Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Planar P_6E_6 (E = S, Se) Macrocycles Incorporating P_2N_2 Scaffolds[**]

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Experimental Section

NMR spectra were recorded using a BRUKER Avance II 400 spectrometer (^{1}H, ^{13}C, ^{31}P, ^{77}Se) on samples dissolved in a deuterated solvent or by using the reaction mixture at ambient temperature. 85 % H_3PO_4/D_2O was employed as external standard for ^{31}P NMR, TMS was used for ^{1}H and ^{13}C NMR and Ph_2Se was the external standard for ^{77}Se NMR. The solid-state ^{31}P NMR spectra were recorded at 298 K using a Bruker AMX300 or a 400 MHz Bruker Avance III spectrometer at B_0 0f 7.05 T or 9.4 T corresponding to the ^{31}P Larmor frequency of 121.5 or 161.9 MHz. The experiments were carried out using Bruker 4 mm (outside diameter) zirconia rotors with a MAS rate of 14 and 10 KHz. The pulse sequence used was cross-polarisation magic-angle spinning (CP-MAS); the spectra were referenced to NaH_2PO_4. The MALDI TOF mass spectrum was obtained on a Bruker Autoflex II MALDI-Tof/Tof with Smartbeam laser system using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile as the matrix and $Ag[OOCCF_3]$ as the marker. Infrared spectroscopy was performed using a Nicolet Nexus 470 with CsI windows, FT-IR and ATR accessory. Raman spectra were recorded on a Perkin-Elmer FT-IR/Raman System 2000 spectrophotometer in the range of 4000-400 cm^{-1}.

The crystallographic data for **2a, 2b** and **3** were obtained by using a Bruker-Nonius Kappa CCD diffractometer. All data were collected with graphite-monochromated *Mo-Kα* radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects. The crystal structures were solved by using direct methods[1] and expanded using Fourier techniques.[2] The non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined using the riding model. All calculations were performed using CrystalStructure[3] crystallographic software package and SHELXL-97.[4] In **2a** one of the *tert*-butyl groups

containing carbon atoms (C5, C6 and C7) was disordered (50:50 and 55:45) in the final refinement. CCDC-867162, 876357 and 867163 contain the supplementary crystallographic data for **2a**, **2b** and **3**, and, respectively. These data can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2a: A cold (-78 °C) solution of I_2 (0.152 g, 0.600 mmol) in THF (15 mL) was added dropwise over 15 min by cannula to a solution of $[Na(THF)_2]_2[^tBuN(Se)P(\mu\text{-}N^tBu)_2P(Se)N^tBu)]$[5] (0.500 g, 0.60 mmol) in THF (20 mL) cooled to -78 °C. The reaction mixture was stirred at -78 °C for 30 min and then allowed to reach room temperature and stirred for an additional 1 h. The precipitate was removed by filtration, dried under vacuum and then treated with dry THF (40 mL) followed by warming to 50 °C prior to filtration to remove the remaining traces of NaI. Drying in vacuo afforded an orange solid. Yield: 35 %. Mp 169 °C. Elemental analysis calcd (%) for $C_8H_{18}N_2PSe$: C 38.10, H 7.19, N 11.11; found: C 38.00, H 6.99, N 10.48. $^1H\{^{31}P\}$ NMR (C_6D_6, 25 °C): δ = 1.56 (s, 54H, *t*Bu), 1.39 (s, 54H, *t*Bu); $^{31}P\{^1H\}$ NMR (d_8-toluene, 25 °C): δ = -67.3 (s, ^1J(P,Se) = 429 Hz, ^2J(P,P) = 19.5 Hz); ^{77}Se NMR (d_8-toluene, 25 °C): δ = 408.6 (^1J(P,Se) = 429 Hz). The ^{31}P NMR spectrum showed that the filtrate contained some additional **2a,** but this could not be separated from $[(HN^tBu)Se{=}P(\mu\text{-}N^tBu)_2P{=}Se(HN^tBu)]$ (H_2**1a**) [$\delta(^{31}P)$ = 26.7, ^1J(P,Se) = 880 Hz)][5] and the tetraselenide **3**, which was identified on the basis of $^{31}P\{^1H\}$ and ^{77}Se NMR spectra (*vide infra*).

2b: Compound **2b** was obtained from the reaction of $[Na(THF)_2]_2[^tBuN(S)P(\mu\text{-}N^tBu)_2P(S)N^tBu)]$[5] (0.500 g, 0.68 mmol) with I_2 (0.173 g, 0.68 mmol) in benzene (30 mL) by using a procedure similar to that described for **2a**. After filtration of the

benzene solution and removal of the solvent, the material was washed with hexane and dried under vacuum resulting in a yellow solid (0.062 g, 22 %). Mp 129 °C. MS (EI, *m/z*); 1231 $[M+H]^+$. Elemental analysis calcd (%) for $C_8H_{18}N_2PS$: C 46.81, H 8.84, N 13.65; found: C 46.69, H 8.91, N 13.59. $^1H\{^{31}P\}$ NMR (C_6D_6, 25 °C): 1.50 (s, 54H, ^{t}Bu), 1.31 (s, 54H, ^{t}Bu); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = -48.7 (s). ^{31}P NMR (161.9 MHz, solid state, 25 °C): -61.0 (s), -34.2(s). [(HN^{t}Bu)S=P(μ-N^{t}Bu)$_2$P=S(HN^{t}Bu)] (H_2**1b**)[6] was identified as a major by-product in the synthesis of **2b**: $^1H\{^{31}P\}$ NMR (C_6D_6, 25 °C): 1.72 (s, 18H, *t*Bu), 1.22 (s, 18H, *t*Bu); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 40.0 (s); ^{31}P NMR (161.9 MHz, solid state, 25 °C): δ [ppm] = 38.3 (s).

3: A cold (-78 °C) solution of Se_2Cl_2 (0.137 g, 0.60 mmol) in toluene (15 mL) was added dropwise (by cannula (15 min.) to a solution of [Na(THF)$_2$]$_2$[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$P(Se)N^{t}Bu)][5] (0.500 g, 0.60 mmol) in toluene (20 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 3 h and then allowed to warm to room temperature and stirred for a further 2 h. The precipitate (NaCl) was removed by filtration and solvent was removed from the filtrate under vacuum to give an orange solid, which was dissolved in *n*-hexane and stored at -40 °C. The deposited crystals of (H_2**1a**) were removed from the cold solution by filtration. The filtrate was reduced in volume until precipitation was visible and the filtrate was stored at -40 °C overnight. The orange solid was filtered off and recrystallized from hexane to give **3** as bright orange crystals. The repeated crystallization of the mother liquids yielded additional batches of **3**. Yield 56 %. Mp. 142 °C (dec.). Elemental analysis calcd (%) for $C_{16}H_{36}N_4P_2Se_4$: C 29.02, H, 5.48, N, 8.46; found: C, 29.16, H, 5.48, N, 8.51. MS (CI^+, *m/z*), 665 $[M+H]^+$. Accurate mass measurement 664.9155 $[M+H]^+$. $^1H\{^{31}P\}$ NMR (C_6D_6, 25 °C): δ = 1.61 (s, 18H, *t*Bu),

1.34 (s, 18H, *t*Bu); $^{31}P\{^{1}H\}$ NMR (d_8-toluene, 25 °C): δ = -50.8 (s, ^{1}J(P,Se) = 524 Hz, ^{2}J(P,P) = 10.0 Hz); ^{77}Se NMR (d_8-toluene, 25 °C): δ = 673.0 (t, ^{2}J(P,Se) = 20.0 Hz, ^{2}J(P,P) = 13 Hz), 336.7 (dd, ^{1}J(P,Se) = 524 Hz, ^{3}J(P,Se) = 6 Hz).

IR and Raman Data

2a: IR (KBr): ν [cm^{-1}] = 2969 (s), 1457 (m), 1364 (s, b), 1249 (m), 1218 (s), 1199 (s), 1047 (s), 930 (m), 899 (s), 849 (w), 822 (s) 737 (w), 703 (w), 658 (w), 595 (s), 542 (m), 515 (w), 485 (m), 434 (w). Raman: ν [cm^{-1}] = 2974 (m), 2928 (m), 1448 (m), 1383 (m), 1245 (w), 1220 (m), 1185 (w), 1131 (w), 1029 (w), 909 (m), 849 (w), 812 (w), 703 (m), 606 (m), 549 (m), 439 (w), 425 (w), 371 (w), 348 (w), 294 (vs), 224 (s), 179 (m).

2b: IR (KBr): ν [cm^{-1}] = 3384.7 (m), 3311.7 (w), 3269.4 (w), 3161.6(w), 2967.0 (s), 2928.1 (s), 2869.2 (m), 2712.5 (w), 2365.9 (w), 2035.9 (w), 1862.3 (w), 1463.3 (m), 1385.2 (s), 1364.6 (s), 1252.1 (m), 1221.7 (s), 1199.2 (s), 1129.4 (w), 1050.7 (s), 1028.6 (s), 929.0 (m), 907.9 (vs), 851.2 (m), 838.2 (m), 818.5 (m), 756.7 (m), 704.9 (w), 656.0 (m), 611.5 (w), 570.4 (w), 522.4 (m), 499.5 (w), 444.7 (w), 429.4 (w), 409.1 (w), 362.1 (w). Raman: ν [cm^{-1}] = 3379.7 (w), 2973.8 (vs), 2931.5 (vs), 2715.6 (w), 1463.3 (s), 1377.7 (m), 1242.2 (w), 1221.2 (m), 1191.0 (w), 1139.7 (w), 1034.3 (w), 919.7 (m), 840.6 (w), 815.8 (m), 760.8 (w), 732.3 (w), 710.1 (m), 664.0 (w), 626.9 (w), 586.2 (s), 552.5 (s), 521.5 (m), 499.5 (m), 464.2 (m), 447.5 (m), 391.0 (m), 359.2 (w), 322.0 (s), 271.2 (s), 242.4 (m), 217.1 (s), 182.6 (m).

3: IR (KBr) ν [cm^{-1}] = 2965 (s), 2891 (m), 2856 (m), 2370 (w), 2329 (w), 1454 (m), 1389 (s), 1378 (s), 1360 (s), 1246 (m), 1218 (m), 1196 (s), 1051 (s), 930 (w), 898 (s), 848 (w),

822 (m), 738 (w), 655 (w), 602 (s), 549 (m), 464 (w), 425 (m). Raman ν [cm^{-1}] = 2969 (m), 2925 (m), 2899 (m), 2767, 2704 (w), 2693 (w), 1459 (m), 1445 (m), 1412 (m), 1381 (m), 1220 (m), 1185 (w), 1134 (w), 1025 (w), 911 (w), 853 (w), 811 (w), 708 (w), 655 (w), 604 (m), 552 (w), 426 (w), 371 (w), 354 (w), 274 (vs), 209 (s), 183 (m).

DFT calculations were performed using the ADF[7] package. Molecular geometries were fully optimized but vibrational calculations were not performed given the large expense of the numerical method with the hybrid potentials.

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Table 1. Crystallographic data for **2a, 2b** and **3**

	2a	**2b**	**3**
Identification code	RTAN1	RTAN10	RTAN9
Empirical formula	C48 H108 N12 P6 Se6	C48 H108 N12 P6 S6	C16 H36 N4 P2 Se4
Formula weight	1513.04	1309.75	662.27
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	trigonal	trigonal	monoclinic
Space group	P 63/m	P 63/m	P 21/a
a (Å), alpha (deg)	16.643(2), 90	16.5400(7), 90	11.2800(5), 90
b (Å), beta (deg)	16.643(2), 90	16.5400(7), 90	14.7500(5), 95.3030(17)
c (Å), gamma (deg)	15.319(3), 120	15.330(4), 120	15.5840(7), 90
Volume ($Å^3$)	3674.7(11)	3680.1(2)	2581.77(18)
Z	2	2	4
Calculated density (mg/m^3)	1.367	1.182	1.704
Absorption coefficient (mm^{-1})	3.155	0.358	5.817
F(000)	1548	1416	1304
Crystal size (mm^3)	0.19 x 0.13 x 0.05	0.25 x 0.22 x 0.15	0.24 x 0.22 x 0.13
Theta range (deg.)	1.9 to 27.50	1.9 to 27.40	1.9 to 27.5
Limiting indices	-19<=h<=19, -16<= k<=16, -18 <=l<=11	-19<=h<=19, -16<= k<=16, -14 <=l<=18	-13<=h<=13, -17<= k<=15, -18 <=l<=18
Reflections collected/unique	7081 / 2244 [R(int) = 0.0547]	7147 / 2249 [R(int) = 0.0678]	7279 / 4181 [R(int) = 0.0867]
Completeness to theta	99.6 %	99.5 %	97.4 %
Max. and min. transmission	0.8582 and 0.5855	0.9483 and 0.9159	0.5185 and 0.3358
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	2244 / 0 / 121	2249 / 0 / 133	4181 / 0 / 247
Goodness-of-fit on F^2	1.084	1.076	1.151
R1, wR2 [I>2sigma(I)]	0.0606, 0.1553	0.0807, 0.1912	0.0798, 0.1465
R1, wR2 (all data)	0.0916, 0.1780	0.1082, 0.2134	0.1259, 0.1728
Largest diff. peak and hole ($e.Å^{-3}$)	0.925 and -0.700	0.561 and -0.357	0.787 and -0.676

Table 2. Bond lengths and angles for **2a**, **2b** and **3**

		2a	
P1–N1	1.507(8)	C1–N1	1.462(11)
P1–N2	1.695(5)	C8–N3	1.468(10)
P2–N2	1.695(6)	P1–Se1	2.253(2)
P2–N3	1.501(7)	P2–Se2	2.262(2)
C4–N2	1.469(10)	Se1–Se2	2.3217(14)
C8–N3	1.468(10)		
C4–N2–P1	132.1(4)	N3–P2–N2	118.6(3)
C4–N2–P2	131.4(4)	N2–P2–N2	83.8(4)
P1–N2–P2	96.0(3)	N3–P2–Se2	111.1(3)
N1–P1–N2	126.2(3)	N2–P2–Se2	111.1(2)
N2–P1–N2	83.8(4)	P1–Se1–Se2	97.79(7)
N1–P1–Se1	104.2(3)	P2–Se2–Se1	98.63(7)
N2–P1–Se1	107.05(19)		
		2b	
P1–N1	1.680(4)	C8–N3	1.465(8)
P1–N2	1.500(6)	C1–N1	1.494(7)
P2–N1	1.690(4)	P1–S1	2.127(2)
P2–N3	1.501(6)	P2–S2	2.124(3)
C5–N2	1.451(9)	S1–S2	2.121(2)
N2–P1–N1	125.7(2)	C1–N1–P1	132.3(4)
N2–P1–S1	106.6(2)	C5–N2–P1	145.7(5)
N1–P1–N1’	83.5(3)	C8–N3–P2	144.9(5)
N3–P2–N1’	119.2(2)	S2–S1–P1	98.83(9)
N3–P2–S2’	109.9(2)	S1’–S2’–P2	100.88(10)
N1–P2–S2’	111.62(16)		
		3	
P1–N3	1.503(10)	Se1–Se3	2.3371(19)
P1–N2	1.686(10)	Se2–Se4	2.3317(19)
P1–N1	1.698(9)	Se3–Se4	2.321(2)
P1–Se1	2.280(3)	N1–C1	1.496(14)
P2–N4	1.494(10)	N2–C5	1.494(15)
P2–N1	1.685(9)	N3–C9	1.457(14)
P2–N2	1.694(10)	N4–C13	1.468(16)
P2–Se2	2.275(3)		
N3–P1–N2	117.0(5)	N4–P2–Se2	113.3(4)
N3–P1–N1	123.0(5)	N1–P2–Se2	108.2(3)
N2–P1–N1	84.1(5)	N2–P2–Se2	107.9(4)
N3–P1–Se1	112.8(4)	P1–Se1–Se3	103.68(10)
N2–P1–Se1	108.2(4)	P2–Se2–Se4	104.65(10)
N1–P1–Se1	108.0(3)	Se4–Se3–Se1	103.20(7)
N4–P2–N1	116.6(5)	Se3–Se4–Se2	103.41(7)
N4–P2–N2	122.9(5)	P2–N1–P1	95.3(5)
N1–P2–N2	84.2(5)	P1–N2–P2	95.4(5)

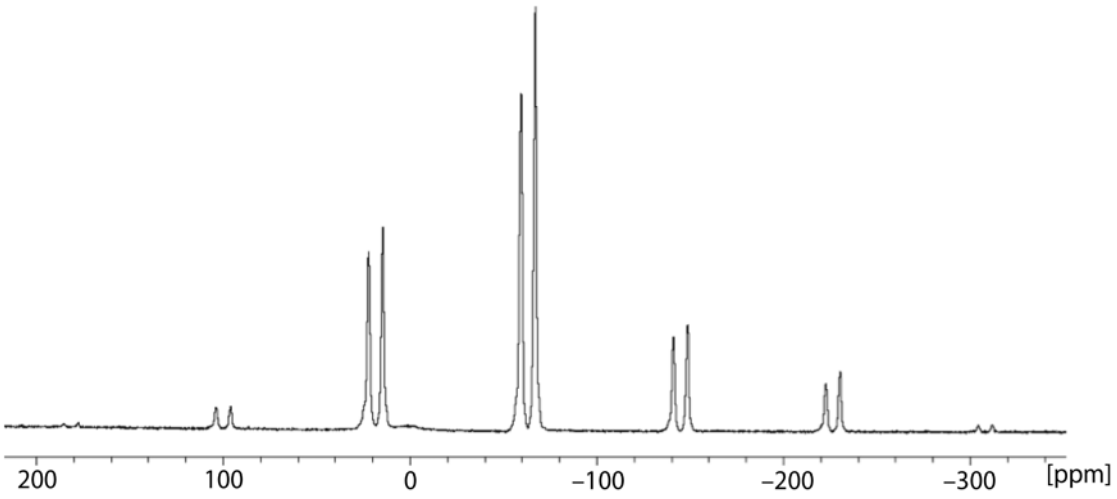

Fig S1. ^{31}P CP-MAS NMR (7.05 T) of **2a** recorded at a MAS rate of 10.0 kHz

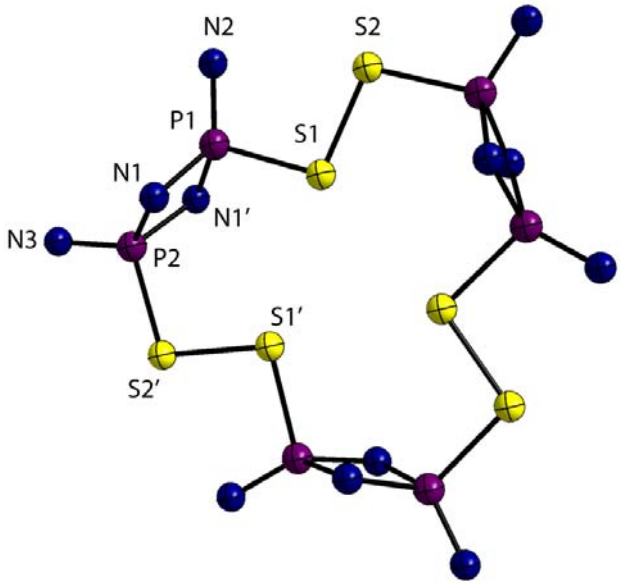

Fig. S2 Molecular structure of **2b**. Hydrogen atoms have been omitted for clarity View from on top showing the atomic numbering scheme

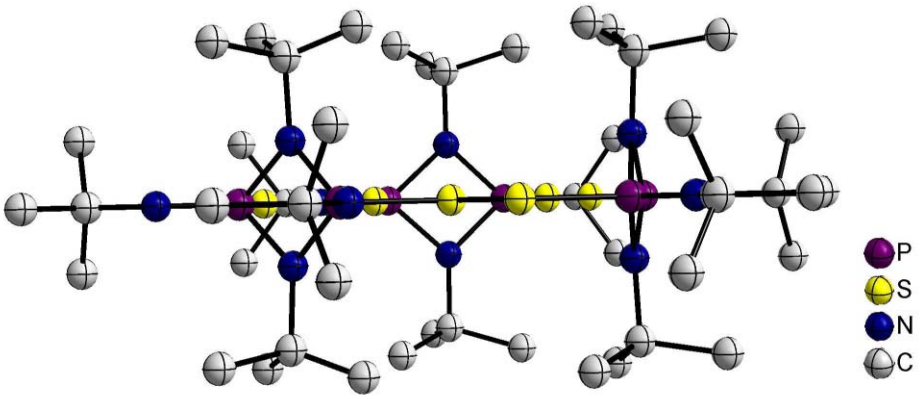

Fig. S3 Molecular structure of **2b**; side-on view showing the planarity of the P_6S_6 framework

Crystal data for **2a**: C48H108N12P6Se6, M = 1513.04, trigonal, space group P63/m, a = b = 16.643(2), c = 15.319(3) Å, α = β = 90.00, γ = 120.00o, V = 3674.7(11) Å3, Z = 2, ρcalcd = 1.367 g cm-3, μ = 3.155 mm-1, T = 173(2) K, 7081 reflections collected (θ range 1.9 - 27.50), 2244 unique (Rint = 0.0547), R1 = 0.0606 for 1628 reflections with I > 2σ(I)] and wR2 = 0.1553 (for all data).

Crystal data for **2b**. C6H6: C54H114N12P6S6, M = 1309.75, trigonal, space group P63/m, a = b = 16.5400(7), c = 15.5330(4) Å, α = β = 90.00, γ = 120.00o, V = 3680.1(2) Å3, Z = 2, ρcalcd = 1.182 g cm-3, μ = 0.358 mm-1, T = 173(2) K, 2249 reflections collected (θ range 1.9 -27.50), 1706 unique (Rint = 0.0678), R1 = 0.0807 for 1706 reflections with I > 2σ(I)] and wR2 = 0.1912 (for all data).

Crystal data for **3**: C16H36N4P2Se4, M = 662.27, monoclinic, space group P21/a, a = 11.2800(5), b = 14.7500(5), c = 15.5840(7) Å, α = γ = 90.00, β = 95.303(2)o, V = 2581.8(2) Å3, Z = 4, ρcalcd = 1.704 g cm-3, μ = 5.817 mm-1, T = 173(2) K, 7279 reflections collected (θ range 1.9 -27.50), 4181 unique (Rint = 0.0867), R1 = 0.0798 for 2888 reflections with I > 2σ(I)] and wR2 = 0.1465 (for all data).