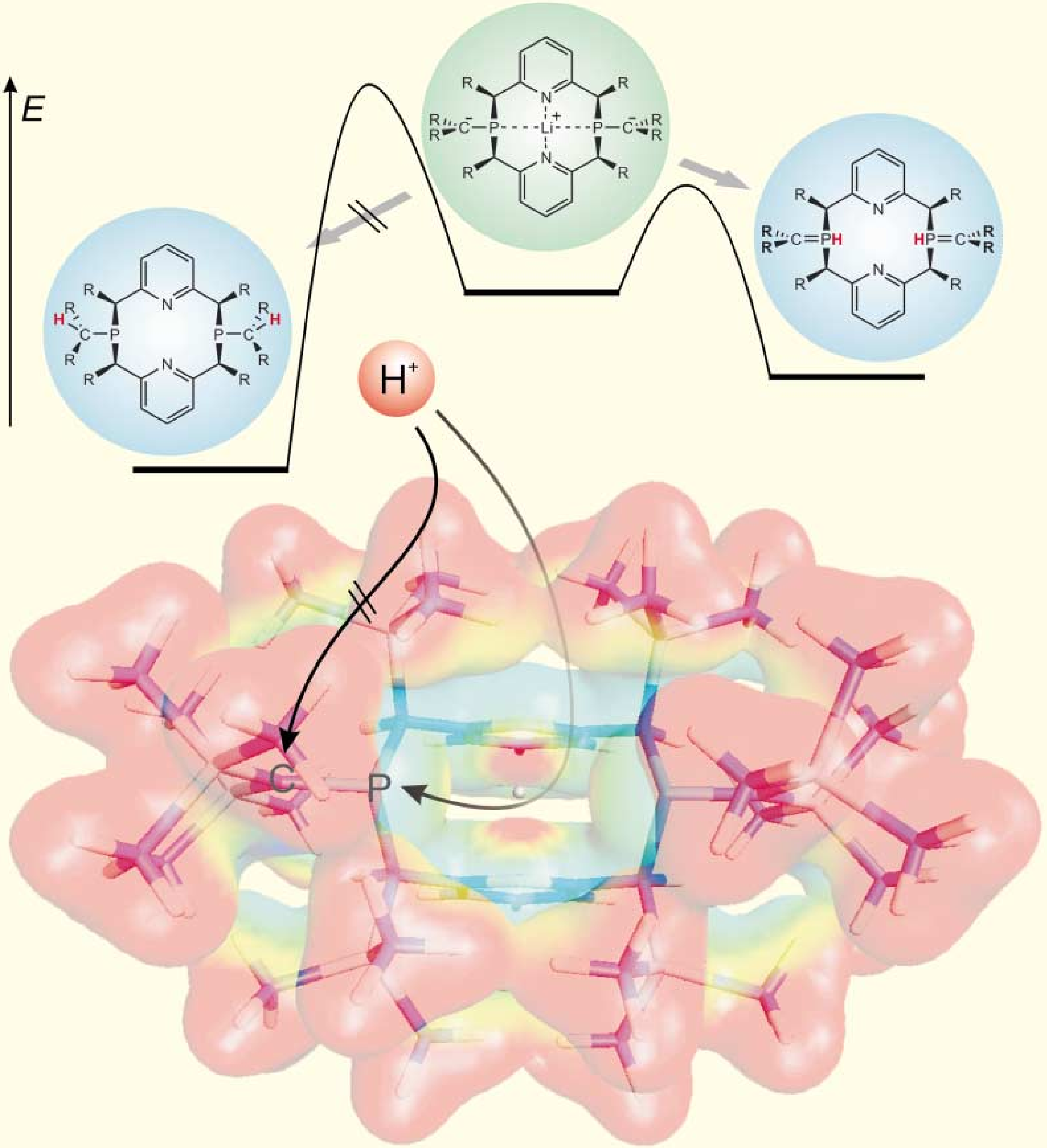
Kinetically Controlled Protonation of a Phosphamethanide



The positive electrostatic potential (red) on the surface of the macrocycle inhibits the protonation of the methanide carbon atom, whereas the negatively charged tunnel (blue) through the macrocycle facilitates an approach of the proton to the phosphorus atom. This favors the formation of the thermodynamically less stable PH-phosphonium ylide instead of the phosphane. For more information see the following pages.

Kinetically Controlled Protonation of a Cyclic Phosphamethanide Complex to a PH-Phosphonium Ylide**

Sahir Ekici, Dietrich Gudat, Martin Nieger,
Laszlo Nyulaszi,* and Edgar Niecke*

Dedicated to Professor Rüdiger Mews
on the occasion of his 60th birthday

The parent phosphonium ylide, $H_3P{=}CH_2$, and the tautomeric, methylphosphane, $H_2P{-}CH_3$, which is energetically more stable by 56 kcal mol^{-1}, are separated by a sufficiently high isomerization barrier of 34 kcal mol^{-1} which renders the former a stable gas-phase species.[1] In solution, PH-phosphonium ylides are generally thermodynamically less stable than the alkyl phosphane form.[2] However, NMR studies of bis(alkoxycarbonyl)methylphosphanes suggested that even in solution the PH tautomer may be populated if an effective stabilization of the negative charge is provided.[3] We report here on the synthesis and crystal structure of a PH-phosphonium ylide that exists as a kinetically stable species in condensed phases.[4]

Recently, we described the coupling reaction between the lithium salt of the bifunctional carbanion **1a** ($R' = Ph$) with the bifunctional, electrophilic bis(phosphaethene)s *rac/meso*-**2a** ($R = SiMe_3$) to yield the macrocyclic complex **3a**, and its subsequent conversion into the neutral ligand **4a** (Scheme 1).[5] The analogous reaction of the bis(phosphaethene)s *rac/meso*-**2b** ($R = SiMe_3$), which were accessible from **1b**[6] and $ClP{=}C(SiMe_3)_2$,[7] respectively, with an excess of **1b** affords the phosphamethanide complex **3b**[$Li(OEt_2)_x$], which was, after exchange of the donor, isolated as a crystalline salt **3b**[$Li(tmeda)_2$].[8] Quite surprisingly, protonation of **3b** with Et_3NHCl in THF yielded no bisphosphane, as in the case of **3a**, but a mixture of the PH-ylides **5b** (80 %) and **6b** (20 %). Isomer **5b** was formed exclusively when the protonation was carried out using NH_4Cl in THF/CH_2Cl_2 (1:1) and was isolated as a crystalline product from this reaction. It was found that a mutual conversion between both isomers, or their further transformation into a bisphosphane **4b**, could be induced neither by heating to 100 °C nor by means of acid or base catalysis; reaction with an excess of *n*-butyllithium proceeded under re-formation of the ate complex **3b**.

The constitution of the macrocycles **3b** and **5b** and **6b** followed from NMR investigations and was, in the case of **3b** and **5b**, confirmed by X-ray diffraction studies. The constitution of the ate complex **3b**, which features coordination of a lithium atom in the macrocycle, is substantiated by the ^{31}P and ^{7}Li NMR data ($\delta(^{31}P) = 14.1$ ppm, $^{1}J_{P,Li} = 58$ Hz; $\delta(^{7}Li) = 2.5$ ppm (t, $^{1}J_{P,Li} = 58$ Hz), 0.6 (s)). The number of ^{1}H and ^{13}C NMR signals implies that **3b** exhibits effective C_{2v} symmetry in solution at 30 °C. Interestingly, this symmetry is conserved even at −80 °C, while at the same time a reduction of the $^{1}J_{P,Li}$ coupling to 50 Hz was observed which points presumably to temperature-dependent changes in the solvation of the lithium ion. The constitution of **5b** as a PH-ylide is confirmed by the occurrence of a characteristic coupling ($^{1}J_{P,H} = 453$ Hz). As in the case of **3a**, the number of ^{1}H and ^{13}C NMR signals indicates an effective molecular C_{2v} symmetry at 30 °C, with the occurrence of two chemically inequivalent exocyclic $SiMe_3$ groups suggesting that the $C(SiMe_3)_2$ moieties (whose carbon atoms are considered to exhibit planar geometries) do not rotate freely, but are frozen in a position similar to that in the crystal (see below). At low temperatures, a dynamic line broadening and finally a doubling of the signals of the $CH(SiMe_3)$ fragments in the macrocycle and the *meta*-CH moieties of the pyridine rings is observed. The coupling patterns and NOE measurements suggest the presence of a C_2-symmetric molecular structure at −80 °C that adopts a conformation similar to that found in the crystal. The isomer **6b** gives rise to two ^{31}P NMR signals of which only one exhibits the typical $^{1}J_{P,H}$ coupling (457 Hz) of a PH-ylide. The ^{1}H NMR spectrum displays broadened signals at 30 °C that decoalesce at lower temperatures. The number of signals at −80 °C implies the presence of a C_1-symmetric molecular structure that is rationalized by assuming that the rotation of the $CH(SiMe_3)_2$ group is frozen and the substituent adopts a conformation close to the one depicted in Scheme 1. This hypothesis was validated by NOE measurements and by the determination of the magnitudes and signs of the $^{1,2}J_{P,X}$ (X = H, C, Si) coupling constants involving the tervalent phosphorus atom.[9] High-temperature NMR spectra of **6b** revealed that rapid rotation of the $CH(SiMe_3)_2$ moiety on the NMR time scale is only observed above 100 °C.

The molecular structure of **3b** and the resulting PH-ylide **5b** are shown in Figure 1 and Figure 2, respectively.[10] The twelve-membered ring of **3b** displays a *syn* conformation with a boat–boat arrangement of the phosphorus atom, and is folded along the P–P axis. The coordination of the lithium by the phosphorus and nitrogen atoms can be described in terms of a strongly distorted tetrahedral, "seesaw"-like geometry (P-Li-P 171°; N-Li-N 85°). The trigonal-planar coordination of the carbon atoms (sum of bond angles 360°) and the P–C distances (175.3(3), 175.5(3) pm) in the phosphoniomethanide moieties match the data of similar compounds.[11]

The protonation to give **5b** induces no substantial changes in the macrocycle conformation. The former coordination space of the lithium atom is occupied by the P-bound hydrogen atoms, each of which displays a weak hydrogen bond to one of the nitrogen atoms (PH···N 283(4), 298(4) pm; P-H-N 88–94(2)°). Comparable structural features have been observed for SH···N and PH···O moi-

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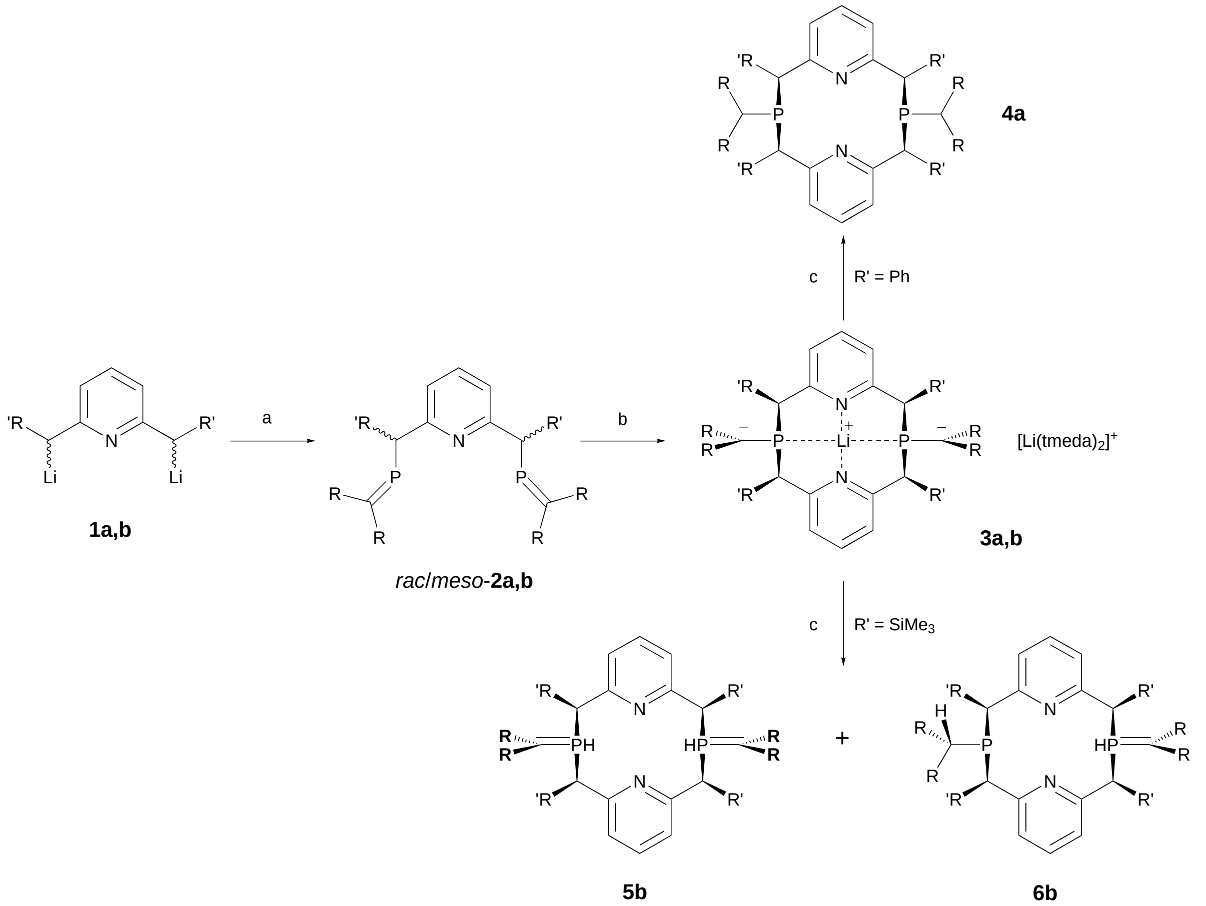

Scheme 1. Synthesis and reactions of **3ab** (**1a**–**4a**: R = SiMe$_3$, R′ = Ph; **1b**–**3b**, **5b**, **6b**: R = R′ = SiMe$_3$); a) ClP=C(SiMe$_3$)$_2$ (2 equiv), Et$_2$O, −78 °C; b) **1a,b** (1 equiv), Et$_2$O, −78→−30 °C, TMEDA (2 equiv); c) Et$_3$NHCl or NH$_4$Cl, THF/CH$_2$Cl$_2$.TMEDA = tetramethylethylenediamine.

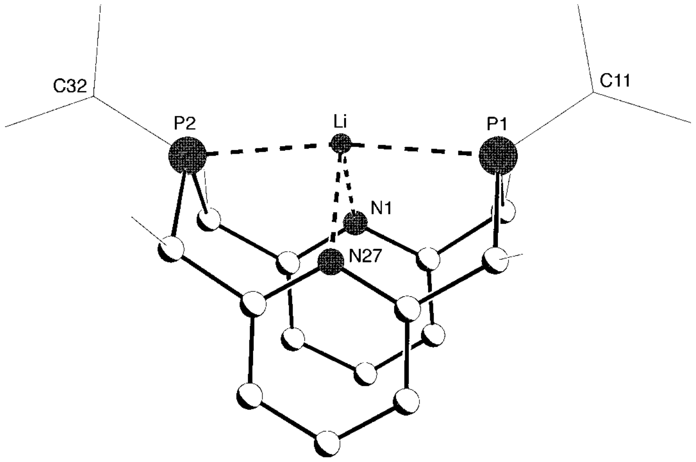

Figure 1. Molecular structure of **3b** in the crystal (without hydrogen atoms and peripheral groups). Selected bond lengths [pm] and angles [°]: Li-N1 212.1(5), Li-N27 211.5(5), Li-P1 245.8(4), Li-P2 245.7(4), P1-C11 175.5(3), P2-C32 175.3(3); N1-Li-N27 85.1(2), N1-Li-P1 85.9(2), N1-Li-P2 87.3(2), N27-Li-P1 87.0(2), N27-Li-P2 86.5(2), P1-Li-P2 171.0(2).

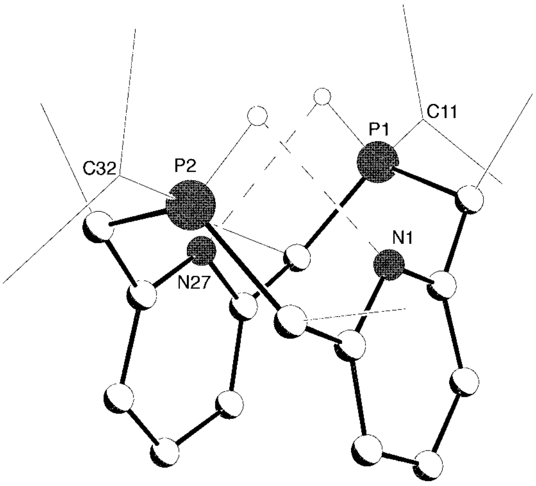

Figure 2. Molecular structure of one of the two independent molecules of **5b** in the crystal (without hydrogen atoms and peripheral groups; data for the second independent molecule in brackets). Selected bond lengths [pm] and angles [°]: P1-C11 168.2(5) [169.3(5)], P2-C32 169.7(5) [169.1(5)], H(P1)···N27 292(4) [283(4)], H(P2)···N1 296(4) [298(4)]; P1-H(P1)···N27 91(2) [94(2)], P2-H(P2)···N1 88(2) [89(2)].

eties.[12] The trigonal-planar coordination of the carbon atoms (sum of bond angles 360°) and the P−C distances (168.2(5)–169.7(5) pm) in the ylide moieties are similar to those of other C(SiMe$_3$)$_2$-substituted phosphonium ylides (P−C 168(3) pm).[13]

To rationalize the unexpected formation of the PH-ylides **5b** and **6b**, quantum-mechanical calculations were carried out.[14] In view of the extreme computational expense of ab initio computations on the Me$_3$Si-substituted molecules studied, we first assessed the reliability of semiempirical

PM3 calculations, using a smaller model system in which all $SiMe_3$ groups were replaced by SiH_3 groups. The relative energies given in Table 1 reveal that, at this level of theory, the phosphane structure with C-bound hydrogen atoms is more stable than the ylide structure by some 10 kcal mol^{-1}. The application of density functional methods (B3LYP functional with different basis sets, with or without zero-point-energy corrections) yielded comparable results. As the replacement of SiH_3 by $SiMe_3$ groups has only a minor influence on the relative energies (as shown by single-point B3LYP/3-21G(*)//PM3 calculations), we consider the phosphane **4b** to be thermodynamically more stable than the ylide **5b**, and attribute the observed formation of the latter to kinetic hindrance of the competing reaction. To elucidate the origin of this effect, we have computed the electrostatic potential on the surface of a lithiated anion whose macrocyclic ligand carries two SiH_3 substituents on one side, and two $SiMe_3$ substituents on the other side of the ring. The representation shown in Figure 3 reveals the potential on the inner side of the macrocycle to be negative, and that on the outer side of the $SiMe_3$-substituted region to be positive. This potential should inhibit the approach of a proton to the reactive, negatively charged carbon atom, whereas the approach to the phosphorus atom and the formation of the PH-ylide should be readily feasible. Since the attack of a proton at the carbon atom on the SiH_3-substituted region is not obstructed, it becomes clear that the observed ylide formation is an immediate consequence of the unfavorable steric and electrostatic effects of the $SiMe_3$ groups, and that with smaller substituents the formation of thermodynamically more stable phosphanes is to be expected. To elucidate the possibility of a ylide/phosphane conversion by an intramolecular 1,2-H shift, we have also computed the corresponding transition states (Table 1). As the resulting energies lie more than 40 kcal mol^{-1} above the ground state at all levels studied, an intramolecular rearrangement seems unlikely. An intermolecular hydrogen exchange should be likewise inhibited by the sterically protecting $SiMe_3$ groups.

Table 1. Relative energies (in kcal mol^{-1}) of the ylide and phosphane form of model compounds.[a]

	R^1, $R^2 = SiH_3$				$R^1 = SiMe_3$, $R_2 = SiH_3$		R^1,$R^2 = SiMe_3$
model[b]	PM3	B3	B6//B3	B6	PM3	B3//PM3	PM3
phosphane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
transition state	56.9	66.0	66.9	66.8	52.1/55.7[b]	82.5/85.7[b]	
ylide	13.6	13.0	13.8	14.0	8.1	37.7	7.7

[a] Model: PM3 = PM3, B3 = B3LYP/3-21g*, B6 = B3LYP/6-31g*. [b] The values separated by slashes refer to the energies of hydrogen shifts in the SiH_3- and $SiMe_3$-substituted region of the molecule, respectively.

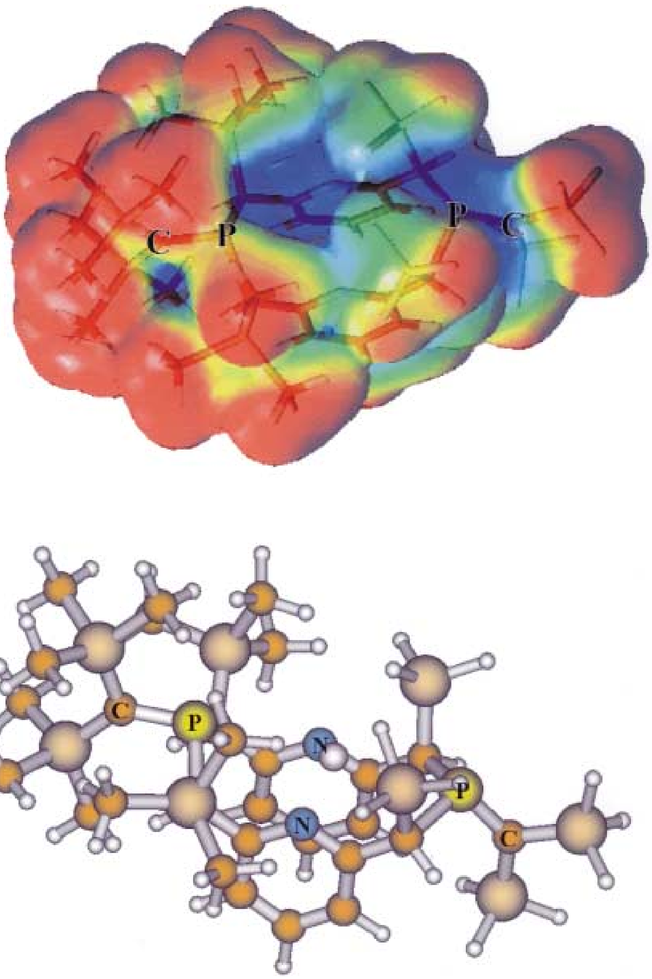

Figure 3. Representation of the electrostatic potential (with molecular structure incorporated as ball-and-stick model) on the surface of an anionic lithium complex whose macrocyclic ligand carries $SiMe_3$ groups on one, and SiH_3 groups on the other side of the ring.

Experimental Section

Synthesis of **2b**: A 1.6 M solution of *n*BuLi (5.6 mL, 9 mmol) was added at −78 °C to a solution of bis(trimethylsilyl)pyridine (1.13 g, 4.5 mmol) in Et_2O (30 mL), and the mixture was stirred for 0.5 h at −78 °C and then for 5 h at room temperature. This solution was then added dropwise at −78 °C to Cl−P=C($SiMe_3$)$_2$ (2.02 g, 9.0 mmol) in Et_2O (30 mL). The mixture was stirred for 1 h, and after it had been warmed to room temperature, the solvents were evaporated in vacuo and the remaining residue was dispersed in *n*-hexane. Filtration and evaporation of the solvents in vacuo yielded a yellow oil consisting of a 4:1 isomer mixture of *rac/meso*-**2b**, which was used for subsequent reactions without further purification. MS (16 eV): *m*/*z* (%): 554 (3) [*M*−$SiMe_3$]$^+$, 73 (100) [$SiMe_3$]$^+$; ^{31}P NMR (CH_2Cl_2, 25 °C): δ = 399.1, 401.2 ppm (*rac/meso*-**2b**).

3b: A solution of **1b** (4.5 mmol) was prepared as described above and was added dropwise at −78 °C to a solution of *rac/meso*-**2b** (2.83 g, 4.5 mmol) in Et_2O (30 mL). The stirred reaction mixture was warmed to −30 °C and kept at this temperature for 24 h. Addition of TMEDA (1.10 g, 9.4 mmol) and storing the mixture for two days at −30 °C produced red crystals of **3b**. Yield 4.6 g (83 %).

5b, 6b: A solution of **3b** (1.0 g, 0.9 mmol) in THF (20 mL) was added dropwise at 0 °C to a stirred suspension of Et_3NHCl (0.10 g, 1.8 mmol) in THF (30 mL). Stirring was continued for 2 h at room termperature, the solvent evaporated in vacuo, and the remaining residue was dispersed in Et_2O (30 mL), and filtered. Concentration of the filtrate to half of the original volume and storage at 0 °C for 2–3 days produced 0.72 g (91 %) of a 4:1 mixture of **5b** and **6b**. Carrying out the protonation of **3b** with NH_4Cl in CH_2Cl_2 under otherwise identical conditions afforded, after analogous work-up, pure **5b** as colorless crystals, yield: 0.67 g (85 %); MS (16 eV): *m*/*z* (%): 878 [*M*]$^+$ (7), 628 [*M*−$C_{11}H_{25}Si_2N$]$^+$ (5), 251 [$C_{11}H_{25}Si_2N$]$^+$ (100).

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[10] X-ray structure analyses at 123 K: **3b**: $[\mathrm{C_{40}H_{82}LiN_2P_2Si_8}]$ $[\mathrm{Li(tmeda)_2}]\cdot 1.5\,\mathrm{Et_2O}$; $M_r = 1235.21$; orthorhombic, space group *Pbca* (no. 61), $a = 18.0563(3)$, $b = 23.8365(4)$, $c = 35.6988(7)$ Å, $V = 15\,364.7(5)$ Å^3, $Z = 8$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.220\ \mathrm{mm^{-1}}$, $F(000) = 5432$, 83 170 reflections ($2\theta_{\max} = 50°$), 13 345 independent reflections, $wR2(F^2) = 0.1095$, $R(F) = 0.0442$ for 693 parameters and 119 restraints. **5b**: $\mathrm{C_{40}H_{84}N_2P_2Si_8}\cdot 1.5\,\mathrm{CH_2Cl_2}$; $M_r = 1007.14$; monoclinic, space group $P2_1/n$ (no. 14), $a = 16.6685(3)$, $b = 35.3065(6)$, $c = 19.6393(4)$ Å, $\beta = 92.147(1)°$, $V = 11\,549.7(4)$ Å^3, $Z = 8$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.409\ \mathrm{mm^{-1}}$, $F(000) = 4344$; 48 157 reflections ($2\theta_{\max} = 50°$), 19 957 independent reflections, $wR2(F^2) = 0.1706$, $R(F) = 0.0627$ for 1018 parameters and 89 restraints. A further X-ray diffraction study of a polymorph **5b′** (*C*2/*c*, $Z = 12$) gave very similar results. CCDC-182888 (**3b**), CCDC-182889 (**5b**). and CCDC-182890 (**5b′**) contain the supplementary crystallographic data for this paper. 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.ac.uk).

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Self-Assembly of Trigonal-Prismatic Metallocages Encapsulating $\mathrm{BF_4^-}$ or $\mathrm{CuI_3^{2-}}$ as Anionic Guests: Structures and Mechanism of Formation**

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The use of metal ions to promote the self-assembly of discrete, well-defined supramolecular architectures has become an important synthetic strategy during recent years, especially for encapsulating structures which possess an internal cavity capable of accommodating guest molecules.[1] Various large polyhedral structures have been constructed and rationally classified.[2] Among these are the $\mathrm{M_{18}L_6}$ (M = metal, L = ligand) hexahedral cage,[3] $\mathrm{M_{12}L_8}$ and $\mathrm{M_6L_8}$ cube-like cages,[4] and 50-component dodecahedra[5] with high symmetry. However, lower-symmetry hosts can ultimately be expected to show enhanced guest selectivity.[6] Surprisingly, the simplest three-dimensional (3D) canonical cage structure with the fewest number of components ($\mathrm{M_3L_2}$ or $\mathrm{M_2L_3}$), the trigonal prism,[2a] has remained rather uncommon in comparison with the various high-symmetry polyhedra.[7] In contrast to the well studied helical structures,[8] and despite the rapid progress in the construction of various molecular architectures with defined shapes and sizes, the mechanisms of formation for such species are often unknown.[9] To develop synthetically viable pathways for a rational design of discrete molecular architectures, it is important to understand the dynamic behavior of such molecular architectures in solution. In the course of our work on the construction of supramolecular assemblies from tripodal ligands,[10] we now describe the self-assembly of the $\mathrm{M_3L_2}$ trigonal prismatic molecular boxes $[\mathrm{BF_4}{\subset}\{\mathrm{Ag_3(MsTBim)_2}\}](\mathrm{BF_4})_2$ (**1**; MsTBim = 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene) and $[\{\mathrm{CuI_3}{\subset}[\mathrm{Cu_3(MsTBim)_2}]\}_2](\mathrm{Cu_2I_4})$ (**2**). The solution ^{1}H NMR spectroscopic study of **1** indicates that the box structure is the thermodynamically stable but kinetically labile product.

The semi-rigid ligand MsTBim,[10e] with an arene core connecting three benzimidazolyl arms is expected to facilitate cage-structure formation instead of encapsulating one or

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