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.

\(^1\)H (270 Hz), \(^{13}\)C (67.9 Hz), \(^{31}\)P-{\(^1\)H} (109 Hz) and \(^{77}\)Se-{\(^1\)H} (51.4 Hz referenced to external Me\(_2\)Se) 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)-3H,1,2,3-diselenaphosphole-3-selenide (1) and 3,3',4,4'-tetraphenyl-3H,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-disphenylbutadiyne (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 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 C\(_{22}\)H\(_{15}\)PSe\(_3\) (%): C, 53.9, H, 3.1; found (%): 53.8, H, 3.3; Selected IR data (KBr) v/cm\(^{-1}\): 2145 (m, v\(_{C≡C}\)), 536 (s, v\(_{P=Se}\)); \(\delta_H = 7.24\) - 7.28 (m, 13H, Ph) ppm; \(\delta_C = 140.6, 139.6, 134.7, 134.0, 132.9, 132.6, 132.4, 132.2, 131.9, 129.8, 129.7, 129.3, 129.1, 128.7, 128.5, 128.3 ppm; \(\delta_P = 67.7\) (s, \(^1J(P,Se) = 359\) Hz, \(^1J(P,Se) = 784\) Hz) ppm; \(\delta_{Se} = 543.1\) (d, \(^2J(P,Se) = 10\) Hz) ppm, 394.9 (d, \(^1J(P,Se) = 358\) Hz) ppm, -34.1 (d, \(^1J(P,Se) = 784\) Hz) ppm; MS (Cl, m/z): 548 [M+H]\(^+\).
Compound 2a: Elemental analysis: calcd for C_{28}H_{20}P_{2}Se_{6} \cdot CHCl_{3} (%): C, 37.7, H, 2.3; found (%): C, 37.5, H, 2.4; Selected IR data (KBr) v/cm\(^{-1}\): v = 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, \(^{1}J(P,Se) = 362\) Hz, \(^{1}J(P,Se) = 798\) Hz) ppm; \(\delta_{Se} = 536.2\) (d, \(^{2}J(P,Se) = 7\) Hz) ppm; 409.1 (d, \(^{1}J(P,Se) = 360\) Hz) ppm; -41.9 (d, \(^{1}J(P,Se) = 797\) Hz) ppm; MS (Cl, m/z): 893 [M+H]\(^{+}\).

Compound 2b: Elemental analysis: calcd for C_{28}H_{20}P_{2}Se_{6} (%): C, 37.7, H, 2.3; found (%): C, 37.3, H, 2.5; selected IR data (KBr) v/cm\(^{-1}\): v = 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, \(^{1}J(P,Se) = 362\) Hz, \(^{1}J(P,Se) = 790\) Hz) ppm; \(\delta_{Se} = 534.3\) (d, \(^{2}J(P,Se) = 7\) Hz) ppm; 395.8 (d, \(^{1}J(P,Se) = 360\) Hz) ppm; -43.3 (d, \(^{1}J(P,Se) = 787\) 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_{3}Si_{2} (%): C, 35.6, H, 4.3; found (%): C, 35.8, H, 4.1; selected IR data (KBr) v/cm\(^{-1}\): 2067 (s, \(\nu_C=C\)), 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, \(^{1}J(P,Se) = 329\) Hz, \(^{1}J(P,Se) = 767\) Hz) ppm; \(\delta_{Se} = 680.9\) (d, \(^{2}J(P,Se) = 12\) Hz) ppm, 438.9 (d, \(^{1}J(P,Se) = 334\) Hz) ppm, 34.1 (d, \(^{1}J(P,Se) = 770\) Hz) ppm; MS (ES\(^{+}\), m/z): 562 [M+Na\(^{+}\)].
Compound 4a: Elemental analysis: calcd for C\textsubscript{22}H\textsubscript{28}P\textsubscript{2}Se\textsubscript{6}Si\textsubscript{2} (%): C, 29.88, H, 3.19; found (%): C, 29.78, H, 3.11; \(\delta\text{H} = 8.01-8.10\) (m, 4H, Ph) ppm, 7.32-7.50 (m, 6H, Ph) ppm, 0.11 (s, 9H, CH\textsubscript{3}) ppm; \(\delta\text{C} = 132.8, 132.6, 128.6, 128.4, 88.0, 86.0, -0.4\) ppm; \(\delta\text{P} = 87.5\) (s, \(1^J(P,Se) = 333\) Hz, \(1^J(P,Se) = 770\) Hz) ppm; \(\delta\text{Se} = 681.0\) (d, \(1^J(P,Se) = 12\) Hz) ppm, 438.8 (d, \(1^J(P,Se) = 334\) Hz) ppm, 34.8 (d, \(1^J(P,Se) = 770\) Hz) ppm; MS (ES\textsuperscript{+}, m/z): 907 [M+Na\textsuperscript{+}].

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-2\textsubscript{H}-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\textsubscript{18}H\textsubscript{23}PSe\textsubscript{2} (%): C, 50.5, H, 5.4; found (%): C, 50.3, H, 5.5; selected IR data (KBr) v/cm\textsuperscript{-1}: 2144 (m, \(\nu\text{C}≡\text{C}\)), 561 (s, \(\nu\text{P=Se}\)); \(\delta\text{H} = 8.15-8.23\) (m, 2H, Ph) ppm, 7.47-7.50 (m, 3H, Ph) ppm, 1.22 (s, 9H, CH\textsubscript{3}) ppm, 1.29 (s, 9H, CH\textsubscript{3}) ppm; \(\delta\text{C} = 134.8, 131.9, 131.7, 128.9, 128.7, 50.5, 40.4, 30.2, , 29.0\) ppm; \(\delta\text{P} = 12.6\) (s, \(1^J(P,Se) = 106\) Hz, \(1^J(P,Se) = 805\) Hz) ppm; \(\delta\text{Se} = 768.4\) (d, \(1^J(P,Se) = 107\) Hz) ppm, -161.4 (d, \(1^J(P,Se) = 801\) Hz) ppm; MS (Cl, m/z): 429 [M+H\textsuperscript{+}].

Compound 6a: Elemental analysis: calcd for C\textsubscript{24}H\textsubscript{28}PSe\textsubscript{4} (%): C, 41.44, H, 4.06; found (%): C, 41.42, H, 4.11; selected IR data (KBr) v/cm\textsuperscript{-1}: 537 (s, \(\nu\text{P=Se}\)); \(\delta\text{H} = 8.15-8.23\) (m, 4H, Ph) ppm, 7.17-7.53 (m, 6H, Ph) ppm, 1.30 (s, 9H, CH\textsubscript{3}) ppm; \(\delta\text{C} = 133.8, 132.8, 132.6, 132.1, 131.8, 128.9, 128.7, 128.3, 128.1, 29.1\) ppm; \(\delta\text{P} = 56.3\) (s, \(1^J(P,Se) = 352\) Hz, \(1^J(P,Se) = 801\) Hz) ppm; \(\delta\text{Se} = 399.1\) (d, \(1^J(P,Se) = 352\) Hz) ppm, -161.4 (d, \(1^J(P,Se) = 805\) Hz) ppm; MS (Cl, m/z): 695 [M+H\textsuperscript{+}].