Formation and Selection of the Macrocycle [{^{t}BuN=)P(μ-N^{t}Bu)}$_2$(μ-Se)$_2${P(μ-N^{t}Bu)}$_2$]$_3$

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1. General remarks

All manipulations were carried out under dry, O_2-free nitrogen on a vacuum-line, using standard inert-atmosphere techniques for isolation and characterisation. All NMR spectra were recorded on a Bruker Advanced 400 QNP 500 MHz cryo spectrometer with $SiMe_4$, H_3PO_4 (85%, D_2O), selenoxanthenone (0.1M, $CDCl_3$) as external standards. Elemental analysis was obtained using a Perkin Elmer 240 Elmer 240 Elemental Analyser. Synthesis of the phosphazanes [ClP(μ-N^{t}Bu)]$_2$ (**A**) and [HN^{t}Bu (Se=)P(μ-N^{t}Bu)]$_2$ were carried out as stated in literature, using freshly-distilled PCl_3. NaHMDS was purchased from Sigma Aldrich (1M in thf).[1,2]

2. Selected NMR Spectra (all at room temperature).

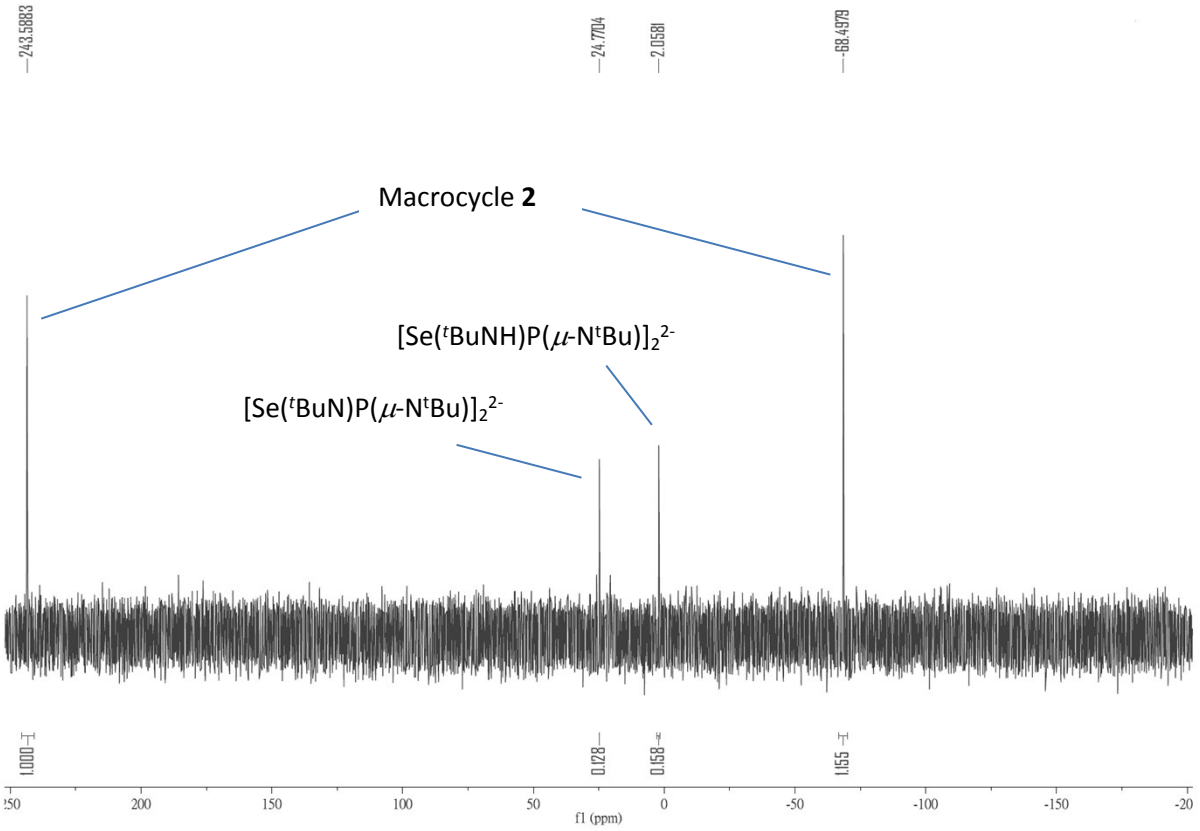

Figure 1 *In situ* ^{31}P NMR spectrum of the reaction of the electrophilic component **A** with the nucleophilic component **1b** (25°C, 161.98 MHz, using an internal d_6-acetone capillary to obtain a lock).

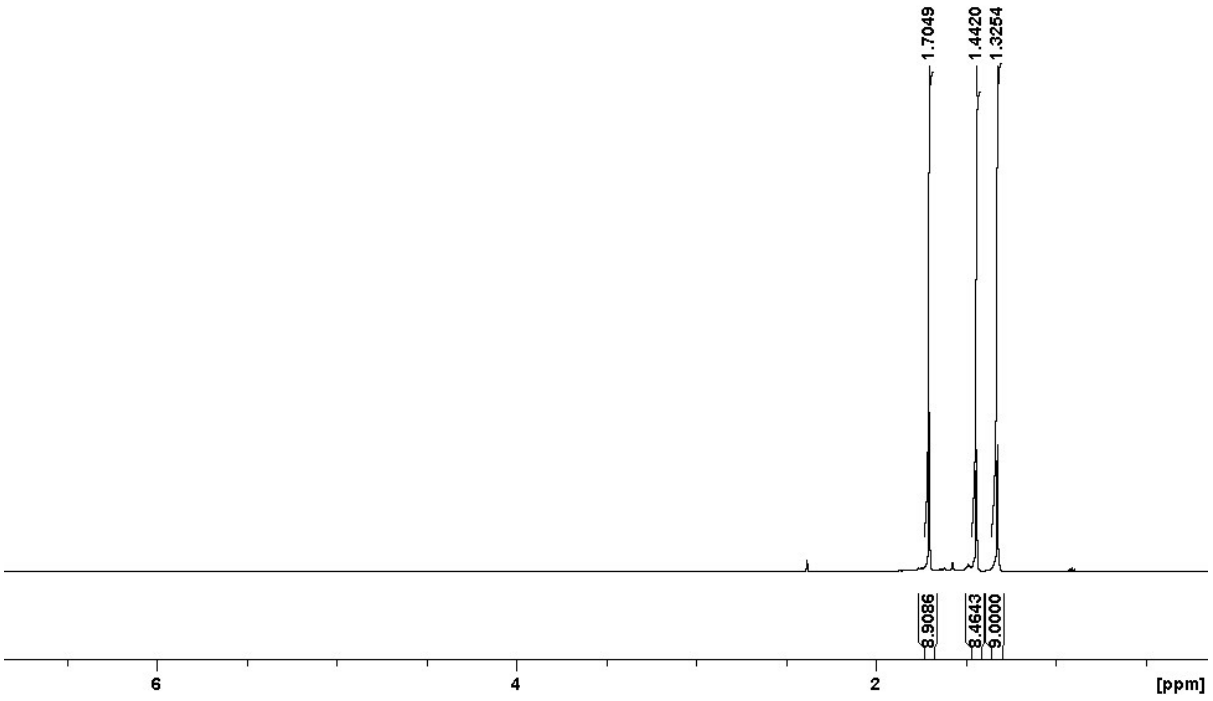

Figure S2a: ^{1}H NMR (25°C, CD_3Cl 500.12 MHz) of **2** (isolated after prolonged drying under vacuum at *ca.* 0.1 bar for *ca.* 20 mins)

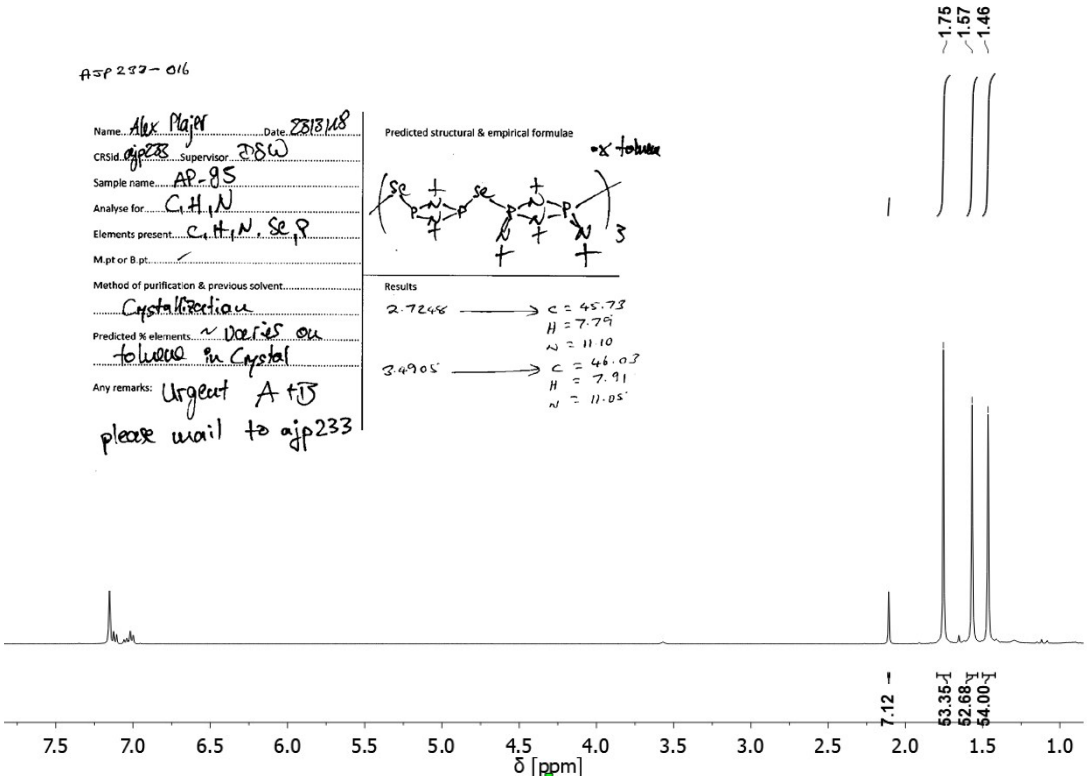

Figure S2b: ^{1}H NMR (25°C, CD_3Cl 500.12 MHz) of **2**·2toluene (isolated after drying under vacuum for *ca.* 5-10 mins at *ca.* 0.1 bar). The inset shows the original elemental analysis slip on this sample.

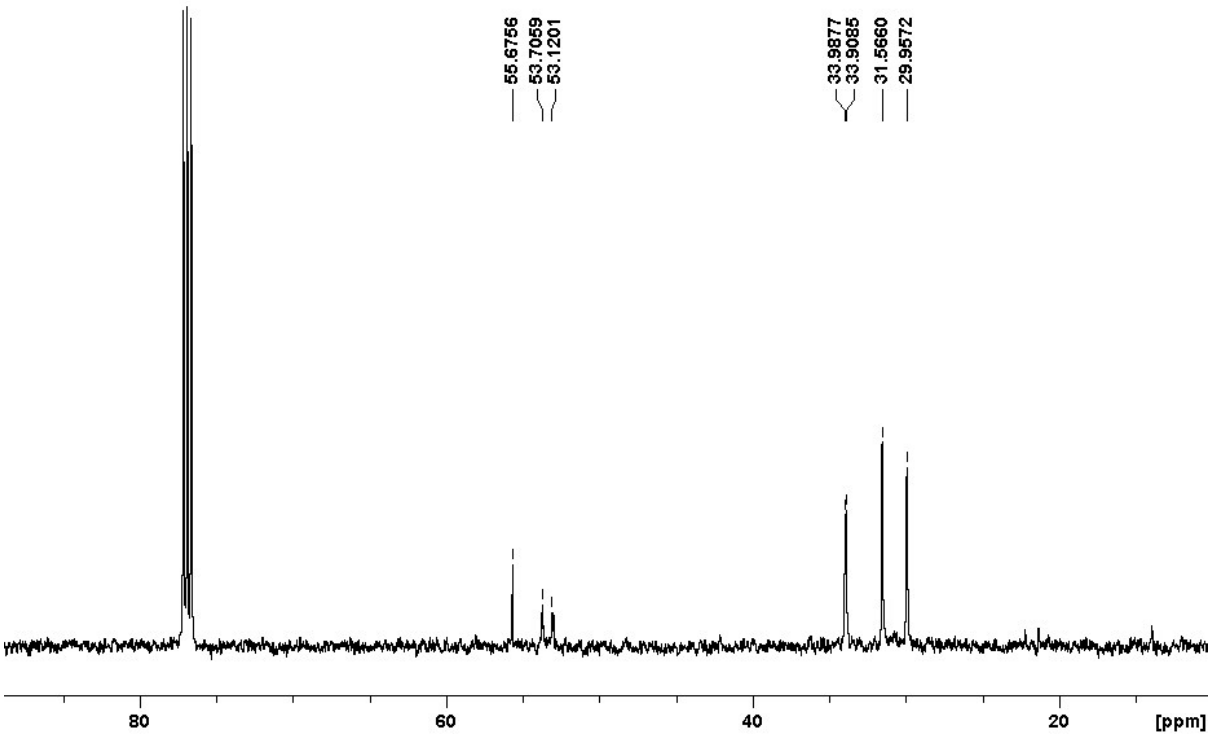

Figure S3: ^{13}C NMR (25°C, CD_3Cl, 125.78 MHz) of **2**

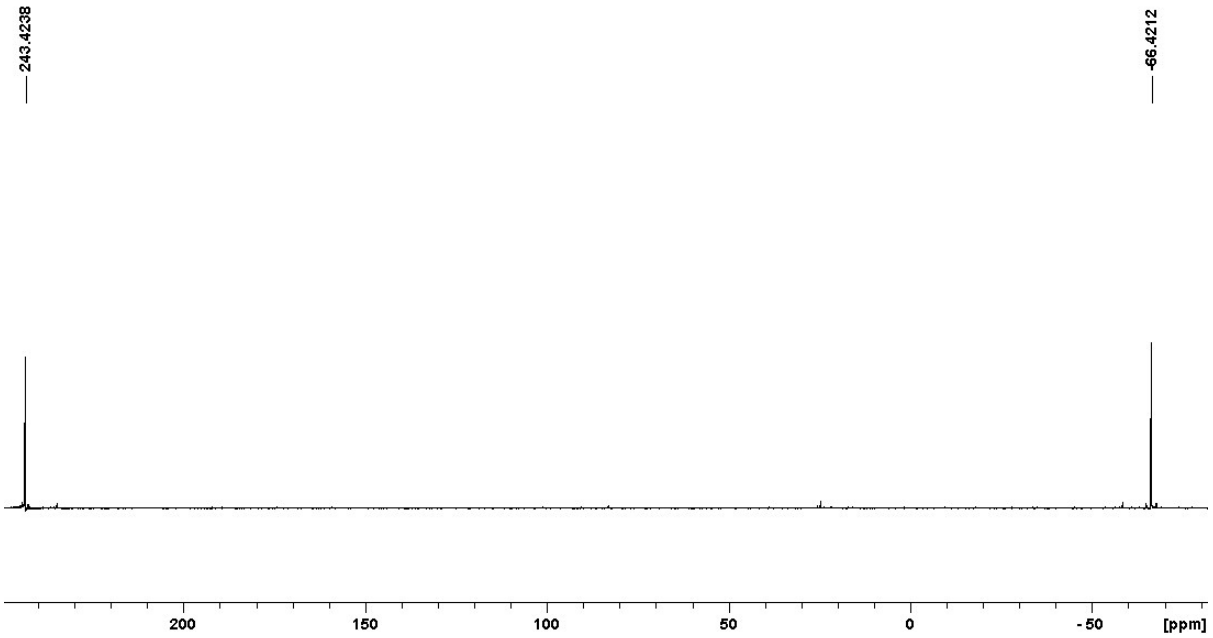

Figure S4: $^{31}P\{^1H\}$NMR (25°C, CD_3Cl, 161.7 MHz) of **2**

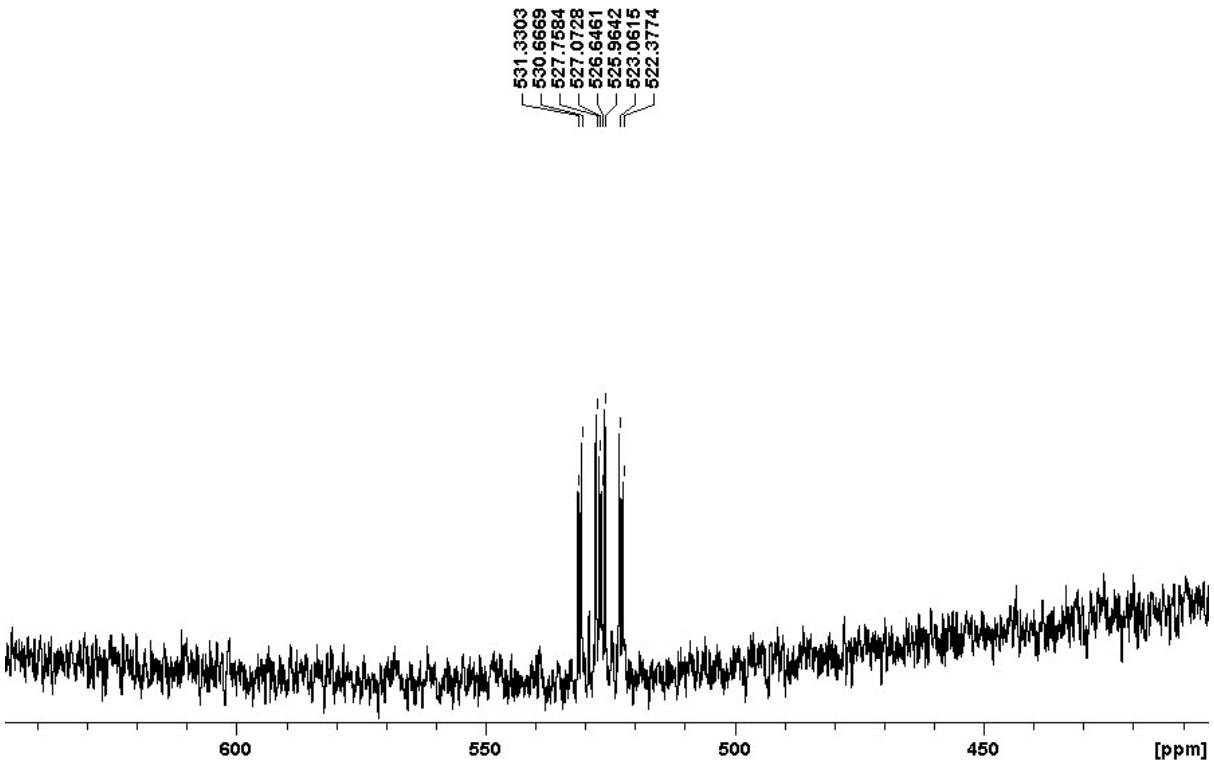

Figure S5: $^{77}Se\{^{1}H\}$ NMR (95.4 MHz, CD_3Cl, +25°C) of **2**

1 T. Roth, H. Wadepohl, D. S. Wright and L. H. Gade, *Chem. - A Eur. J.*, 2013, **19**, 13823–13837.

2 A. Nordheider, K. Hüll, K. S. Athukorala Arachchige, A. M. Z. Slawin, J. D. Woollins, R. Thirumoorthi and T. Chivers, *Dalt. Trans.*, 2015, **44**, 5338–5346.s

3. X-ray Crystallography

Single-crystal X-ray diffraction data were collected on a Bruker D8-QUEST PHOTON-100 diffractometer equipped with an Incoatec IμS Cu microsource. Data integration and reduction were undertaken with SAINT in the APEX3 software suite. Multi-scan empirical absorption corrections were applied using SADABS. Structures were solved using SHELXT-2014 and refined using full-matrix least squares on F^2 using SHELXL-2014/7.

Several ^{t}Bu groups were disordered over two positions, necessitating distance and angle (DANG and DFIX) restraints, along with thermal parameter restraints (SIMU). Two molecules were modelled over symmetry positions, where half the toluene molecule was present in the asymmetric unit (occupancy set to 0.5). One of these was modelled as a rigid group disordered over two sites (Part -1).

G. M. Sheldrick, A. F. H., B. H. M., B. I. J., G. C. R., C. S. C., B. H.-B., D. B., G. S., J. D., et al., Acta Crystallogr. Sect. C Struct. Chem. 2015, 71, 3–8. G. M.

Sheldrick, B. M. C., Y. H., E. S. H., D. R. T., O. M. J., B. M. C., C. B., C. G. L., G. C., et al., Acta Crystallogr. Sect. A Found. Adv. 2015, 71, 3–8.

Table 1: Crystal data and structure refinement for **2**

Identification code	p1-_a - FINAL
Empirical formula	$C_{100}H_{194}N_{18}P_{12}Se_6$
Formula weight	2494.12
Temperature/K	180(2)
Crystal system	triclinic
Space group	P-1
a/Å	13.853(3)
b/Å	17.290(3)
c/Å	28.760(4)
α/°	75.917(12)
β/°	84.957(13)
γ/°	74.512(12)
Volume/Å^3	6437.3(18)
Z	2
ρ_{calc}g/cm^3	1.287
μ/mm^{-1}	3.784
F(000)	2608.0
Crystal size/mm^3	0.300 × 0.200 × 0.200
Radiation	CuKα (λ = 1.54178)

2Θ range for data collection/°	5.448 to 134.332
Index ranges	$-16 \leq h \leq 16$, $-19 \leq k \leq 20$, $-34 \leq l \leq 34$
Reflections collected	65225
Independent reflections	22732 [R_{int} = 0.0374, R_{sigma} = 0.0390]
Data/restraints/parameters	22732/568/1374
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.0975
Final R indexes [all data]	R_1 = 0.0526, wR_2 = 0.1051
Largest diff. peak/hole / e $Å^{-3}$	0.98/-0.72