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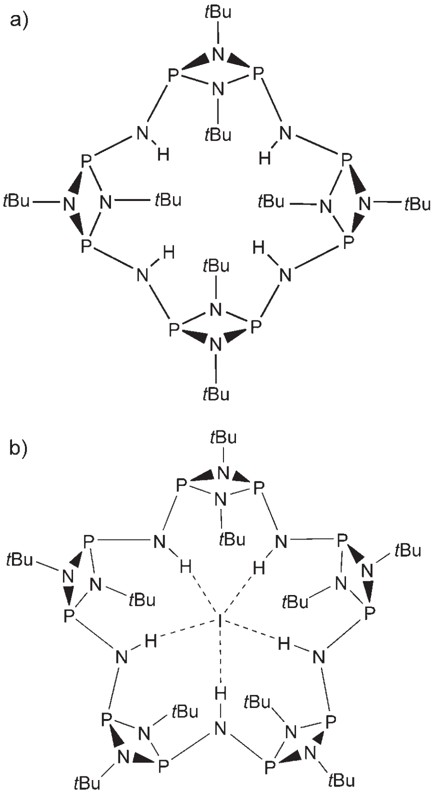
Inorganic Macrocycles

The Selenium-Based Hexameric Macrocycle $[(Se{=})P(\mu\text{-}NtBu)_2P(\mu\text{-}Se)]_6$**

Silvia González-Calera, Dana J. Eisler, James V. Morey, Mary McPartlin, Sanjay Singh, and Dominic S. Wright**

Recently, we have developed logical approaches to a family of phosphorus–nitrogen-based macrocycles of the type $[\{P(\mu\text{-}NR)\}_2(\mu\text{-}Y)]_n$.[1,2] The tetrameric, nitrogen-bridged macrocycle $[\{P(\mu\text{-}NtBu)\}_2(\mu\text{-}NH)]_4$ (Scheme 1 a) is obtained by the condensation of the dimers $[ClP(\mu\text{-}NtBu)]_2$ and $[(NH_2)P(\mu\text{-}NtBu)]_2$ in the presence of Et_3N.[3] However, the pentameric homologue is produced exclusively if this reaction is undertaken in the presence of I^- ions, resulting in the host–guest complex $[\{P(\mu\text{-}NtBu)\}_2(\mu\text{-}NH)]_5I^-$ (Scheme 1 b).[4] The toroidal structures of the tetramer and pentamer and the presence of *endo* N−H functionalities combine the appearance and host–guest characteristics of organic macrocycles such as calixarenes and porphyrins.



Scheme 1. Structures of a) the tetramer and b) the pentamer.

Less progress has been made in attempts to extend this class of new ligands to macrocycles containing other bridging elements, owing largely to the inability to generalize the synthetic methods used for N-bridged species. Indeed, the only representative of this type reported to date is the oxygen-bridged dimer $[\{P(\mu\text{-}N(2\text{-}py)\}_2(\mu\text{-}O)]_2$ (2-py = 2-pyridyl), obtained by hydrolysis of $[ClP\{\mu\text{-}N(2\text{-}py)\}]_2$ in the presence of CuCl and pyridine.[5] However, we reported a key synthetic step in the potential extension of this methodology to a broader range of macrocycles by showing that oligomerization can be effected between P_2N_2 units by the reaction of a deprotonated P(H)=O group with a P−Cl bond (Scheme 2).[6] This reaction can be rationalized by a change from a P-centered to an O-centered nucleophile. In this sense, the reaction can be seen to involve an intermediate possessing "masked" functionality. However, it should be noted in this regard that the ambiguous nature of species containing $[R_2P{=}E]^-$ anions (E = O, S, Se, NR, etc.) is well established by previous structural and theoretical studies, as is the fact that the negative charge normally lies primarily over to the side of E.[7]

We report herein the success of this approach by showing that the reaction of the dimer $[(Cl)(Se{=})P(\mu\text{-}NtBu)]_2$ (**1**) with excess sodium metal in toluene at reflux gives the macrocyclic, selenium-bridged hexamer $[(Se{=})P(\mu\text{-}NtBu)_2P(\mu\text{-}Se)]_6$ (**2**) as a crystalline product in good yield (45%) by formal head-to-tail cyclization of the intermediate anion. The formation of the P-Se-P bridge again stems from the ambidentate nature of the intermediate anion (Scheme 3). Evidence of the resulting presence of alternate P^{III} and P^{V} centers within the backbone of **2** is seen in the room-temperature $^{31}P\{^1H\}$ NMR spectrum in toluene, which shows P^{III} (d, $\delta = 206.8$ ppm) and P^{V} centers (d, $\delta = 54.4$ ppm) that are coupled to each other with a coupling constant that is typical of a P-(μ-NR)-P bridge ($^2J_{^{31}P\text{-}^{31}P} = 44$ Hz).[8] This spectrum can be compared to that of the precursor **1**, which shows two singlet resonances in the P^{V} region only, for the *cis* ($\delta = 22.1$ ppm, major) and *trans* ($\delta = 22.7$ ppm, minor) isomers (together with ^{77}Se satellites attributed to the AA′X isotopomer containing one ^{77}Se atom ($I = 1/2$, 7.6%)).[8] The structural characterization of **1**[9] also strongly supports the presence of isomers in a maximum ratio *cis*/*trans* of 7:1 (3:1 according to the relative integration of the ^1H, ^{31}P, and ^{77}Se NMR spectra). This situation contrasts with previous studies of the dimers $[R(H)N(Se{=})P(\mu\text{-}NtBu)]_2$, which show the presence exclusively of the *cis* isomer.[8] The greater

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[*] S. González-Calera, Dr. D. J. Eisler, J. V. Morey, Prof. M. McPartlin, Dr. S. Singh, Dr. D. S. Wright
Chemistry Department, Cambridge University
Lensfield Road, Cambridge CB2 1EW (UK)
Fax: (+44) 122-333-6362
E-mail: ss724@cam.ac.uk
dsw1000@cus.cam.ac.uk

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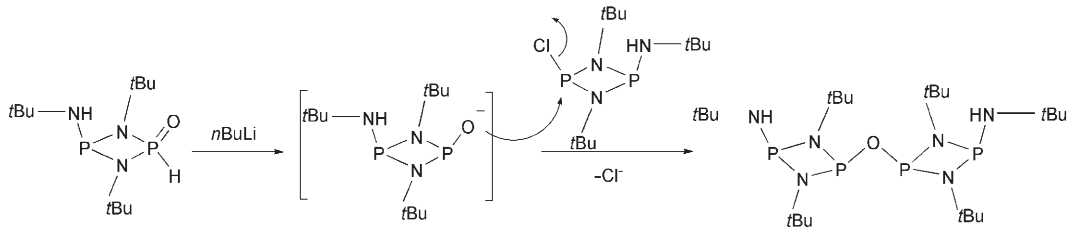
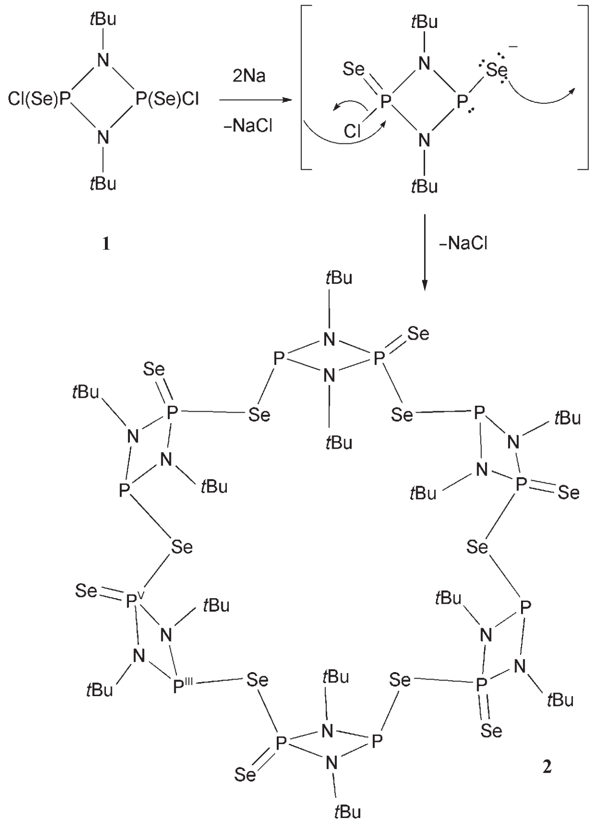


Scheme 2.



Scheme 3.

proportion of the *cis* isomer of **1** over the *trans* may have an influence on the formation of a macrocyclic (rather than oligomeric or polymeric) product.[1,3,4]

Owing to the low solubility of the macrocycle **2** in organic solvents (such as $CHCl_3$, toluene, and THF), further elucidation of the chemical environments and bonding of the Se atoms in its macrocyclic backbone using ^{77}Se NMR spectroscopy was not possible. This situation, and the fact that only the dimer $[(Se{=})P(\mu\text{-}NtBu)_2P(\mu\text{-}Se)]_2^+$ could be observed in the positive-ion electrospray mass spectrum of **2** (*m*/*z* 726), meant that the exact nature and size of the macrocycle could not be ascertained prior to its structural characterization. However, the low-temperature X-ray structure of the solvate **2**·2 toluene·THF shows that molecules of **2** are formed from six $[(Se{=})P(\mu\text{-}NtBu)_2P(\mu\text{-}Se)]$ units linked together into a macrocyclic arrangement through bridging Se atoms (Figure 1 a).[9] All six of the *endo* Se atoms (Se(2), Se(4), Se(6), and the symmetry equivalents) are within a plane which defines a toroidal cavity measuring approximately 8.2 Å in diameter and 6.1 Å from top to bottom.[10] The molecule is only slightly distorted from overall planarity, with the eighteen atoms within the macrocyclic $[(P\cdots P)(\mu\text{-}Se)]_6$ fragment deviating by a maximum of approximately 0.14 Å from the mean plane. Like the related nitrogen macrocycles $[\{P(\mu\text{-}NtBu)\}_2(\mu\text{-}NH)]_n$ ($n = 4$, 5),[3,4] the P_2N_2 ring units are approximately perpendicular to the mean plane of the macrocycle (dihedral angles 95.4–97.6°) so that the molecules have a toroidal shape. An interesting feature of the structure of the solvate is the presence of the lattice THF molecule within the sheath of the *t*Bu groups in **2**, above the centroid of the macrocycle (Figure 1 b). This situation is like that found in the host–guest solvate $[\{P(\mu\text{-}NtBu)\}_2\{1,8\text{-}(O)C_{10}H_6\}]_3\cdot THF$[11] and reminiscent of the host–guest behavior of calixarenes.[12] The ranges of P–N (1.684(7)–1.722(7) Å), P-(μ-Se) (2.245(2)–2.380(2) Å), and P=Se (2.063(8)–2.081(2) Å) bond lengths as well as the P-(μ-Se)-P angles (range 99.93(9)–100.30(8)°) in the structure of **2** are similar to those reported previously in the literature[13] as well as those noted above for **1**.

Sulfur and selenium macrocycles have been the focus of considerable attention in the past two decades owing to their unusual redox properties and their ability to stabilize low-oxidation-state metals.[14] Most attention has been paid to

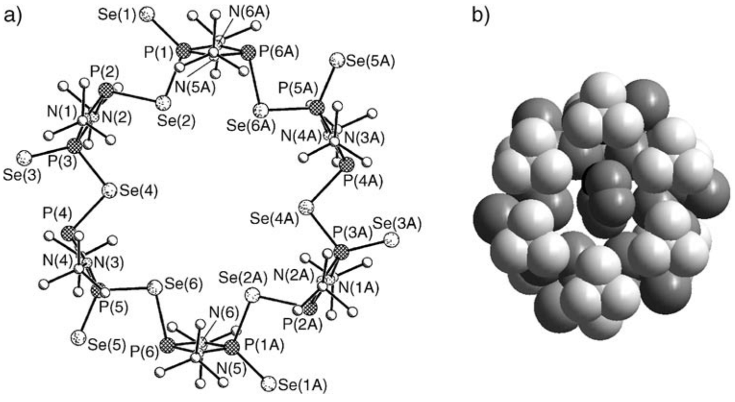


Figure 1. a) Crystal structure of the macrocycle **2**. b) Space-filling diagram, showing inclusion of a THF molecule within the cavity. H atoms, rotational disorder of one of the *t*Bu groups, and site disorder of the Se atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P–N range 1.684(7)–1.722(7), P-(μ-Se) range 2.245(2)–2.380(2), P=Se range 2.063(8)–2.081(2), Se···centroid mean 4.10; P-(μ-Se)-P range 99.93(9)–100.30(8), N-(μ-P)-N range 96.7(4)–97.5(4), P-(μ-N)-P range 81.8(3)–83.7(4). Symmetry transformations used to generate equivalent atoms A: $-x+1$, $-y$, $-z$.

selenium coronands, which are directly related to crown ethers. However, larger Se_6 macrocycles such as $[(CH_2)_3Se]_6$[15] and $[(CH_2)_3Se(CH_2)Se]_3$[16] (and **2**) are still rare. Compound **2** represents a completely new type of Se (or indeed any other Group 16) macrocyclic arrangement, unique in possessing a rigid, crown-like arrangement combined with a large cavity size. The structure of **2** is related to the previously reported hexameric antimony(III) imido macrocycles $[\{Sb(\mu\text{-}NR)\}_2(\mu\text{-}NR)]_6$ (R = 2-MeO-C_6H_4,[17] Ph[18]). However, in both of these cases the dimer-bridging μ-NR groups adopt *trans* conformations with respect to the Sb_2N_2 ring constituents, so as to place all of the associated R groups *exo* to the cavity. The result of this arrangement is that (unlike in **2**) there are no available donor atoms for metal coordination within the backbones of these macrocycles. Significantly, in **2** (where there are no organic substituents bonded to the μ-Se atoms), a cisoid geometry of the μ-Se atoms with respect to the P_2N_2 rings is adopted (similar to that seen in the related nitrogen-based torocycles $[\{P(\mu\text{-N}t\text{Bu})\}_2(\mu\text{-NH})]_n$ ($n = 4$, 5), Scheme 1),[3,4] thus allowing donor Se atoms to be available for potential metal coordination.

In conclusion, we have obtained an unprecedented hexameric, Se-based macrocycle using a simple and logical synthetic procedure. This methodology may well be extendable to other large main-group macrocycles. The large size of the molecular cavity of the new Se macrocycle and its rigidity should make its host–guest chemistry of particular interest, especially with respect to softer metals or even metal–metal-bonded fragments. In addition, there is a potential for the formation of networks through coordination of metal ions using the *exo* Se atoms. Another issue to explore is the ability of the alkali-metal cations in templating macrocycles like **2**.[19]

Experimental Section

1: A mixture of solid $[ClP(\mu\text{-N}t\text{Bu})]_2$ (5.50 g, 20.0 mmol) and gray selenium powder (44.0 mmol) was heated to 200 °C under argon for 30 min. The mixture turned yellow while heating. This mixture was allowed to cool to room temperature and subsequently extracted with hexane (100 mL) and filtered to remove unreacted selenium. The filtrate was evaporated to dryness, giving **1** in sufficient purity for analysis and further reactions. Yield: 6.93 g, 80%. M.p. 105 °C. $^1H\{^{31}P\}$ NMR (25 °C, C_6D_6, 500.12 MHz): $\delta = 1.643$ (s; *t*Bu, *trans* isomer), 1.637 ppm (s; *t*Bu, *cis* isomer); ratio 3:1. $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6, 161.95 MHz, 85% H_3PO_4/D_2O): $\delta = 22.1$ (s, with two satellite doublets arising from $[(^{77}Se{=})ClP(\mu\text{-N}t\text{Bu})_2PCl({=}Se)]$ ($^1J_{^{31}P\text{-}^{77}Se} = 991$ Hz, $^2J_{^{31}P\text{-}^{31}P} = 21$ Hz)], 22.7 ppm (s, with a satellite doublet arising from $[(^{77}Se{=})ClP(\mu\text{-N}t\text{Bu})_2PCl({=}Se)]$ ($^1J_{^{31}P\text{-}^{77}Se} = 990$ Hz, $^2J_{^{31}P\text{-}^{31}P} \approx 0$ Hz)]. A common contaminant in samples of **1** is $[(Se{=})ClP(\mu\text{-N}t\text{Bu})_2PCl]$ ($\delta = 43.5$ (d, $^1J_{^{31}P\text{-}^{77}Se} = 961$, $^2J_{^{31}P\text{-}^{31}P} = 16$ Hz), 152.2 ppm (s, $^2J_{^{31}P\text{-}^{31}P} = 16$ Hz)). ^{77}Se NMR (25 °C, C_6H_6, 95.40 MHz, Me_2Se in C_6D_6): $\delta = 170.7$ (dd, $^1J_{^{31}P\text{-}^{77}Se} = 1001$ Hz, $^2J_{^{31}P\text{-}^{77}Se} = 13$ Hz; *cis* isomer), 170.5 ppm (dd, $^1J_{^{31}P\text{-}^{77}Se} = 990$ Hz, $^2J_{^{31}P\text{-}^{77}Se} = 11$ Hz; *trans* isomer). Electrospray MS: *m/z*: 399 $[M^+{-}Cl]$, 379 $[M^+{-}t\text{Bu}]$. Elemental analysis (%) calcd for **1**: C 22.2, H 4.2, N 6.5; found: C 22.7, H 4.2, N 6.4.

2: A mixture of **1** (1.3 g, 3.0 mmol) and sodium metal (0.30 g, 13.5 mmol) in toluene (40 mL) was brought to reflux (16 h). The resulting brown residue was filtered off and the filtrate concentrated well past the formation of a white precipitate. THF (4.0 mL) was added, and gentle heating gave a yellow solution. Storage at 4 °C (24 h) gave colorless crystals of **2**·2 toluene·THF. Once placed under vacuum during isolation (10^{-1} atm, 15 min), however, elemental analysis reveals that only one toluene molecule is present for each molecule of **2** in the amorphous powder produced. The following analysis refers to this material. Yield: 0.50 g, 45%. M.p. 235 °C. $^1H\{^{31}P\}$ NMR (25 °C, C_6D_6, 500 MHz): $\delta = 1.54$ (s; *t*Bu), 6.9–7.2 (m; toluene), 2.12 ppm (s; Me of toluene). $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6, 161.95 MHz, 85% H_3PO_4/D_2O): $\delta = 206.8$ (d; P^{III}), 54.4 ppm (d; P^V); $^2J_{^{31}P\text{-}^{31}P} = 44$ Hz. The material was too insoluble in organic solvent for a ^{77}Se NMR spectrum to be obtained Electrospray MS: *m/z*: 726 [dimer$^+$]. Elemental analysis (%) calcd for **2**·toluene: C 29.2, H 5.2, N 7.4; found C 29.2, H 5.2, N 7.9. Using the correct stoichiometric ratio of Na metal relative to **1** resulted in a slightly reduced yield of **2**.

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weakly at high angles. This may be attributed to extensive disorder of the two independent molecules (A and B), with rotational disorder of the *t*Bu groups (three ca. 60:40 and one ca. 80:20) and site disorder of the Se and Cl atoms (asymmetric occupancies in the range 75:25 to 50:50 in molecule A and 60:40 in molecule B). The occupancies of the Se and Cl sites (which are well resolved) cannot be explained by any random distribution of either a pure *cis* or of a *trans* isomer of **1** but only as a mixture of the two. Crystal data for **2**·2 toluene·THF: $C_{66}H_{96}N_{12}OP_{12}Se_{12}$, $M_r = 2392.71$, monoclinic, space group $P21/n$, $a = 16.247(3)$, $b = 14.118(3)$, $c = 26.140(5)$ Å, $\beta = 91.53(3)°$, $V = 5994(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.326$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 3.848$ mm^{-1}, reflections collected 39888, independent reflections 8280 [$R_{int} = 0.059$]. $R1 = 0.066$ [$I > 2.0\sigma(I)$], $wR2 = 0.188$. On average there is one THF and two independent toluene molecules in the lattice for each molecule of the macrocycle. The THF solvate is disordered on both sides of **2** in sites of half occupancy. One *t*Bu group exhibits rotational disorder (64:36). In addition, there is a minor disorder (86:14) of the macrocycle explained by a random distribution of a second orientation related to the first by C_2 rotation such that all the atoms except two Se atoms superimpose. Data for **1** and **2** were collected on a Nonius KappaCCD diffractometer at 180(2) K, solved by direct methods and refined by full-matrix least squares on F^2 (G. M. Sheldrick, SHELX-97, Göttingen, **1997**). CCDC-658497 (**1**) and CCDC-658498 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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