15-8.23 (m, 4H, Ph) ppm, 7.17-7.53 (m, 6H, Ph) ppm, 1.30 (s, 9H, CH_3) ppm; δ_C = 133.8, 132.8, 132.6, 132.1, 131.8, 128.9, 128.7, 128.3, 128.1, 29.1 ppm; δ_P = 56.3 (s, $^1J(P,Se)$ = 352 Hz, $^1J(P,Se)$ = 801 Hz) ppm; δ_{Se} = 399.1 (d, $^1J(P,Se)$ = 352 Hz) ppm, -161.4 (d, $^1J(P,Se)$ = 805 Hz) ppm; MS (Cl, m/z): 695 $[M+H]^+$.

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