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A Tetrameric Lithiated Phosphazene Containing a Lithium Atom Bound Exclusively to Four sp^3-Hybridized Carbanionic Centers: A Key Intermediate for Understanding Structure−Reactivity Relationships of Phosphazenyllithium Compounds

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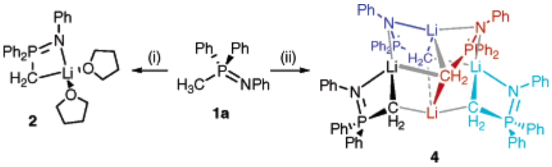
The structure of the first tetrameric α-lithiated *N*-phenylphosphazene has been determined in the solid state and shown to persist in toluene solution, an observation that gives insight into the variation in stereoselectivity found for reactions of α-lithiated phosphazenes with aldehydes.

Introduction

C_α-lithiated phosphazenes have found widespread application as reactive intermediates in many carbon−Z bond-forming reactions (where Z = C, metal).[1,2] Understanding the reactivity of these synthetically important anionic species is often complicated by the diversity of structures they may adopt in solution. Where available, solid-state structures and multinuclear magnetic resonance studies provide useful models for rationalizing the observed regio- and/or stereoselectivities in reactions with electrophiles. A limited number of α-lithium monophosphazenes $[Li\{C(R^3)_2P(R^2)_2{=}NR^1]$ have been characterized at the molecular level. In ethereal solvents monomeric complexes are preferentially formed.[3] The treatment of $CH_3P(Ph)_2{=}NPh$ (**1a**) with $LiBu^n$ in THF results in the disolvated monomer $[Li\{CH_2P(Ph)_2{=}NPh\}(THF)_2]$ (**2**) (Scheme 1).[3a] When the solvent of choice is hexane, self-aggregation occurs, furnishing dimers[4] and tetramers (e.g., $[Li\{CH_2P(Me)_2{=}NSiMe_3\}]_4$ (**3a**)[4a] and $[Li\{CH(Me)P(Et)_2{=}NSiMe_3\}]_4$ (**3b**); see Chart 1).[5] Generally, the repeating motif of the aggregates consists of LiCPN four-membered rings. Lithiated *N*-methoxycarbonylphosphazenes react differently compared to *N*-aryl analogues, and this has been correlated to their distinct structures[6] since conjugation of the nitrogen atom with the CO_2Me group promotes the chelation of lithium with the carbonylic oxygen atom, leading to six-membered metallacycles.[7] In all structurally characterized phosphazenyl lithium complexes to date chelation of lithium involves the coordination to a nitrogen or oxygen atom. Herein we report the synthesis and crystal and solution structure in toluene of the unprecedented tetramer $[LiCH_2P(Ph)_2{=}NPh]_4$, **4**, containing a lithium exclusively coordinated to carbon atoms. Elucidation of this remarkable complex provides a rationalization of the stereochemical course of the reactions of phosphazenes **1** lithitated at the C_α carbon (henceforth represented as $\mathbf{Li^+1^-}$) with aldehydes, which is shown to be highly dependent on the nature of the solvent.

Scheme 1. Synthesis of Complexes 2 and 4[a]



[a] Reaction conditions: (i) $LiBu^n$, −30 °C to rt, THF; (ii) $LiBu^n$, −30 °C to rt, toluene.

Experimental Section

General Data. All compounds were treated as air- and moisture-sensitive; accordingly all reactions and manipulations were carried out in an atmosphere of dry, pure N_2 or argon gas, using standard

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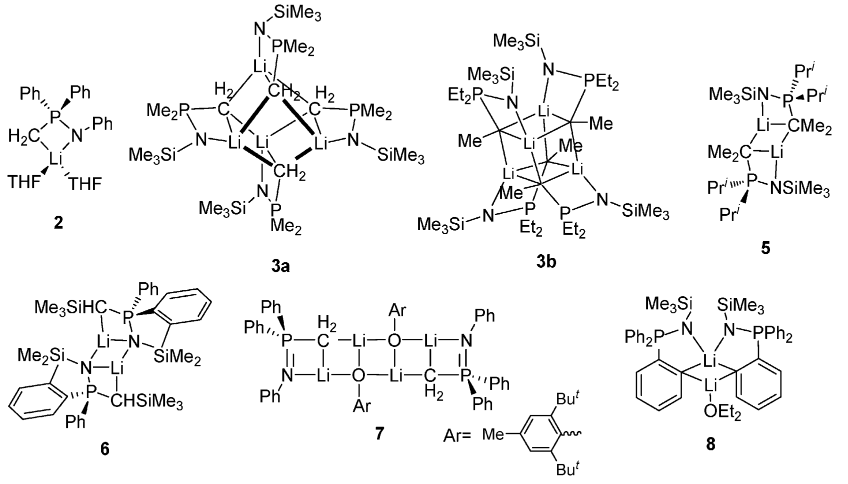
Chart 1



procedures. Solvents were freshly distilled over Na/K alloy. Phosphazenes **1** were prepared as described elsewhere.[8] All other reagents were obtained from Acros and used as received.

All spectra were measured on a Bruker Avance 500 spectrometer equipped with a third radio frequency channel. A 5 mm triple probe head was used. The outer coil was doubly tuned for ^{1}H and ^{31}P, and the inner coil was tunable in the frequency range ^{109}Ag to ^{31}P. The 90° pulse widths and operating frequencies were 10.5 μs (^{1}H, 500.13 MHz), 29.5 μs (^{7}Li, 194.37 MHz), 10.0 μs ^{13}C (125.75 MHz), and 11.8 μs (^{31}P, 202.46 MHz). The attenuation levels used were −3 dB for the proton channel and 0 dB for all the other nuclei. The spectral references used were TMS for ^{1}H and ^{13}C, 85% H_3PO_4 for ^{31}P, and 1 M LiBr in D_2O for ^{7}Li. A set of two complementary ^{31}P/^{7}Li selective band-pass/stop frequency filters were used for the acquisition of the ^{31}P{^{7}Li,^{1}H} and ^{7}Li {^{31}P,^{1}H} NMR spectra.

Synthesis of 4. To a toluene solution (2 mL) containing *P*-methyl-*P*,*P*-diphenyl(*N*-phenyl)-λ^5-phosphazene, **1a** (0.29 g, 1 mmol), was added dropwise 1.2 equiv of *n*-butyllithium (1.2 mmol, 0.8 mL of a 1.6 M solution in hexanes) at −30 °C. The solution was stirred and allowed to warm to room temperature, affording a white precipitate, which was dissolved upon gentle heating. On standing at room temperature for 24 h, the resulting solution yielded a crop of X-ray-quality colorless blocks of **4** suitable for X-ray analysis. Isolated yield: 0.18 g (61%). Anal. Calc for $C_{19}H_{17}LiNP$: C, 76.8; H, 5.8; N, 4.7. Found: C, 76.8; H, 6.4; N, 4.4. Selected NMR data for **4** at −80 °C in toluene-d_8: ^{1}H NMR (500.13 MHz): δ 0.24 (d, 2H, $^2J_{PH}$ 8.6 Hz), 0.38 (d, 2H, $^2J_{PH}$ 8.3 Hz), 6.4−7.3 (22 ArH), 7.5−7.8 (8 ArH). ^{13}C NMR (125.75 MHz): δ 5.88 (CH_2, $^1J_{PC}$ 41.8 Hz), 6.00 (CH_2, $^1J_{PC}$ 40.8 Hz), 117.0−142 (CAr 152.1 (C_{ipso}), 153.3 (C_{ipso}). ^{31}P NMR (202.46 MHz): δ 31.37 (bs) and 39.96 (bs). ^{7}Li NMR (194.37 MHz): δ −0.04 (d, $^2J_{P,Li}$ = 2.7 Hz), 0.21 (m), and 1.02 (d, $^2J_{P,Li}$ = 3.9 Hz).

General Procedure for the Synthesis of β-Hydroxyphosphine Oxides 11 and 12. To a solution of 0.6 mmol of the corresponding phosphazene **1a**−**c** in 25 mL of toluene or THF was added 0.72 mmol of *n*-BuLi at −35 °C. The metalation was completed in 30 min. Then, the corresponding aldehyde (0.72 mmol) was added and the reaction was stirred 3−4 h until it reached room temperature. The solvent was removed under reduced pressure, and the crude mixture was dissolved in 20 mL of acetone. To this solution was added 2 N HCl at room temperature and the mixture refluxed during 4 h, except in the case of pivalaldehyde, which required 24 h of reaction to complete the hydrolysis. The mixture was poured into water and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried with $MgSO_4$, and solvents were evaporated under reduced pressure. ^{1}H, ^{1}H{^{31}P}, and ^{31}P NMR spectra of the reaction crude were measured in order to determine the diastereomeric ratio **11**:**12** obtained. Compounds **11**,**12a**,[9] **11**,**12b**,[9] and **11**,**12c**[10] have been described previously. Their ^{1}H and ^{31}P NMR data are in agreement with those reported in the literature. The assignment of the *like/unlike* stereoisomers was based on the magnitude of $^3J_{HH}$ for the methine protons of the compounds.

4-(Diphenylphosphinoyl)-2,2-dimethylheptan-3-ol (11d and 12d) ($CDCl_3$, 298 K). Identified from a mixture **11d**:**12d** (41:59). **11d**: ^{1}H NMR (500.13 MHz): δ 0.51−2.72 (18H), 3.67 (m, $^3J_{PH}$ 11.6 Hz), 4.91 (d, $^3J_{HH}$ 7.8 Hz), 7.32−7.58 (6 ArH), 7.63−7.94 (4 ArH). ^{31}P NMR (202.46 MHz): δ 41.41 ppm. **12d**: ^{1}H NMR (500.13 MHz): δ 0.51−2.48 (18H), 3.67 (dd, $^3J_{PH}$ 14.2, $^3J_{HH}$ 1.6 Hz), 3.84 (d, $^3J_{HH}$ 1.6 Hz), 7.32−7.58 (6 ArH), 7.63−7.94 (4 ArH). ^{31}P NMR (202.46 MHz): δ 42.04 ppm.

Crystallography. Crystals of **4** suitable for an X-ray structural determination were obtained as described above. Crystals were removed directly from solution under a stream of dinitrogen and coated in an inert perfluorinated oil prior to mounting on a glass fiber and immediate transfer to the diffractometer. The data were measured on a Bruker SMART three-circle diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation and equipped with an Oxford Cryosystems cryostream. Intensities were measured using ω scans. The structures were solved by direct methods using SHELXS-97,[11] and refinement, based on F^2 of all data, was by full matrix least-squares techniques and SHELXL-97.[12] All non-hydrogen atoms in **4** (except those in disordered solvent molecules) were refined anisotropically. All hydrogen atoms were placed in idealized positions and allowed to ride on heavy atoms. The asymmetric unit consists of one-half of the lithiated phosphazene tetramer, one full molecule of toluene, one partial toluene, and a fragment of very disordered solvent. Details of treatment of the disordered solvent are given in the Supporting Information. This disorder results in the high *R*-factor.

$C_{90}H_{76}Li_4N_4P_4\cdot 2.8(C_7H_8)$: M = 1623.16, 0.1 × 0.1 × 0.2 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 18.763(4) Å, b = 20.181(4) Å, c = 25.127(5) Å, β = 104.52(3)°, V = 9211(3) Å^3, Z = 4, D_c = 1.171 g/cm^3, F_{000} = 3424, Mo Kα radiation, λ = 0.71073 Å, T = 150(2) K, $2\theta_{max}$ = 48.0°, 29 115 reflections collected, 7191 unique (R_{int} = 0.0956). Final GooF = 1.062, R_1 =

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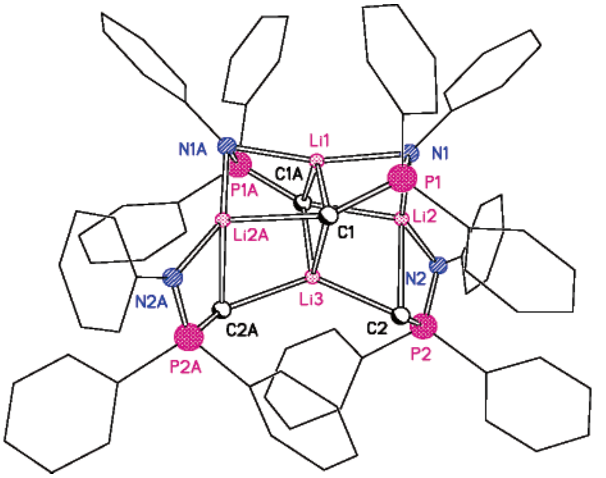


Figure 1. Molecular structure of **4** (for clarity, all H atoms and lattice solvent omitted and organic framework shown as wire frame). Selected bond distances (Å) and angles (deg): Li(1)−N(1), 2.046(9); Li(1)−C(1), 2.231(9); Li(2)−N(1) 2.160(7); Li(2)−N(2), 1.968(7); Li(2)−C(2), 2.431(8); Li(2)−C(1a), 2.409(8); Li(3)−C(1), 2.527(8); Li(3)−C(2), 2.139(8); P(1)−N(1), 1.618(5); P(1)−C(1), 1.751(6); P(2)−N(2), 1.618(5); P(2)−C(2), 1.721(6). N(1)−Li(1)−N(1a), 163.6(4); N(1)−Li(2)−N(2), 150.3(4); C(1)−Li(1)−N(1), 77.8(3). C(1)−Li(1)−N(1a), 110.4(4); C(2)−Li(2)−N(2), 73.4(2); C(2)−Li(2)−N(1), 122.0(3); C(1)−Li(1)−C(1a), 122.6(4); C(2)−Li(2)−C(1a), 104.8(3); C(2)−Li(3)−C(2a), 134.4(4); C(1)−Li(3)−C(2a), 98.3(3); C(1)−Li(3)−C(1a), 101.5(3).

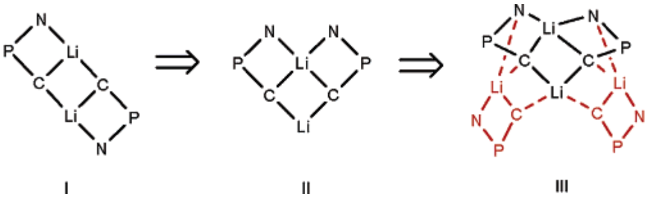
0.0999, $wR_2 = 0.2391$, R indices based on 4467 reflections with $I > 2\sigma(I)$ (refinement on F^2), 512 parameters, 1 restraint. CCDC 603907.

Results and Discussion

Treatment of a toluene solution of *P*-methyl-*P*,*P*-diphenyl-(*N*-phenyl)-λ^5-phosphazene (**1a**) with 1.2 equiv of $LiBu^n$ afforded quantitatively $[LiCH_2P(Ph)_2{=}NPh]_4$ (**4**). Upon recrystallization from toluene, colorless crystals suitable for X-ray analysis were obtained (Scheme 1).

X-ray crystallography reveals **4** to consist of an aggregate of four $LiCH_2P(Ph)_2{=}NPh$ units (Figure 1). Each lithium atom is four coordinated: Li(1) and Li(2) via two N and C donors and Li(3) via four C anions. To the best of our knowledge, this is the first example of a lithium phosphazene containing the metal atom bound exclusively to four sp^3-hybridized carbanionic centers.[13] While C(1)−Li(1) and C(2)−Li(3) exhibit short C−Li contacts [2.231(9) and 2.139(8) Å, respectively], C(1A)−Li(2), C(1)−Li(3), and C(2)−Li(2) distances are significantly longer [2.409(8), 2.527(8), and 2.431(8) Å, respectively]. A similar spread of C−Li bond distances has been found in other tetrameric lithium complexes (cf. $[LiEt]_4$ (2.20−2.50 Å),[14] $[LiBu^t]_4$ (2.15−2.37 Å),[15] **3a** (2.35−2.50 Å)[4a]). The rest of the bonds lengths within the ligands are similar to those previously reported,[3−6] although the mode of aggregation in **4** imposes highly distorted tetrahedral geometries on the N-bound lithium atoms [for example: N(1)−Li(1)−N(1a) and N(1)−Li(2)−N(2) angles, 163.6(4)° and 150.3(4)°, respectively].

Scheme 2. Conceptual Formation of 4 from a Dimeric $(LiCPN)_2$ Ladder (I) via Rearrangement (II) and Addition of Two Further Monomer Units (III)



Self-aggregation of LiCPN units in lithium phosphazenes takes place by monomers sharing either one N−Li or one C−Li bond, giving rise to ladder motifs,[16] as shown by complexes **3a**, **3b**, **5**. and **6**, respectively (Chart 1).[4,5] This oligomerization mode also persists in the mixed aggregate $[(LiCH_2P(Ph)_2{=}NPh)\cdot(LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}\text{-}4\text{-}CH_3)]_2$ (**7**) formed in the lithiation of **1a** in the presence of a 2,6-di-*tert*-butyl-4-methylphenol (Chart 1).[17] The structures shown in Chart 1 sugggest that the process of aggregation takes place preferentially by C−Li networking and is mainly determined by the interplay of two factors: the coordinating ability of the solvent and the bulkiness of the carbanionic moiety. Complex **2**, containing a primary carbanion, crystallizes from THF as a monomer, whereas the analogous lithium phosphazene $[LiCH_2P(Me)_2{=}NSiMe_3]$ forms tetramers **3a** upon crystallization from hexane. In the same solvent the complex $[LiCH(Me)P(Et)_2{=}NSiMe_3]$ also aggregates to give tetramers **3b**. Although **3a** and **3b** are configurational isomers, one might conclude that the tetrameric aggregation tolerates well the slight difference of steric hindrance at the carbanionic center produced by a CH(Me) moiety as compared with a CH_2 group. However, self-aggregation of $[LiC(Me)_2P(Pr^i)_2{=}NSiMe_3]$ does not progress beyond the dimeric stage. The isolation of the ladder complex **5** from hexane indicates that the presence of a tertiary carbanion and two bulky Pr^i substituents linked to the phosphorus in the phosphazenyl fragment inhibited the aggregation of dimers into tetrameric cubanes due to steric effects. In complex **6** the situation is somehow more exacerbated than in **5**. In this case, the phosphazenyl moiety is part of a rigid benzoheterocyclic system and the carbanion bears a bulky $SiMe_3$ substituent. One may understand that the aggregation is limited to dimers and that binding monomers through N−Li contacts is preferred over the C−Li bonds as a means of avoiding the steric congestion derived from a $[LiCH(SiMe_3)]_2$ core. In the extended ladder mixed dimer complex **7** the very bulky aryl fragments prevent the formation of cubane-like aggregates.

The aggregation of tetramer **4** deviates from the norm shown by **3a** and **3b** presumably as a result of steric inability to maintain a cubane superstructure based on C−Li connections. The larger size of the phenyl substituents linked to the phosphorus as compared with the *P*-methyl and *P*-ethyl groups of **3a** and **3b**, respectively, favored the alternative tetrameric structure shown by **4**. Conceptually, it can be viewed as a reorganization of a C−Li edge-sharing ladder followed by addition of two further monomer units (Scheme 2). Interestingly, the model fragment **II** resembles the structural motif found in complex **8** resulting from the dimerization of an *ortho*-lithiated phosphazene.[18]

The solution structure was determined by variable-temperature NMR studies performed in toluene-d_8 on a 0.075 M sample.

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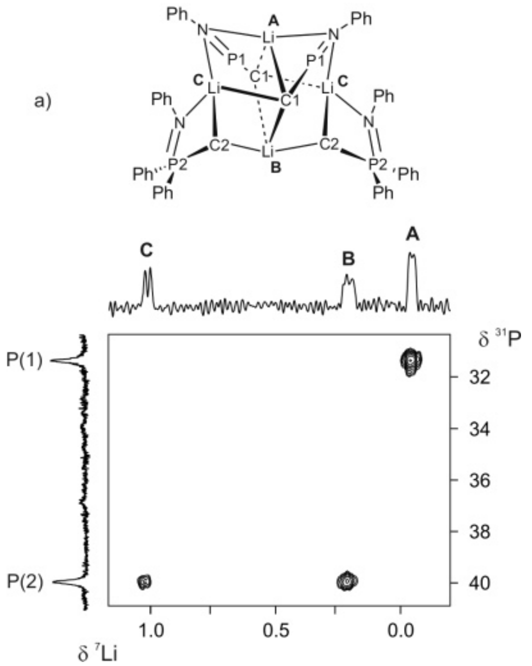

Figure 2. 2D ^{7}Li,^{31}P{^{1}H} HMQC NMR spectrum (194.37 MHz) of complex **4** at −80 °C in toluene-d_8. Spectral width, 5000 Hz for ^{31}P and 880 Hz for ^{7}Li; 64 increments recorded; final matrix after zero filling, 2048 × 64; evolution delay of $^{n}J(^{31}\mathrm{P},^{7}\mathrm{Li})$ 24 ms; 400 scans per increment in F1; qsine multiplication in F2 and Gaussian multiplication of LB = −18, GB = 0.2 in F1 prior to transformation (magnitude mode). Repetition delay of 0.3 s.

NMR spectra of **4** measured at −80 °C show the presence of essentially a single species (ca. 12% of unidentified products). In the ^{1}H NMR spectrum two signals of methylene protons are observed as doublets due to the coupling with one phosphorus atom at δ 0.24 ($^{2}J_{\mathrm{PH}} = 8.6$ Hz) and δ 0.38 ($^{2}J_{\mathrm{PH}} = 8.3$ Hz) ppm. The corresponding methylene carbons appear in the ^{13}C spectrum at δ 5.88 ($^{1}J_{\mathrm{PC}} = 41.8$ Hz) and 6.00 ($^{1}J_{\mathrm{PC}} = 40.8$ Hz) ppm. The upfield shift of the CH_2 protons and carbons of **4** as compared with **1a** [δ_{H} 2.14 ppm ($^{2}J_{\mathrm{PH}} = 12.9$ Hz), δ_{C} 15.13 ppm ($^{1}J_{\mathrm{PC}} = 74.8$ Hz)] reflects the carbanionic nature of these moieties. In the temperature range −80 to −100 °C the ^{31}P spectrum exhibits two broad singlets P(1) and P(2) at δ 31.37 and 39.96 ppm, respectively (Figure 2, left projection), shifted downfield by about 26.55 and 35.14 ppm relative to **1a**. Both signals become sharper when the ^{31}P spectrum is recorded under simultaneous ^{1}H and ^{7}Li decoupling, thus confirming that the width observed results from the existence of ^{31}P,^{7}Li couplings. The two ^{31}P resonances remain observable up to 0 °C as very broad signals. At temperatures above −20 °C new signals begin to appear in the ^{31}P NMR spectrum. Comparing the NMR spectra of different samples we noticed that their number and relative concentration were also dependent on the aging of the lithium base solution used for the metalation. An EXSY spectrum measured at −20 °C showed exchange between P(1) and P(2) exclusively. On recooling the sample, the low-temperature pattern of ^{31}P NMR signals was recovered.

The ^{7}Li{^{1}H} NMR spectrum revealed (after suitable resolution enhancement) the presence of two doublets, A (poorly resolved) and C, as well as a multiplet B (Figure 2, top projection) at δ −0.04 ($^{2}J(^{31}\mathrm{P},^{7}\mathrm{Li}) = 2.7$ Hz), 1.02 ($^{2}J(^{31}\mathrm{P},^{7}\mathrm{Li}) = 3.9$ Hz) and 0.21 ppm, respectively. Signals A and B are notably broader than C. Doublets A and C indicate that these lithiums are coupled to one phosphorus nucleus. The unresolved multiplicity of B may arise from the coupling to two different phosphorus nuclei. All signals transform into singlets in the ^{7}Li{^{31}P,^{1}H} NMR spectrum (see Supporting Information). The three multiplets merged into a broad signal at −30 °C. Thus, the pattern of NMR signals observed at low temperature is consistent with the retention in solution of the tetrameric structure characterized in the solid state.

Table 1. Stereoselectivity in the Reaction of Li^{+}1^{-} with Aldehydes in THF and Toluene[a]

entry	1	R^{1}	product	R^{2}	solvent	yield (%)[b]	*u*:*l*[c]
1	**a**	H	**9/10a**	Ph	THF	79[d]	
2	**b**	Me	**9/10b**	Ph	THF	88[d]	>95:5
3	**c**	*n*-Pr	**11/12c**	Ph	THF	>97	78:22
4	**c**	*n*-Pr	**11/12d**	^{t}Bu	THF	94	76:24
5	**b**	Me	**9/10b**	Ph	toluene	92[e]	58:42
6	**c**	*n*-Pr	**11/12c**	Ph	toluene	>97	53:47
7	**c**	*n*-Pr	**11/12d**	^{t}Bu	toluene	89	59:41

[a] All reactions were carried out in a 20 mM scale using 30 min of lithiation at −30 °C and 3 h of quench with the aldehyde. [b] Crude yield. [c] *Unlike*:*like* ratio determined by ^{31}P{^{1}H} NMR. [d] Reference 9. [e] Reference 17.

The assignment of the ^{31}P and ^{7}Li NMR spectra was carried out through the 2D shift correlation between the two heteronuclei (Figure 2).[19] Lithium C is significantly deshielded as compared with lithiums A and B, shows the largest ^{31}P,^{7}Li coupling, and correlates with P(2). These features are consistent with the assignment of lithium C as Li(3) in the crystal structure. Its coordination mode (C_4Li) is notably distinct from lithiums A and B (both C_2N_2Li), and it exhibits the shortest C−Li bond distance. P(2) also correlates with lithium B, which must therefore be Li(2). Lithium A correlates with P(1) and corresponds to Li(1) in the crystal structure. The fact that C(1)−Li(1) represents the second shortest distance in the crystal supports this assignment.

1D gROESY spectra of **4** establish the connectivity within phosphazenyl fragments through the ROEs observed between the *ortho* protons of the *P*-phenyl rings and the adjacent methylenic protons. The assignment was completed by correlating the phosphazenyl protons with the respective phosphorus atom through the 2D ^{1}H,^{31}P gHMQC NMR spectrum measured at −20 °C.

It has been reported that lithium phosphazenes react with aldehydes to give β-hydroxyphosphazenes **10** in good yields and with high diastereoselectivity (Scheme 3, Table 1, entries 1, 2).[9] However, in toluene as solvent, the reaction of **1b** with benzaldehyde proceeds with practically no stereocontrol (entry 5).[17] We have now assayed further examples of this chemistry (Scheme 3, Table 1). To avoid complex mixtures derived from partial hydrolysis during aqueous workup,[17] the adducts were treated with diluted hydrochloric acid to yield the corresponding phosphine oxides **11** and **12** (entries 3, 4, 6, and 7). The acid hydrolyses of the phosphazene linkage do not affect the diastereomeric ratio of the β-hydroxy derivatives. Products of *unlike* configuration were predominantly obtained in THF. Increasing the bulkiness of R^{1} produced a decrease in the stereoselectivity. In toluene as solvent almost no face discrimination in the attack to the carbonyl group was observed.

The lack of selectivity of the reactions performed in toluene can be rationalized through the participation of a reactive species such as **4**. Although complex **4** contains a primary carbanion, we might assume that the derivatives having a secondary carbanionic center will show a similar tetrameric structure, as it has been already mentioned for the lithium phosphazenes **3a** and **3b** (Chart 1). On the basis of this assumption, it is reasonable

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(19) Fernández, I.; López-Ortiz, F. *Chem. Commun.* **2004**, 1142.

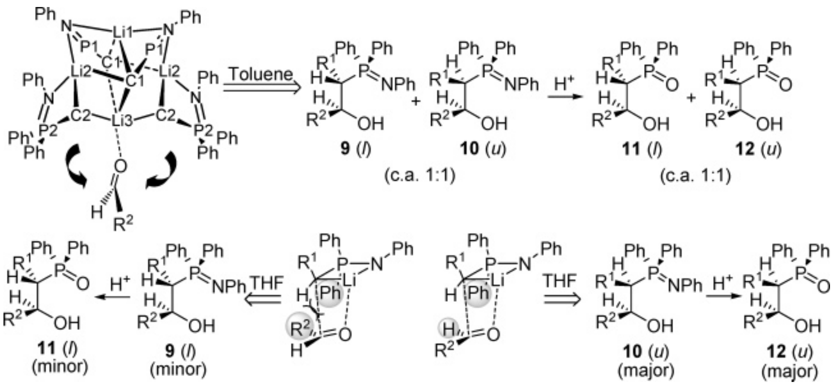
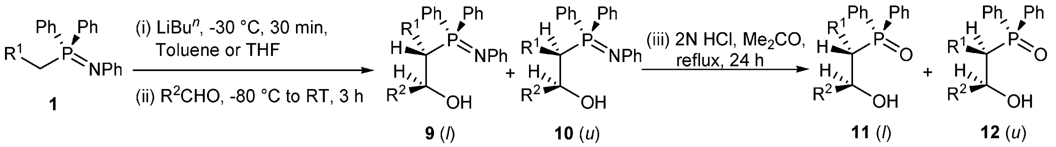


Figure 3. Proposed mechanism for the solvent-dependent formation of β-hydroxyphosphine oxides **11** and **12**.

Scheme 3. Synthesis of β-Hydroxyphosphine Oxides



to suggest that initial complexation of an aldehyde to **4** will preferentially occur at Li(3) (Figure 3). The large deshielding of this lithium center as compared with Li(1) and Li(2) is indicative of its higher electrophilicity, probably caused by the reduced electronic stabilization afforded by the distant C(1) anions, relative to Li(1) and Li(2). In the resulting complex a carbanion is available for attack at either face of the carbonyl moiety, and therefore, poor face selectivity can be expected. It is worthy of note that the proposed coordination of an aldehyde to **4** is similar to the binding of the Et_2O molecule in dimer **8** to the lithium atom lacking nitrogen contacts (Chart 1). In THF as solvent, however, the coordination of the oxygen of the aldehyde with the lithium cation of monomer **1** might provide two different complexes (Figure 3). According to this model,[20] the *unlike* products **10**/**12** would be formed preferentially due to unfavorable steric interactions in the transition state leading to **9**/**11**.

In conclusion, the solid-state structure of the uncomplexed α-lithiated phosphazene **4** is based on a unique tetrameric aggregate incorporating three distinct lithium environments, one of which involves coordination exclusively to sp^3 carbon atoms. We have shown that this structure persists in solution and that it provides a rationalization of the degree of stereocontrol observed in reactions of phosphazenyl anions with aldehydes.

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Supporting Information Available: Crystallographic data, synthetic details, NMR experimental details, $^{31}P\{^1H\}$, $^7Li\{^1H\}$, and $^7Li\{^{31}P, ^1H\}$ spectra of **4**. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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[20] A similar model has been proposed for the reaction of aldehydes with C_α-lithiated phosphine oxides: Armstrong, D. R.; Barr, D.; Davidson, M. G.; Hutton, G.; O'Brien, P.; Snaith, R.; Warren, S. *J. Organomet. Chem.* **1997**, *29–33*, 529.