Facile P_2N_2 macrocycle formation promoted by lithium templating. The X-ray crystal structures of *syn*-Li_2(thf)(P_2N_2) and *anti*-Li_2(thf)$_2$(P_2N_2) [P_2N_2 = PhP($CH_2SiMe_2NSiMe_2CH_2$)$_2$PPh]

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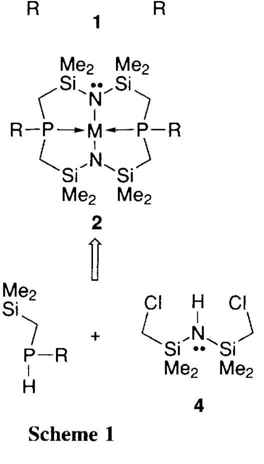
Lithium ions act as templates in the formation of twelve-membered ring macrocycles that contain both amido and phosphine donors.

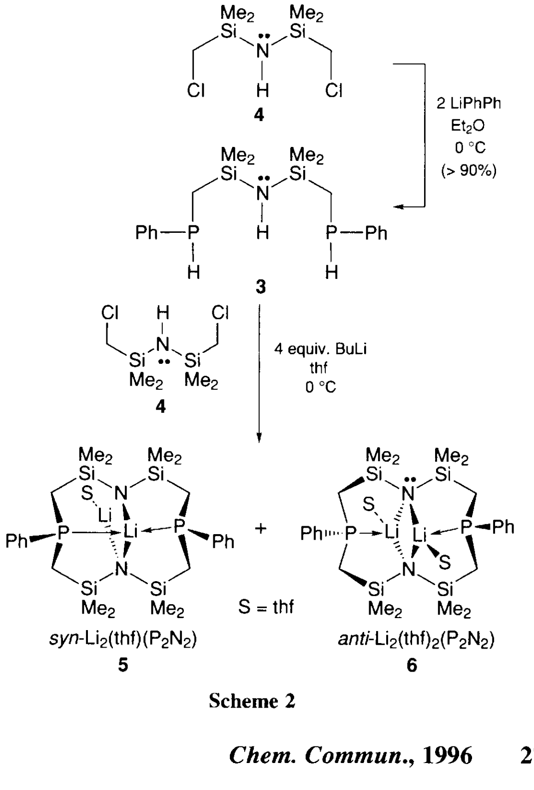
The synthetic procedures for the preparation of macrocyclic ligands can be broadly subdivided into two categories: (*i*) direct cyclization generally using high-dilution techniques, and (*ii*) metal template reactions.[1] While many nitrogen-based macrocyclic ligands such as porphyrins and phthalocyanines are well entrenched in inorganic coordination chemistry, phosphorus-containing macrocycles are less common.[2] This is in large part due to the fact that synthetic procedures can be arduous[1] and control of stereochemistry at the trigonal-pyramidal phosphorus centres is difficult. Although early work in this area used both high-dilution techniques[3] and metal template reactions[4] to prepare phosphine-containing macrocycles, recently the template procedure has been exploited to not only improve yields but also control stereochemistry.[5] Here, we report the stereoselective preparation of two new phosphorus-containing macrocycles that also incorporate amido nitrogen donors; these large twelve-membered heterocyclic rings are made up of two disilylamido donors and two phenylphosphine units mutually *trans* disposed. In addition, lithium ions serve to template the phosphorus–carbon bond formation resulting in extremely high yields and with excellent control of stereochemistry.

As a consequence of our interest in early-metal chemistry with the ancillary ligand **1**[6–8] and the recent surge of investigations of the ligation of nitrogen-based macrocycles for these elements,[9–11] we decided to examine the preparation of a macrocyclic version of **1** by closing up the open end with another disilylamido unit to give derivatives of the type **2**. Because of the formal dinegative charge of **2** there is some analogy to porphyrin-type systems, admittedly without conjugation. From a retrosynthetic analysis, the analogous secondary diphosphine equivalent of the acyclic ligand, *i.e.* **3**, and the bis(chloromethyldimethylsilyl)amine **4** seemed like obvious precursors, particularly since **4** is the starting material for **3** (Scheme 1).



Scheme 1

Reaction of 2 equiv. of LiPHPh with HN($SiMe_2CH_2Cl$)$_2$ **4** leads to the formation of the secondary diphosphinosilazane (**3**, R = Ph) in almost quantitative yield (Scheme 2). We have investigated a variety of conditions for macrocyclic ring formation between **3** and **4**; in general we find that solvent plays an important role and lithium bases are critical. For example, reaction of a mixture of **3** and **4** at low temp. in thf in the presence of 4 equiv. of either butyllithium (BuLi) or lithium diisopropylamide (LDA) leads to the formation of just two products in very high yields; after separation of LiCl, fractional crystallization from hexanes allows for the separation and crystallization of two colourless, crystalline solids, the more soluble material having the formula Li_2(thf)(P_2N_2) **5** and the less soluble product with the formula Li_2(thf)$_2$(P_2N_2) **6** [P_2N_2 = PhP($CH_2SiMe_2NSiMe_2CH_2$)$_2$PPh]. Both **5** and **6** display 1 : 1 : 1 : 1 quartets in their ^{31}P{^{1}H} NMR spectra due to coupling to ^{7}Li (I = 3/2, 92.6% natural abundance); also the corresponding ^{1}H NMR spectra are very similar. However, it is the ^{7}Li NMR spectra that indicate that these materials are quite different. For **5**, the ^{7}Li NMR spectrum consists of a binomial triplet and a broad singlet, while for **6**, only one type of lithium environment is evident from the observed doublet resonance. Thus the structure of **5** requires two distinct Li environments of



Scheme 2

which only one is attached to two equivalent phosphine donors. In **6**, both lithiums are equivalent and each is bound to a single phosphine. In Scheme 2, the proposed structures are indicated. Single-crystal X-ray structural analyses not only confirmed these proposals but provided the additional information on relative stereochemistry at the pyramidal phosphorus centres.

The solid-state structures‡ are shown in Fig. 1 along with some important bond lengths and bond angles. A common structural motif found in each material is the presence of two lithium ions bridged by two disilylamide moieties. This is in accord with numerous lithium amides that have been shown to display this kind of structure.[12,13] In addition, the relative stereochemistry at phosphorus is evident from these two structures: in **5**, the phenyl groups are *syn* across the macrocycle, while in **6**, these substituents are disposed in an *anti* relationship.

Some additional comments on the synthetic procedure are worth mentioning. When the reaction is performed in thf at 0 °C as shown in Scheme 2, the ratio of *syn*-$Li_2(thf)(P_2N_2)$ **5** to *anti*-$Li_2(thf)_2(P_2N_2)$ **6** is reproducibly 3 : 1 in a combined isolated yield of 90%. The ratio of **5** to **6** is temperature dependent such that as the temperature is lowered, increased amounts of the *anti* product **6** are formed without loss of chemical yield; thus, at −60 °C, the ratio is 1 : 2.4 in favour of *anti* **6**. More interesting is the effect of solvent alluded to above. If diethyl ether is used, only the *syn* isomer **5** is detected and it is isolated in greater than 80% yield; in this case, we isolate the dioxane adduct of **5**, *syn*-$Li_2(dioxane)(P_2N_2)$, upon workup, which in turn converts to the original thf adduct **5** upon addition of thf.

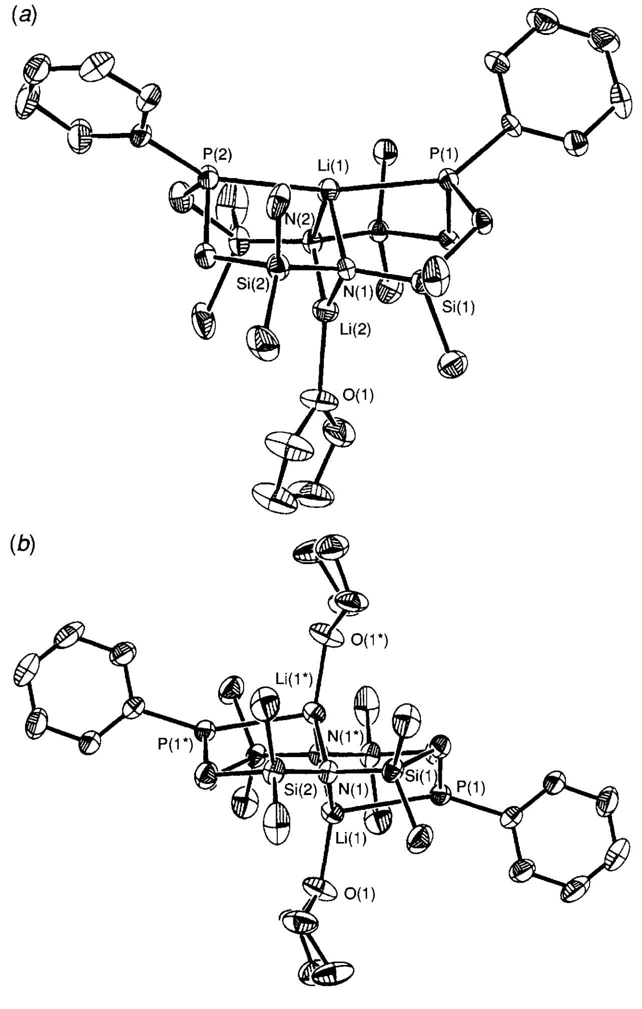


Fig. 1 Molecular structure, numbering scheme and selected bond lengths (Å) and bond angles (°) for: (*a*) *syn*-$Li_2(thf)(P_2N_2)$ **5** N(1)–Li(1) 2.19(2), N(1)–Li(2) 2.06(2), N(2)–Li(1) 2.10(2), N(2)–Li(2) 2.03(2), P(1)–Li(1) 2.53(2), P(2)–Li(2) 2.53(2), O(1)–Li(1) 1.91(2), Li(1)–Li(2) 2.55(2); Li(1)–N(1)–Li(2) 73.6(7), Li(1)–N(2)–Li(2) 76.2(7), N(1)–Li(1)–N(2) 101.4(8), N(1)–Li(2)–N(2) 108.7(9), C(13)–P(1)–Li(1) 143.5(5), C(19)–P(2)–Li(1) 149.3(6), P(1)–Li(1)–P(2) 167.9(8); (*b*) *anti*-$Li_2(thf)_2(P_2N_2)$ **6** N(1)–Li(1*) 2.064(8), N(1)–Li(1) 2.117(7), P(1)–Li(1) 2.722(7), O(1)–Li(1) 1.964(8), Li(1)–Li(1*) 2.54(1), Li(1)–N(1)–Li(1*) 74.7(3), N(1)–Li(1)–N(1*) 105.3(3), C(7)–P(1)–Li(1) 152.0(2)

It is clear that the relative stereochemistry at the phosphorus centres is controllable by the use of temperature and solvent; however, the precise nature of this control remains speculative at this point. We suggest that the structural motif of two lithium ions with bridging amides serves as the template to both determine stereochemistry and facilitate the cyclization step; after the first P–C bond formation, the dilithium unit bridged by two amides orients the remaining phosphide nucleophile and chloromethyl group, with the solvent playing an important role. In addition, the actual cyclization step is undoubtedly enhanced by the presence of the geminal dimethylsilyl units.[14]

We are presently investigating the coordination properties of these new macrocycles that contain both amide and phosphine donors.

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Footnotes

† Professional Officer: UBC Crystallographic Service.

‡ *Crystal data*: **5**, $C_{28}H_{50}Li_2N_2OP_2Si_4$. M = 618.89, monoclinic, space group Cc (no. 9), a = 56.344(3), b = 10.380(5), c = 25.227(2) Å, β = 90.176(7)°, U = 14754(7) Å^3, D_c = 1.114 g cm^{-3}, Z = 16, μ = 24.79 cm^{-1}, number of reflections used = 7727 (16057 unique measured, R_{int} = 0.057), R = 0.050, R_w = 0.045, Rigaku AFC6S diffractometer, at 21.0 °C, graphite monochromator, Cu-Kα = 1.54178 Å.

6, $C_{32}H_{48}Li_2N_2O_2P_2Si_4$. M = 680.91 monoclinic, space group $P2_1/c$, a = 10.959(1), b = 10.992(1), c = 17.4213(7) Å, β = 100.289(5)°, U = 2064.7(3) Å^3, D_c = 1.095 g cm^{-3}, Z = 2, μ = 23.04 cm^{-1}, number of reflections used = 2280 (4495 unique measured, R_{int} = 0.053), R = 0.048, R_w = 0.048, data collection as above. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/284.

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