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The first example of stereoselective self-assembly of a cryptand containing four asymmetric intracyclic phosphane groups

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ABSTRACT

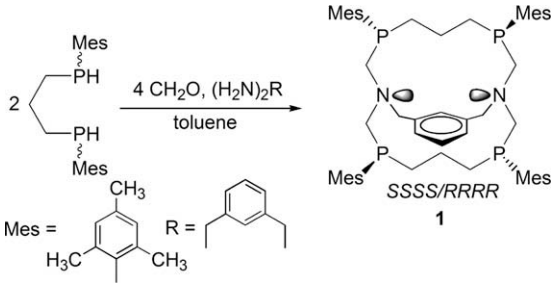
The *rac* stereoisomer of a novel cryptand containing two bridgehead nitrogen and four asymmetric phosphorus atoms in the 16-membered core cycle was obtained stereoselectively via the reaction of bis(mesitylphosphino)propane, formaldehyde, and *meta*-xylylenediamine in the course of a covalent self-assembly process.

Cryptands are able to encapsulate cations of alkali and alkaline earth metals,[1] transition metals,[2] and lanthanoids;[3] display high selectivity in such reactions;[4] and stabilize the resulting complexes (*cryptate effect*). These remarkable properties have led to the development of original sensors,[5] catalysts,[6] organic electrides,[7] and luminescent materials.[8] While for effective binding of alkali metals and alkaline earth metals O-donor cryptands are commonly used, N-donor cryptands are generally applied with transition metals and lanthanoids. It is well known that the phosphorus(III) atom in phosphanes is an excellent donor center for transition metals, however, there are only a few reports on the synthesis of phosphane cryptands.[9,10] The large number of isomers that can be formed in the case of polyphosphorus molecules[11] is probably the reason for the lack of attention to phosphane cryptands.

Recently, our research group reported an efficient stereoselective covalent self-assembly of the macrocyclic tetraphosphanes 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes resulting from the Mannich-type condensation of bis(arylphosphino)propanes, primary amines, and formaldehyde.[12] In the present Letter we have expanded the covalent self-assembly approach to the stereoselective synthesis of a novel phosphorus-containing cryptand consisting of a 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecane 16-membered core ring and a *m*-xylylene bridge connecting the two nitrogen atoms.

Cryptand **1** was prepared in a moderate yield via a one-pot Mannich-type condensation reaction of *m*-xylylenediamine, formaldehyde and a diastereomeric mixture of 1,3-bis(mesitylphosphino)propane[13] (Scheme 1). The two bifunctional reagents (bisphosphane and diamine) were used without high dilution conditions or template reagents, so in principle, the formation of many oligomers is possible.

According to the ^{31}P NMR spectrum of the reaction mixture, cryptand **1** was formed in 55% yield relative to all the other products and the crystalline racemic *SSSS/RRRR* isomer of **1** was isolated in 38% yield. The relatively good yield and stereoselectivity can be explained by the covalent self-assembly of the ther-



Scheme 1. The Mannich-type condensation reaction of *m*-xylylenediamine, formaldehyde and a diastereomeric mixture of 1,3-bis(mesitylphosphino)propane.

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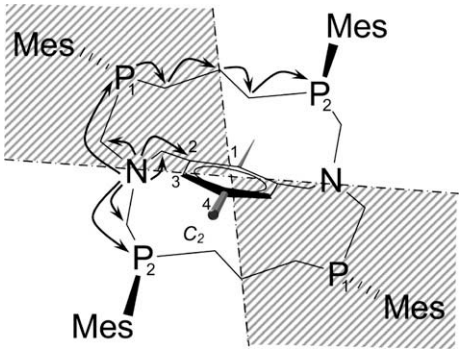


Figure 1. Schematic presentation of the macrocyclic structure with a C_2 axis and the main $^1H–^{15}N/^1H–^{31}P/^1H–^{13}C$ HMBC correlations.

modynamically most stable product in the course of the Mannich-type reaction.

Cryptand **1** was isolated as an air-stable white crystalline solid which was soluble in common organic solvents ($CHCl_3$, CH_2Cl_2, and C_6H_6). Compound **1** was characterized by FAB-MS, elemental analysis, 1D/2D ^1H, ^{13}C, ^{15}N, and ^{31}P NMR spectroscopic experiments,[14] and X-ray analysis.[15]

The 3D structure of cryptand **1** can be divided into four subunits, which have been established unambiguously by NMR spectroscopic methods including $^1H–^{15}N/^1H–^{31}P/^1H–^{13}C$ HMBC correlations[16] starting from nitrogen to the two nonequivalent phosphorus atoms P1 and P2 and the xylylene bridge[†] (Fig. 1). All the identified protons of the P,N-macrocyclic part were represented twice in the ^1H NMR spectra and two phosphorus signals were apparent in the ^{31}P NMR spectrum. Thus, the second part of the molecule could be generated either by rotation around the axis passing through the xylylene protons H1/H4 (C_2 symmetry operation) or by reflection (mirror symmetry operation). However, the latter can be excluded due to the existence of only one type of side chain linking the phosphorus atoms P1···P2. Therefore, the two subunits can be superimposed by a C_2 axis and at the same time the xylylene moiety is symmetrically orientated relative to the two P···P linkers. Finally, the configuration of P1 and P2 (being nonequivalent in the NMR spectra) must be the same (e.g., *RR* or *SS*). Thus, the cryptand possesses C_2 symmetry and the configurations of all four phosphorus atoms are *RRRR* or *SSSS*. This structure is also strongly supported by the nonequivalence of the geminal protons in most of the CH_2 groups in the ^1H NMR data ($\Delta\delta$ 1.35–2.22 ppm), which can be explained by anisotropic effects of the phosphorus and nitrogen lone pairs of electrons. To confirm this observation, the ^1H chemical shifts[17] of the title compound possessing a symmetrical structure with *endo–endo* nitrogen lone pairs of electrons were calculated. These were found to exhibit a very good correlation between the experimental and calculated data ($R^2 = 0.992$, GIAO B3LYP/6-31G(d)//HF/6-31G[18]).

X-ray crystallographic analysis confirmed the structure of the bicyclic tetrakisphosphane **1** (Fig. 2).

Cryptand **1** crystallizes in the centrosymmetric monoclinic space group *C*2/*c* with four molecules in the unit cell, and with only half of the molecule being located in the asymmetric unit and the other half being generated by a C_2 axis on which the atoms C26, C27, H26, and H27 are located. Compound **1** forms a true racemic mixture of the two enantiomers with *SSSS* and *RRRR* configuration of the four phosphorus atoms. The packing diagram of cryptand **1** (Fig. 3) shows that each enantiomer forms

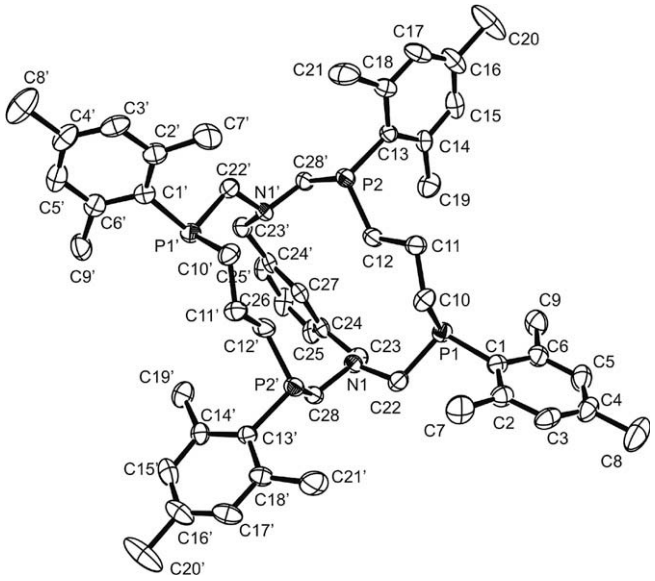


Figure 2. Molecular structure of cryptand **1** in ORTEP view (ellipsoids at 50% probability).

separated columns arranged along the *b* axis.

Cryptand **1** represents an *endo–endo* isomer with only the lone pairs of electrons of the bridgehead nitrogen atoms pointing directly into the cavity (Scheme 1). The geometry of both nitrogen atoms is tetrahedral (the sum of the bond angles is 333.64°). The lone pairs of electrons of the phosphorus atoms P1 and P2 have an axial orientation and are located in opposite directions relative to the 16-membered ring.

The rigidity of compound **1** leads to a considerable distortion of the 16-membered ring (Table 1) as compared to 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes (Scheme 2).

Thus, (*RSSR*)-1,9-dibenzyl-3,7,11,15-tetramesityl-1,9-diaza-3,7,11,15-tetraphosphacyclohexadecane (**2**)[12a] and 1,9-di-*R,R* (or *S,S*)-α-methylbenzyl-3,7,11,15-tetramesityl-1,9-diaza-3,7,11,15-*(RSSR)*-tetraphosphacyclohexadecane (**3**)[12b] have intramolecular N···N distances of ca. 7.4 Å, whereas cryptand **1** has an intramolecular N1···N1′ distance of 4.988 Å. The distortion is also apparent in the intramolecular P···P distances (Table 1).

Thus, only the racemic *RRRR*/*SSSS* isomer is obtained in the described reaction although at least six additional forms could theoretically have been produced. What is the driving force for such high stereoselectivity? With the purpose of seeing if this phenomenon is due to thermodynamic control of the reaction, we analyzed the energies of all the possible isomers of a simpler model cryptand (**1a**) with mesityl radicals at phosphorus atoms which were substituted for methyl groups. The results of the HF/6-31G//HF/6-31G[18] calculations are summarized in Table 2. According to the calculations, the most stable is the *RRRR* isomer and this is in accord with the experiment. The next two forms (*RRRS* and *RRSR*) are higher in energy (by 4.2 and 8.2 kcal/mol, respectively). Moreover, a nonsymmetrical orientation of the xylylene aromatic ring also destabilizes the structure. Consequently, the displayed stereoselectivity may result from thermodynamic control of the reaction.

In conclusion, cryptand **1** has been successfully synthesized via covalent self-assembly in the Mannich-type condensation and exists as one isomer in both the solid states and the solution despite the presence of four chiral intracyclic phosphorus atoms and the possible *endo* or *exo* orientation of nitrogen lone pairs of electrons.

[†] Details of the NMR experiments, as well as calculation data will be published later in a separate paper.

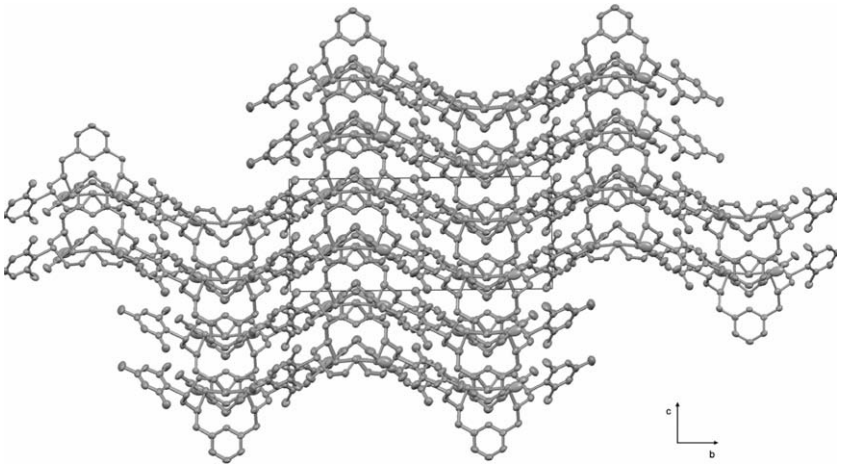
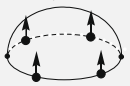
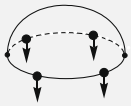
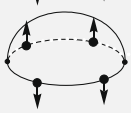
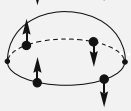
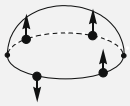
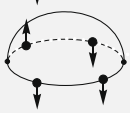


Figure 3. Packing diagram of cryptand **1** (viewed along the *a* axis).

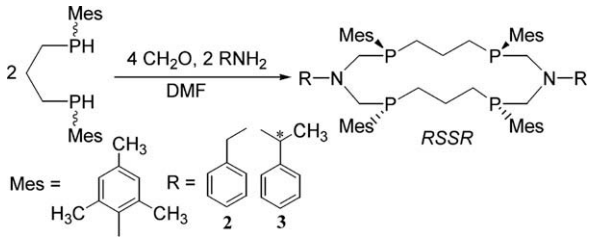
Table 1
Selected interatomic distances (Å) for **1**, **2** and **3**

Compd	N···N	P1···P1′	P2···P2′	Ref.
1	4.988	7.579	6.015	This work
2	7.279	8.845	4.953	12a
3	7.571	8.634	4.968	12b

Table 2
Relative energies (kcal/mol)[a] of different isomers[b] of **1a**

P1P2P1′P2′ configuration	Isomer[c]	sym[d]	nsym[d]
RRRR		0.0	4.3
RSRS		8.3	17.8
SRSR		17.3	13.8
RRSS		12.9	ns[e]
RSSR		ns	7.9
RRRS (*RSRR*)		4.2	ns
RRSR (*SRRR*)		8.2	ns

[a] (HF/6-31G//HF/6-31G[18]).
[b] Corresponding enantiomers are not shown.
[c] Schematic orientation of phosphorus lone pairs are shown by arrows.
[d] Isomers with symmetrical (sym) and nonsymmetrical (nsym) orientation of the xylylene aryl moiety in relation to the 16-membered macrocycle of the molecule.
[e] ns = nonstable conformation.



Scheme 2. The Mannich-type condensation reaction of bis(mesitylphosphino)propane, primary amines and formaldehyde.

Acknowledgments

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14. *m*-Xylylenediamine (0.21 g, 1.5 mmol) was slowly added to a solution of 1,3-bis(mesitylphosphino)propane (1.08 g, 3.1 mmol) and paraformaldehyde (0.18 g, 6.0 mmol) in toluene (15 ml) over 3 h at 70 °C. The mixture was then stirred at rt. and the formation of a crystalline product was observed after 5 days. The resulting white crystals were collected by filtration and dried under vacuum. Yield: 0.52 g, 38%, mp 215–217 °C. ^{31}P NMR ($CDCl_3$, 242.94 MHz, 303 K): −38.4, −44.3 ppm. ^{15}N NMR ($CDCl_3$, 60.81 MHz, 303 K): 32.4 ppm. ^{1}H NMR ($CDCl_3$, 600.13 MHz, 303 K): 1.68 (m, 2H, $PCH_2CH_2CH_2P$), 1.95 (m, 2H, $PCH_2CH_2CH_2P$), 2.12 (m, 2H, $PCH_2CH_2CH_2P$), 2.24 (s, 6H, *p*-$CH_3^{I\ or\ II}$ in Mes), 2.25 (s, 6H, *p*-$CH_3^{II\ or\ I}$ in Mes), 2.30–2.50 (m, 10H, signals of $PCH_2CH_2CH_2P$ overlapped with the signals of P–$CH_2^{I+II\ A}$–N), 2.51 (s, 12H, *o*-$CH_3^{I\ or\ II}$ in Mes), 2.53 (s, 12H, *o*-$CH_3^{II\ or\ I}$ in Mes), 2.76 (m, 2H, $PCH_2CH_2CH_2P$), 3.19 (d, 2H, $^{2}J_{HH}$ 15.4 Hz, CH_2^{A} in xylylene), 3.75 (m, 2H, P–$CH_2^{II\ B}$–N), 4.62 (m, 2H, P–$CH_2^{I\ B}$–N), 4.99 (m, 2H, CH_2^{B} in xylylene), 6.85 (s, 8H, *m*-H in Mes), 7.05 (d, 2H, $^{3}J_{HH}$ 7.4 Hz, H-3 in xylylene), 7.26-7.29 (signals of H-4 in xylylene overlapped with the $CHCl_3$ signal), 8.24 (s, 1H, H-1 in xylylene) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz, 303 K): 20.88 (s, *p*-CH_3 in Mes), 23.53 (d, $^{3}J_{PC}$ 18.2 Hz, *o*-$CH_3^{I\ or\ II}$ in Mes), 23.72 (d, $^{3}J_{PC}$ 18.8 Hz, *o*-$CH_3^{II\ or\ I}$ in Mes), 26.53 (dd, $^{2}J_{PC}$ 23.7 Hz, $^{2}J_{PC}$ 23.4 Hz $PCH_2CH_2CH_2P$), 27.26 (dd, $^{1}J_{PC}$ 14.4 Hz, $^{3}J_{PC}$ 12.2 Hz, $PCH_2CH_2CH_2P^{I}$), 29.07 (dd, $^{1}J_{PC}$ 15.1 Hz, $^{3}J_{PC}$ 14.7 Hz, $PCH_2CH_2CH_2P^{II}$), 56.42 (d, $^{1}J_{PC}$ 11.1 Hz, P–CH_2^{I}–N), 58.06 (d, $^{1}J_{PC}$ 8.3 Hz, P–CH_2^{II}–N), 59.39 (d, $^{3}J_{PC}$ 7.7 Hz, CH_2 in xylylene), 125.05 (s, C-3 in xylylene), 126.21 (s, C-1 in xylylene), 127.70 (s, C-4 in xylylene), 129.40 (s, *m*-C in Mes), 130.96 (d, $^{2}J_{CP}$ 20.5 Hz, *o*-$C^{I\ or\ II}$ in Mes), 131.61 (d, $^{2}J_{CP}$ 17.1 Hz, *o*-$C^{II\ or\ I}$ in Mes), 138.73 (s, *p*-$C^{I\ or\ II}$ in Mes), 138.78 (s, *p*-$C^{II\ or\ I}$ in Mes), 140.77 (s, C-2 in xylylene), 144.37 (d, $^{1}J_{PC}$ 14.9 Hz, *ipso*-$C^{I\ or\ II}$ in Mes), 144.52 (d, $^{1}J_{PC}$ 14.9 Hz, *ipso*-$C^{II\ or\ I}$ in Mes) ppm. FAB-MS (*m*/*z*, $I_{rel.}$, %): 873 ($[M]^+$, 13.5), 874 ($[M+H]^+$, 7.2), 889 ($[M+O]^+$, 4.3). Anal. Calcd for $C_{54}H_{72}N_2P_4$ [873.02]: C, 74.2; H, 8.3; N, 3.2; P, 14.1. Found: C, 73.9; H, 8.1; N, 3.0; P, 13.9.
15. Crystal data of **1** were collected on a CCD Oxford Xcalibur S diffractometer ($\lambda(0_\alpha)$ = 0.71073 Å) using ω and φ scans mode. Semi-empirical absorption corrections were carried out with SCALE3 ABSPACK[19] and the structures were solved by direct methods.[20] Structure refinement was carried out with SHELXL-97.[21] All non-hydrogen atoms were refined anisotropically, H atoms were calculated and refined isotropically. CCDC 696882 (**1**) contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk). Crystal data, structure refinement for compound **1**. $C_{54}H_{72}N_2P_4$ (**1**); *M* = 873.02, monoclinic, space group *C*2/c, *a* = 23.9070(4), *b* = 9.4781(1), *c* = 22.3124(5) Å, α = 90, β = 98.584(2), γ = 90°, *V* = 4999.2(2) Å^3, *Z* = 4, *D* calcd = 1.160 g cm^{-3}; μ(Mo-Kα) = 0.188 mm^{-1}; 41740 reflections measured, 4670 independent reflections. Final R_1 = 0.0527, *R*w = 0.1002 for reflections with $I \geqslant 2\sigma(I)$, and R_1 = 0.0997, *R*w = 0.1170 for all reflections.
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