Supplementary Material (ESI) for Dalton Transactions

Supplementary Information.

Unless otherwise stated, all reactions were carried out under on 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, ^{13}C, ^{31}P and ^{77}Se NMR spectra were recorded on a JEOL GSX 270 MHz spectrometer with δ referenced to external SiMe4. IR spectra were recorded as KBr pellets in the range of 4000-250 cm^{-1} on a Perkin-Elmer 2000 FTIR/Raman spectrometer. Mass spectrometry and microanalysis were performed by the University of St Andrews Mass Spectrometry and Microanalysis Services.

X-ray crystallographic data were collected at 93 K by using a Rigaku MM007 High brilliance RA generator and Mercury CCD system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. Hydrogen atoms bound to carbon were idealised. Structural refinements were obtained with full-matrix least-squares based on F^2 by using the program SHELXTL.

General experimental procedure for formation of olefins: A mixture of ketone (2.2 mmol) or aldehyde (2.2 mmol) and **WR** (1 mmol) in 10 ml of dry toluene was refluxed for 20 h to give a slightly yellow solution along with a layer of grey elemental selenium at the bottom of flask. Upon cooling to room temperature the solution was column chromatographied on silica gel (toluene or 9:1 = toluene/ethyl acetate as eluant), yielding olefins as crystals or solids from dichloromethane / *n*-hexane.

Tetraphenylethylene (1): 100% yield based on WR (colourless crystal). Selected IR (KBr, cm^{-1}): 3049(w), 3017(w), 1594(w), 1490(m), 1441(m), 1074(m), 1027(m), 761(m), 746(m), 699(s), 625(m); ^{1}H NMR ($CDCl_3$): δ_H = 7.10 (m, 1H, ^{1}J = 1.2 Hz), 7.07 (m, 1H, ^{1}J = 2.2 Hz), 7.03 (m, 1H, ^{1}J = 2.4 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 143.82, 144.06, 131.43, 127.75, 126.51 ppm; MS (ESI^+, m/z): 355 $[M+23]^+$. The structure was confirmed crystallogrophically and is in accord with the literature [I.Ino, L P Wu, M Munakata, T

Kuroda-Sowa, M Mackawa, Y.Suenaga, R. Sakai, *Inorg.Chem.*, 200, **39**, 5430.CCDC code TPHETY]

T**etrakis(*p*-methoxyphenyl)ethylene (2):** 99% yield based on WR (colourless crystal). Selected IR (KBr, cm^{-1}): 1606 (m), 1510 (s), 1246 (s), 1174 (m), 1034 (m), 833 (m); ^{1}H NMR ($CDCl_3$): δ_H = 6.92 (d, 1H, ^{1}J = 7.4 Hz), 6.62 (d, 1H, ^{1}J = 8.7 Hz), 3.73 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 157.85, 138.44, 136.98, 132.61, 113.10, 55.15 ppm; MS (ESI^+, m/z): 475 $[M+23]^+$. The structure was confirmed by X-ray crystallography and is in accord with the literature [R.Rathore, S.V.Lindeman, A.S.Kumar, J.K.Kochi
Journal: J.Am.Chem.Soc., 1998, **120**, 6931 CCDC code GEYGOG]

T**etrakis(p-dimethylaminophenyl)ethylene (3):** 99% yield based on WR (colourless crystal). Selected IR (KBr, cm^{-1}): 1609 (s), 1519 (s), 1351 (m), 1165 (w), 817 (m), 547 (w); ^{1}H NMR ($CDCl_3$): δ_H = 7.72 (d, 1H, ^{1}J = 133 Hz), 6.72 (d, 1H, ^{1}J = 118 Hz), 2.89 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 148.30, 140.01, 132.16, 128.60, 111.81, 40.61 ppm; MS (ESI^+, m/z): 504 $[M+23]^+$.

T**etrakis(*p*-bromophenyl)ethylene (4):** 87% yield based on WR (white solid). Selected IR (KBr, cm^{-1}): 1582 (w), 1484 (s), 1393 (m), 1071 (m), 1009 (s), 793 (s), 491(m); ^{1}H NMR ($CDCl_3$): δ_H = 7.25 (d, 1H, ^{1}J = 8.7 Hz), 6.83 (d, 1H, ^{1}J = 8.7 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 141.56, 139.70, 132.84, 131.39, 121.38 ppm; MS (ESI^+, m/z): 671 $[M+23]^+$.

T**etrakis(*p*-chlorophenyl)ethylene (5):** 69% yield based on WR (white solid). Selected IR (KBr, cm^{-1}): 1590 (w), 1489 (s), 1397 (m), 1089 (s), 1014 (s), 828 (m), 798 (s), 526 (m), 499 (m). ^{1}H NMR ($CDCl_3$): δ_H = 7.09 (d, 1H, ^{1}J = 8.4 Hz), 6.90 (d, 1H, ^{1}J = 8.4 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 141.18, 139.64, 133.05, 132.53, 128.40 ppm; MS (ESI^+, m/z): 493 $[M+23]^+$.

T**etrakis(p-fluorophenyl)ethylene (6):** 53% yield based on WR (white solid). Selected IR (KBr, cm^{-1}): 3073(w), 1649(s), 1599(s), 1503(m), 1408(m), 1296(m), 1282(m),

1229(s), 1154(m), 931(m), 856(s), 763(s), 694(m), 578(m), 495(m); ^{1}H NMR ($CDCl_3$): δ_H = 6.93 (d, 1H, ^{1}J = 5.4 Hz), 6.80 (d, 1H, ^{1}J = 8.7 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 163.41, 159.78, 139.16, 132.90, 115.17 ppm; MS (ESI^+, m/z): 427 $[M+23]^+$.

[9,9']-Bifluorenylidene (7): 92% yield based on WR (white solid). Selected IR (KBr, cm^{-1}), 1604 (w), 1475 (m), 1443 (s), 1348 (m), 1280 (w), 763 (s), 721 (vs), 585 (w), 421 (m); ^{1}H NMR ($CDCl_3$): δ_H = 8.37 (d, J = 6.9 Hz, 4H), 7.69 (d, J = 7.7 Hz, 4H), 7.32 (m, J = 6.2 Hz, 4H), 7.20 (m, J = 7.2 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 141.38, 138.35, 129.23, 126.92, 126,81, 126.43, 119.97 ppm; MS (EI, m/z): 328 $[M]^+$.

D**ixanthylene (8):** 78% yield based on WR (brown solid). Selected IR (KBr, cm^{-1}): 3063(w), 1657(w), 1588(m), 1441(s), 1301(m), 1252(s), 1200(m), 1151(m), 1116(m), 1095(m), 939(m), 889(m), 825(m), 765(vs), 739(s), 613(m), 497(m); ^{1}H NMR ($CDCl_3$): δ_H = 8.77 (d, J = 8.2 Hz, 4H), 8.34 (d, J = 7.9 Hz, 4H), 7.90 (dd, J = 6.9 Hz, 4H), 7.71 (dd, J = 6.9 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 155.54, 134.90, 133.16, 128.39, 124.00, 122.69, 117.16 ppm; MS (EI, m/z): 360 $[M]^+$.

(***E)*-bis(benzylbiphenyl)ethylene (9):** 77% yield based on WR (colourless crystal). Selected IR (KBr, cm^{-1}): 3026 (m), 1598 (m), 1486 (s, C=C), 1442 (m), 764 (s), 734 (s), 698 (s); ^{1}H NMR ($CDCl_3$): δ_H = 7.55-7.52 (6H), 7.40-7.24 (6H), 7.15-7.05 (16H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 143.87, 143.84, 142.91, 140.80, 139.05, 131.90, 131.55, 128.79, 127.79, 127.26, 126.97, 126.40, 126.30 ppm; MS (ESI, m/z): 507 $[M+Na]^+$. The structure was confirmed crystallographically.

(***E)*-1,1'-(1,2-dimethyl-1,2-ethenediyl)bis-naphthalene (10)**: 63% yield based on WR (white solid). Selected IR (KBr, cm^{-1}): 1433 (s), 1088 (s), 813 (m), 745 (s), 686 (m), 534 (m), 477 (m); ^{1}H NMR ($CDCl_3$): δ_H = 8.20 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2H), 7.93 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2H), 7.62-6.90 (m, 12H), 2.65 (s, 3H), 2.57 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 142.3, 135.4, 135.2, 134.1, 133.7, 133.0, 132.6, 129.2, 129.0, 128.8, 127.9, 126.9, 125.4 ppm; MS (EI, m/z): 308$[M]^+$.

(***E)*-1,2-di(1,3-benzodioxol-5-yl)ethylene (11)**: 60% yield based on WR (yellowish green solid). Selected IR (KBr, cm^{-1}): 2895(w), 1502(s), 1486(s), 1440(m), 1250(s), 1096(w), 1038(s), 927(m), 812(m); ^1H NMR ($CDCl_3$): δ_H = 7.01 (s, 2H), 6.87 (d, $^3J_{H,H}$ = 8.2 Hz, 2H), 6.83 (s, 2H), 6.76 (d, $^3J_{H,H}$ = 8.2 Hz, 2H), 5.96 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 126.80, 121.24, 108.48, 105.47, 101.16 ppm; MS (EI, m/z): 268 $[M]^+$.

(***E)*-2, 2, 4, 4-Tetramethoxystilbene (12)**: 100% yield based on WR (pale yellow solid). Microanal. Calcd (%) for $C_{18}H_{20}O_2$: C, 71.98, H, 6.71; Found (%): 72.35, H, 6.69; selected IR (KBr, cm^{-1}), 1609 (s), 1580 (s), 1503 (s), 1459 (m), 1453 (m), 1326 (m), 1292 (s), 1267 (m), 1210 (s), 1095 (m), 1029 (m), 746 (m), 687 (m), 529 (m); ^1H NMR ($CDCl_3$): δ_H = 8.15 (s, 2H, Ar), 7.71 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, Ar), 6.96 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, Ar), 6.31 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, Ar), 3.67 (s, 6H, OMe), 3.58 (s, 6H, OMe) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 161.10, 156.90, 132.87, 128.25, 114.31, 104.40, 98.21, 55.47, 55.29 ppm; MS (EI, m/z): 300 $[M]^+$.

(*E*)-4,4'-Dimethoxystilbene (13): 74% yield based on WR (white powder). Selected IR (KBr, cm^{-1}): 2836(w), 1606(s), 1510(s), 1462(m), 1437(m), 1305(m), 1251(s), 1177(m), 1029(m), 833(s), 744(m), 543(m); ^1H NMR ($CDCl_3$): δ_H = 7.41 (d, $^3J_{H,H}$ = 8.9 Hz, 4H, Ar), 6.92 (s, 2H, =CH), 6.87 (d, $^3J_{H,H}$ = 8.6 Hz, 4H, Ar), 3.81 (s, 6H, OMe) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 159.09, 130.56, 127.49, 126.27, 114.18, 55.40 ppm; MS (EI, m/z): 240 $[M]^+$.

(*E*)-3,3'-Dimethoxystilbene (14): 69% yield based on WR (yellow powder). Selected IR (KBr, cm^{-1}): 2830(w), 1595(s), 1486(s), 1433(s), 1261(vs), 1043(m), 689(s); ^1H NMR ($CDCl_3$): δ_H = 8.13 (dd, $^3J_{H,H}$ = 5.9 Hz, 2H, Ar), 7.88 (s, 2H, Ar), 7.24 (s, 2H, HC=CH), 6.98 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, Ar), 6.82 (d, $^3J_{H,H}$ = 7.5 Hz, 2H, Ar), 3.63 (s, 6H, OMe); ^{13}C NMR ($CDCl_3$): δ_C = 159.19, 132.67, 129.31, 129.09, 128.83, 114.96, 114.55, 55.34 ppm; MS (EI, m/z): 240 $[M]^+$.

(*E*)-3,3',5,5'-tetramethoxystilbene (15): 96% yield based on WR (yellow powder). Selected IR (KBr, cm^{-1}): 2833(w), 1593(s), 1460(m), 1435(m), 1205(m), 1155(s), 1063(m), 1017(m), 939(m), 841(m), 753(m), 693(m), 515(m); ^{1}H NMR ($CDCl_3$): δ_H = 7.30 (s, 2H, =CH), 6.92, (d, $^{4}J_{H,H}$ = 2.9 Hz, 4H, Ar), 6.60 (t, $^{4}J_{H,H}$ = 2.5 Hz, 2H, Ar), 3.98 (s, 12H, OMe) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 161.52, 133.42, 128.96, 128.34, 107.90, 102.51, 55.44; MS (EI, m/z): 300 $[M]^+$.

1,2,4,5-Tetraphenylbenzene (16): 83% yield based on WR (colourless needle). Selected IR (KBr, cm^{-1}): 3022(w), 1597(m), 1490(m), 1474(m), 1442(m), 1379(w), 1072(m), 1026(m), 905(m), 756(s), 699(vs), 532(m), 506(m); ^{1}H NMR ($CDCl_3$): δ_H = 7.52 (s, 2H), 7.25 (m, 20H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 141.03, 139.73, 133.07, 129.99, 128.05, 126.72 ppm; MS (CI^+, m/z): 383$[M+H]^+$. The structure was confirmed crystallogrphically.

1,2,3,8-Tetraphenyl-8a*H*-8-phospha-cyclopent[a]indene-8-selenide (17a,b): 70% yield based on WR (brown powder) whose ^{31}P-{^{1}H} NMR spectrum revealed a mixture of two conformational isomers. Layering a dichloromethane solution of the mixture with hexane gave of **17a** (*SR/RS* mixture) (brown powder, 56% yield) and **17b** (*RR/SS* mixture) (brown crystal, 14% yield).

17a (*SR/RS*): Elemental analysis: calcd (%) for $C_{35}H_{25}PSe$: C75.67, H 4.54; found (%): C 74.35, H 4.41; ^{1}H NMR ($CDCl_3$): δ_H = 8.15-7.01 (m, 25H); ^{13}C NMR ($CDCl_3$): δ_C = 132.9, 131.1, 130.5, 130.4, 130.1, 129.9, 129.5, 128.9, 128.5, 128.3, 128.1, 127.1, 123.0, 122.9; ^{31}P NMR ($CDCl_3$): δ_P = 34.7 (^{1}J(P,Se) = 763 Hz) ppm; ^{77}Se NMR ($CDCl_3$): δ_{Se} = -253.2 (^{1}J(P,Se) = 761 Hz) ppm; MS (ESI^+, m/z): 579 $[M+23]^+$; MS (SEI^-, m/z): 555 $[M-H]^+$.

17b (*RR/SS*): Elemental analysis: calcd (%) for $C_{35}H_{25}PSe$: C75.67, H 4.54; found (%): C 75.35, H 4.57; ^{1}H NMR ($CDCl_3$): δ_H = 8.15-7.01 (m, 25H); ^{13}C NMR ($CDCl_3$): δ_C = 131.4, 132.0, 130.7, 130.6, 130.2, 129.4, 128.8, 128.4, 128.1, 128.0, 127.1, 123.3, 123.2; ^{31}P NMR ($CDCl_3$): δ_P = 13.0 (^{1}J(P,Se) = 737 Hz) ppm; ^{77}Se NMR ($CDCl_3$): δ_{Se} = -246.4 (^{1}J(P,Se) = 736 Hz) ppm; MS (ESI^+, m/z): 579 $[M+23]^+$. The structure was confirmed crystallographically.