Organometallics **2004,** *23,* 5934−5938

# The First Mixed-Anion Complex of a Lithium Phosphazene: Synthesis and Crystal and Solution Structure of $[(LiCH_2P(Ph)_2{=}NPh)\cdot(LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}\text{-}4\text{-}CH_3)]_2$

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*Received June 1, 2004*

The crystal and toluene solution structure (X-ray, $^1H$, $^7Li$, $^{13}C$,$^{31}P$ NMR) of a mixed-anion lithium phosphazene-phenolate, **10**, is a six-rung ladder consisting of two LiPCN units fused to a central $Li_2O_2$ core, which provides insight into the function of phosphazenyl-stabilized carbanions as reagents. The mixed aggregate showed decreased reactivity toward benzaldehyde with respect to the uncomplexed anion.

Carbanions stabilized by one phosphazenyl group have attracted much attention due to their unusual coordination chemistry[1] and application as reagents in organic synthesis.[2] The C−P−N fragment of these anions generally acts as a chelate, leading to the formation of Li−C−P−N four-membered rings. Ethereal solvents tend to stabilize monomeric complexes,[1,2b,c,3] with the organolithium compound $[Li\{CH_2P(Ph_2){=}NPh\}(THF)_2]$ (**1**)[3a] being the prototype of this coordination mode (Chart 1). In the absence of coordinating solvents, self-aggregation of the metallocycle is observed leading to dimers[1e,4] and tetramers (Chart 1).[5] Ladders having lithium atoms bridged through either carbon (**2**)[4a] or nitrogen atoms (**3**)[4b] have been previously described. Both the coordination mode and reactivity[6] of lithium phosphazenes are affected by variation of the carbon/nitrogen substituents and solvent effects. For example, the treatment of $4\text{-}MeC_6H_4CH(SiMe_3)P(Ph)_2{=}NSiMe_3$ with $LiBu^n$ in THF leads to the formation of a complex similar to **1**. However, in benzene the dimeric compound **4**, showing a $\eta^6$ coordination, is obtained.[7] Conversely, bulky substituents linked to the phosphazenyl moiety, as in complex **5**, favor the coordination of the lithium atom to the $C_{ipso}$ carbon, giving rise to a formal five-membered ring.[7] Delocalization of the negative charge through electron-withdrawing groups bonded either to the carbanionic center or to the nitrogen atom of the PN linkage results in the formation of six-membered chelates **6**[8] and **7**,[9] respectively.

Interestingly, lithiated *N*-methoxycarbonylphosphazene analogues of **7** exhibit very different reactivity to *N*-aryl systems **1** due to chelation of lithium via the *N*-$CO_2Et$ group.[6a,b,d] To date, the effect of interactions between lithium phosphazenes and potential reaction products has not been structurally investigated. Herein, we report the structural characterization of the first mixed-anion lithium phosphazene system that might give insight into the complexation between a lithium phosphazene and a reaction product. The effect of mixed aggregate formation on the reactivity toward benzaldehyde was also investigated.

## Experimental Section

**General Data.** All compounds were treated as air- and moisture-sensitive. Accordingly, all reactions and manipula-

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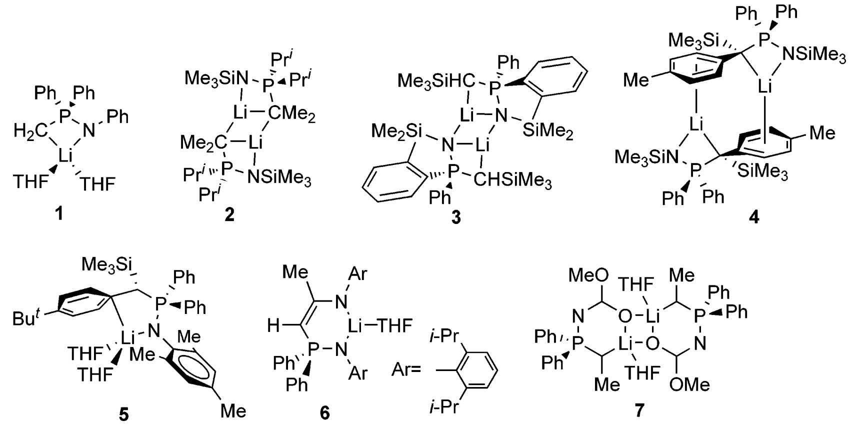
10.1021/om049608x CCC: $27.50
Publication on Web 11/03/2004

**Chart 1**



tions were carried out in an atmosphere of dry, pure $N_2$ or argon gas, using standard procedures. Solvents were freshly distilled over Na/K alloy. *P*-Diphenyl(methyl)(*N*-phenyl)-$\lambda^5$-phosphazene (**8**) and *P*-Diphenyl(ethyl)(*N*-phenyl)-$\lambda^5$-phosphazene (**11**) were prepared as described elsewhere.[10] 2,6-Di-*tert*-butyl-4-methylphenol (**9**) and *n*-butyllithium were obtained from Sigma-Aldrich and used as received.

All spectra were run 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 $^1H$ and $^{31}P$, and the inner coil was tunable in the frequency range corresponding to the nuclei $^{109}Ag$ to $^{31}P$. The pulse widths for the 90° pulses and operating frequencies were 85 $\mu$s ($^1H$, 500 MHz), 15.7 $\mu$s ($^7Li$, 194.37 MHz), and 31 $\mu$s ($^{31}P$, 202.46 MHz). The attenuation levels used were 15 dB for the proton channel and 0 dB for the heteronuclei. The spectral references used were 85% $H_3PO_4$ for $^{31}P$ and 1 M LiBr in $D_2O$ for $^7Li$. A set of two complementary $^{31}P/^7Li$ selective band-pass/stop frequency filters were used for the acquisition of the $^{31}P\{^7Li,^1H\}$ and $^7Li\{^{31}P,^1H\}$ NMR spectra. All spectra were recorded in toluene-$d_8$ at −70 °C, unless otherwise stated.

**Synthesis of $[(LiCH_2P(Ph)_2{=}NPh)\cdot(LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}\text{-}4\text{-}CH_3)]_2$, 10.** To a cooled (0 °C) solution of *P*-methyl-*P*,*P*-diphenyl(*N*-phenyl)-$\lambda^5$-phosphazene (**8**) (0.29 g, 1.0 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (**9**) (0.22 g, 1.0 mmol) in 10 mL of toluene was added dropwise 2.4 equiv of *n*-butyllithium (2.4 mmol, 1.5 mL of a 1.6 M solution in hexane). The solution was stirred for 15 min, affording a white precipitate, which dissolved upon gentle warming. Storage at ambient temperature for 12 h afforded a crop of X-ray quality colorless crystals, which were isolated and stored in a dry, anaerobic glovebox. Yield: 0.25 g, 48%. Anal. Calcd (found) for $C_{34}H_{40}Li_2N_1O_1P_1$: C, 78.0 (79.0); H, 7.7 (7.7); N, 2.7 (3.1). Crystals suitable for X-ray analysis were also obtained from benzene solution. $^1H$ NMR: $\delta$ −0.05 (d, 2H, $^2J_{PH}$ 13.3 Hz), 1.47 (9H), 2.50 (3H), 6.13 (d, 2H, $^3J$ 7.7 Hz), 6.61 (d, 1H, $^3J$ 7.3 Hz), 6.88 (ddd, 4H, $^4J_{PH}$ 2.2, $^3J$ 8.4, $^3J$ 7.3 Hz), 6.92 (dd, 2H, $^3J$ 7.3, $^3J$ 7.7 Hz), 7.00 (d, 2H, $^3J$ 7.3 Hz), 7.25 (dd, 4H, $^3J_{PH}$ 10.2, $^3J$ 8.4 Hz), 7.43 (2H). $^{13}C$ NMR: $\delta$ 7.25 ($CH_2$), 21.48 ($CH_3$), 31.21 ($CH_3$), 34.99 (C), 116.78 (HCAr), 121.76 (d, HCAr, $^3J_{PC}$ 18.0 Hz), 126.84 ($C_{ipso}$), 127.17 (HCAr), 128.00 (d, HCAr, $^3J_{PC}$ 9.9 Hz), 128.50 (HCAr), 129.90 (HCAr), 131.12 (d, HCAr, $^2J_{PC}$ 8.8 Hz), 135.31 (d, $C_{ipso}$, $^1J_{PC}$ 73.8 Hz), 140.61 ($C_{ipso}$), 151.39 ($C_{ipso}$), 156.19 ($C_{ipso}$). $^{31}P$ NMR: $\delta$ 27.38. $^7Li$ NMR, −90 °C: $\delta$ 1.62 (d, $^2J_{PLi}$ 6.9 Hz), 1.83 (d, $^2J_{PLi}$ 4.8 Hz).

**Synthesis of Compounds 12−16 (method A).** To a toluene solution containing *P*-ethyl-*P*,*P*-diphenyl(*N*-phenyl)-$\lambda^5$-phosphazene (**11**) (0.1 g, 0.33 mmol) was added dropwise 1.2 equiv of *n*-butyllithium (0.4 mmol, 0.25 mL of a 1.6 M solution in hexane) at −30 °C. After 30 min the temperature was lowered to −80 °C and benzaldehyde (0.04 mL, 0.4 mmol) added. The reaction mixture was stirred for 3 h and allowed to reach 0 °C. Addition of water (25 mL) followed by extraction with $CH_2Cl_2$ (3 × 15 mL) and solvent evaporation under vacuum afforded a crude reaction mixture containing compounds **12**−**16**. They were identified on the basis of their $^1H$ and $^{31}P$ NMR data ($\delta_P$ 18.98 and 21.48 ppm for **12** and **13**, respectively).[11,12] Following treatment of a dichloromethane solution of the crude mixture with 2 N HCl (2 mL) at room temperature for 30 min and subsequent aqueous workup, the $\beta$-hydroxyphosphazenes **12** and **13** were hydrolyzed to the corresponding phosphine oxides **14** and **15** ($\delta_P$ 43.04 and 40.92 ppm for **14** and **15**, respectively).

The same procedure was applied for the reactions carried out in the presence of 2,6-di-*tert*-butyl-4-methylphenol (**9**) with the exception that 0.074 g (0.33 mmol) of **9** was mixed together with the phosphazene **8** and 2.2 equiv of $LiBu^n$ (method B) or 4.2 equiv of $LiBu^n$ (method C) was used in the lithiation step.

**Crystallography.** Crystals of **10** 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 3-circle diffractometer with a CCD area detector using graphite-monochromated Mo K$\alpha$ radiation and equipped with an Oxford Cryosystems cryostream. Intensities were measured using $\omega$ scans. The structures were solved by direct methods using SHELXS-97,[13] and refinement, based on $F^2$ of all data, was by full matrix least-squares techniques and SHELXL-97.[14] All non-hydrogen atoms in **10** were refined anisotropically. All hydrogen atoms were placed in idealized positions and allowed to ride on heavy atoms. Solvent molecules lie in a zigzag channel parallel to the *c*-axis. There are two benzene molecules, each with occupancy of 50%, and one toluene molecule, with occupancy ∼30%, in the asymmetric unit. The phenyl rings of the solvent molecules were constrained to have idealized geometry. Anisotropic displacement parameters were refined for the carbon atoms of the benzene molecules, while the carbon atoms of the toluene were refined with isotropic displacement parameters. Most of the residual unmodeled electron density left after the final refinement lies around the solvent molecules, and the model only approximates the true

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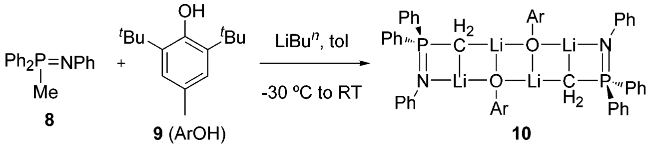
**Scheme 1. Synthesis of Complex 10**



disorder, which results in the high *R*-factor. $C_{84.17}H_{96.77}Li_4N_2O_2P_2$, $M = 1256.08$, colorless blocks, crystal size 0.2 × 0.1 × 0.11 mm, monoclinic, $C2/c$, $a = 25.007(6)$ Å, $b = 13.561(3)$ Å, $c = 24.345(5)$ Å, $\beta = 107.43(5)°$, $V = 7877(3)$ Å$^3$, $Z = 4$, $D_c = 1.061$ g cm$^{-3}$, $T = 100(2)$ K, $\lambda$(Mo K$\alpha$) = 0.71073 Å, 28 193 reflections measured, 7740 unique reflections ($2\theta_{max} = 27.39°$, $R_{int} = 0.0720$) against 493 parameters gave $R_1 = 0.1030$ and $wR_2 = 0.2375$ [$I > 2\sigma(I)$] ($R_1 = 0.1195$ and $wR_2 = 0.2477$ for all data). CCDC 231692.

## Results and Discussion

Treatment of an equimolar toluene solution of *P*-methyl-*P*,*P*-diphenyl(*N*-phenyl)-$\lambda^5$-phosphazene (**8**) and 2,6-di-*tert*-butyl-4-methylphenol (**9**) with 2.4 equiv of LiBu$^n$ afforded quantitatively [(LiCH$_2$P(Ph)$_2$=NPh)·(LiOC$_6$H$_2$-2,6-{C(CH$_3$)$_3$}-4-CH$_3$)]$_2$ (**10**) as a white powder (Scheme 1). Upon recrystallization from benzene, colorless crystals suitable for X-ray analysis were obtained.

In the solid state **10** consists of a six-rung ladder in which a lithium aryloxide core[15] is complexed by two α-lithiated *P*-methyl-*P*,*P*-diphenyl(*N*-phenyl)phosphazene units (Figure 1). A search of the Cambridge Structural Database suggests this to be a unique structural motif for heteroatom-stabilized group 1 metal alkyls. Each lithium is formally three-coordinate, via either one carbanionic and two aryloxide centers [Li(2)] or one neutral phosphazene, one carbanionic, and one aryloxide center [Li(1)]. The Li−C bond that forms a rung of the ladder is toward the upper limit of the expected range [Li(1)−C(1), 2.372(10) Å] and is significantly longer than Li(2)−C(1) [2.164(8) Å]. Although formally three-coordinate, Li(1) also interacts with the *ipso* carbon atom of one aryloxide group [Li(1)−C−(11), 2.371(10) Å]. This interaction is significantly shorter than Li−C$_{aryl}$ distances observed previously for $\eta^6$ and $\eta^1$-C$_{aryl}$ coordination of phosphazenes to Li$^+$ [Li−C$_{aryl}$ 2.434(7)−2.787(4) Å].[7] The P−N bond distance [1.670(4) Å] is the longest seen in α-lithiated alkyldiphenylphosphazene structures (range of 1.574(7) Å for **2**[4a] to 1.634(2) Å for **7**[9]), whereas P(1)−C(1) is normal [1.747(4) Å].[3−5,9]

Given the utility of lithium phosphazenes in synthesis and the well-documented discrepancies between solid state and solution structures of lithium reagents, it is important to also consider the solution structure of **10**.

The solution structure was determined by variable-temperature NMR studies performed in toluene-$d_8$ on a 0.1 M sample. NMR spectra of **10** measured at −70 °C show the presence of essentially a single species (<3% of unidentified products). As expected, metalation of phosphazene **8** to give **10** produced an upfield shift of the methylene protons ($\Delta\delta_H$(**10**−**8**) = −2.18 ppm) and carbon ($\Delta\delta_C$(**10**−**8**) = −7.88 ppm). Similar to other lithium phosphazenes, the *ipso* carbon of the *P*-phenyl rings is also shifted upfield ($\Delta\delta_{Cipso}$(**10**−**8**) = −3.51 ppm) and the $^{31}$P,$^{13}$C coupling constant notably reduced ($\Delta^1J_{PC}$(**10**−**8**) = −30 Hz). In the temperature range −70 to −100 °C the $^{31}$P spectrum exhibits a broad apparent triplet at $\delta$ 27.38 ppm (Figure 2a). This signal becomes a sharp singlet when the $^{31}$P spectrum is recorded under simultaneous $^1$H and $^7$Li decoupling (Figure 2b), thus confirming that the splitting observed results from the existence of a $^{31}$P,$^7$Li coupling. Apparent doublets arising from the coupling of one $^{31}$P nucleus to one $^7$Li nucleus have been observed in a number of cases,[16] and the unusual line shape has been assigned to relaxation effects.[17] The apparent triplet observed for **10** suggests that the $^{31}$P atom is coupled to more than one $^7$Li nucleus.

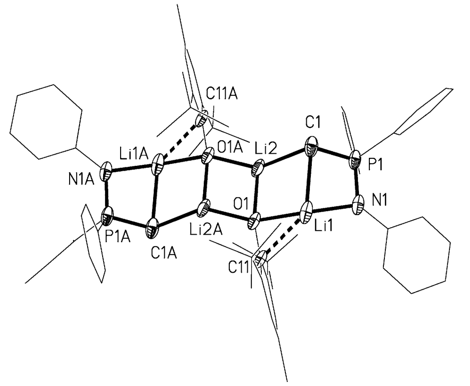


**Figure 1.** Molecular structure of **10** (for clarity, all H atoms and lattice solvent omitted and organic framework shown as wire frame). Thermal ellipsoids at the 50% level. Selected bond distances (Å) in **10**: Li(1)−O(1),1.939(8); Li(1)−N(1) 1.936(8); Li(1)−C(1) 2.372(10); Li(1)−C(11), 2.371(10); Li(2)−O(1), 1.988(9); Li(2)−O(1a), 1.909(7); Li(2)−C(1), 2.164(8); P(1)−N(1), 1.670(4); P(1)−C(1), 1.747(4).

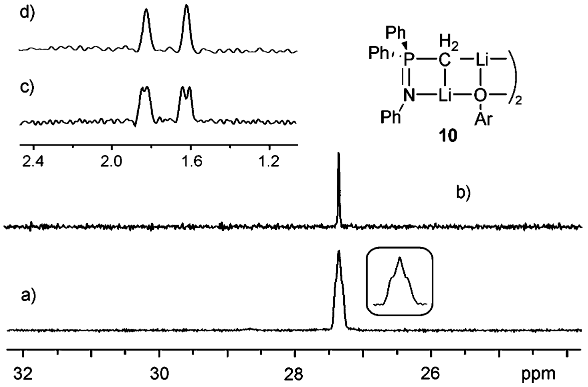


**Figure 2.** NMR spectra of a 0.1 M sample of **10** in toluene-$d_8$. (a) $^{31}$P{$^1$H} (202.46 MHz), −70 °C; (b) $^{31}$P{$^7$Li,$^1$H}, −70 °C; (c) $^7$Li{$^1$H} (194.37 MHz), −90 °C; and (d) $^7$Li{$^{31}$P,$^1$H} NMR, −90 °C. (Ar = C$_6$H$_2$-2,6-{C(CH$_3$)$_3$}-4-CH$_3$.) Gaussian multiplication of the FID (LB = −6, GB = 0.12 for $^{31}$P, and LB = −10, GB = 0.16 for $^7$Li) prior to the Fourier transformation was applied.

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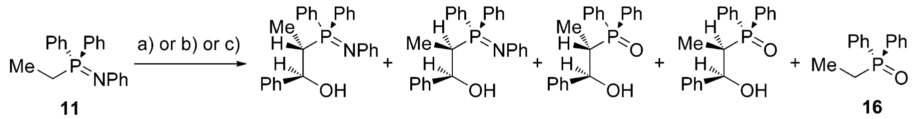
**Scheme 2. Synthesis of $\beta$-Hydroxyphosphazenes 12 and 13 and Phosphine Oxides 14 and 15**[a]



| Reaction conditions | **12** (%) | **13** (%) | **14** (%) | **15** (%) | **16** (%) |
|---|---|---|---|---|---|
| (a) | 53.3 | 38.8 | 2.2 | 1.7 | 4 |
| (b) | 27.7 | 18.1 | 8.8 | 10.3 | 35 |
| (c) | 31.3 | 19 | 9.7 | 15.5 | 24.5 |

[a] (a) (i) LiBu$^n$ (1.1 equiv) toluene, −30 °C, 30 min; (ii) PhCHO (1.2 equiv), −80 to 0 °C, 3 h; (iii) $H_2O$. (b) (i) **9** (1 equiv), LiBu$^n$ (2.2 equiv) toluene, −30 °C, 30 min, (ii) PhCHO (2.2 equiv), −80 to 0 °C, 3 h; (iii) $H_2O$. (c) (i) **9** (1 equiv), LiBu$^n$ (4.2 equiv) toluene, −30 °C, 30 min, (ii) PhCHO (4.2 equiv), −80 to 0 °C, 3 h; (iii) $H_2O$.

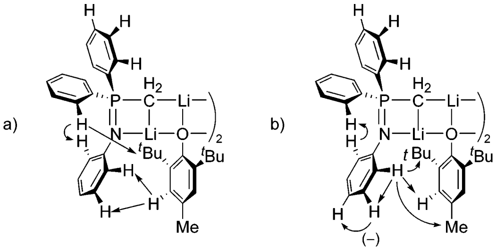


**Figure 3.** (a, b) Selected NOEs extracted from 1D gROESY NMR spectra of **10** (500.13 MHz) at −70 °C in toluene-$d_8$ (spin-lock field of 2.5 kHz, $\tau_m$ 120 ms, NS 128).

$^7$Li NMR spectra confirmed this hypothesis. The $^7$Li-{$^1$H} spectrum measured at −90 °C showed two doublets at $\delta$ 1.62, $^2J(^{31}P,^7Li) = 6.9$ Hz, and 1.83 ppm, $^2J(^{31}P,^7Li) = 4.8$ Hz (Figure 2c), that collapsed into singlets when $^{31}$P decoupling was applied (Figure 2d). This confirms that the single signal found in the $^{31}$P spectrum is indeed coupled to two different $^7$Li nuclei, a fact further evidenced in the $^7$Li,$^{31}$P{$^1$H} HMQC spectrum[16e] through the correlation of both $^7$Li doublets with the unresolved $^{31}$P signal. On the other hand, 1D gROESY spectra of **10** clearly established the proximity between aryloxide and phosphazenyl moieties (Figure 3): the *ortho* protons of the *P*-phenyl ring (Figure 3a) and *N*-phenyl group (Figure 3b) of **10** interact in a dipolar fashion with protons of the aryloxide fragment.

These findings indicate that the monomeric unit of **10** found in the solid state is retained in toluene solution. Considering the tendency of phenolates to aggregate in nondonor solvents and the bulkiness of the *ortho* aryl substituents,[18] we can reasonably assume that **10** adopts a dimeric structure in toluene solution similar to that observed in the solid state.

Once the solid-state and toluene solution structure of the mixed aggregate **10** had been established, we sought to investigate the impact of these complexes in a standard lithium phosphazene reaction involving the participation of phenolates. As such, we used the reaction of lithiated **11** with benzaldehyde. It is known that **Li$^+$11$^-$** adds to benzaldehyde in THF at low temperature giving $\beta$-hydroxyphosphazenes **12** and **13** in high yield and with high stereoselectivity (ratio *l*:*u* > 95:5).[11] We have performed the same transformation in toluene, both in the absence of the bulky phenol **9** and in the presence of 1 equiv of **9**. The control experiment was carried out by adding benzaldehyde to a toluene solution of **Li$^+$11$^-$** at −80 °C and allowing the temperature to slowly increase to 0 °C over 3 h (Scheme 2). Quenching the reaction with water and subsequent aqueous workup afforded a crude reaction mixture consisting of $\beta$-hydroxyphosphazenes **12** and **13** (yield of 92%), the phosphine oxides **14** and **15** (yield of 4%), and **16** (4%). Compounds **14**−**16** arise from the hydrolysis of the P═N linkage of the respective phosphazenes under the reaction conditions used.[19] The overall *like*:*unlike* ratio of the phosphazenes and phosphine oxides of the same relative configuration was 1.4:1. These results indicate that the use of toluene in lieu of THF as solvent does not affect the efficiency of the process. However, there is a very large decrease in the stereoselectivity of the addition reaction. As stated above, in noncoordinating solvents, lithiated phosphazenes exist as dimers or tetramers. Consequently, one may reasonably assume that the decreased stereoselectivity observed in toluene with respect to THF is a consequence of the increased aggregation state in the former solvent.

Repeating the reaction in the presence of 1 equiv of phenol **9**, using in this case 2.2 equiv of LiBu$^n$, leads to a very different distribution of the same mixture of compounds. The yield of hydroxyphosphine oxides **14** and **15** increased to 19% at the expense of hydroxyphosphazenes **12** and **13**, which are obtained in 46% yield. There is a marginal decrease of the *l*:*u* ratio to 1.3:1. The amount of unreacted phosphazene **11** increased, as evidenced by the formation of its hydrolysis product **16** in 35% yield. The relatively large amount of **16** obtained indicates that upon complexation with the phenolate salt, the reactivity of the lithium phosphazene toward benzaldehyde decreased significantly. The yield of **16** decreased to 25% when 4.2 equiv of base was used, probably due to the participation of the excess of lithium base in the formation of new mixed aggregates with the lithiated species present in solution. In this reaction the yield of phosphine oxides **14** and **15** formed further increased to 25% and the overall *l*:*u* ratio decreased to 1.2:1.

In conclusion, the solid-state structure of **10** has been determined and is maintained in toluene solution. It

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[18] Jackman, L. M.; Bortiatynski, J. *Adv. Carbanion Chem.* **1992**, *1*, 45.

[19] Compounds **12** and **13**[11] and **14**−**16**[12] have been previously characterized. The relative configuration of the stereosiomers is straightforwardly assigned on the basis of the magnitude of $^3J_{HH}$ for the sp$^3$-hybridized methine protons and the coupling constants of the $^{31}$P nucleus with the proton and $C_{ipso}$ carbon linked to the C−OH moiety.

may be envisaged as a central $Li_2O_2$ core formed by dimerization of a lithium phenolate with two lithium phosphazenes having the characteristic Li−C−P−N four-membered chelate ring, complexed via C−Li and O−Li bridges. This six-rung ladder structure is, to our knowledge, unprecedented for lithium phosphazenes. The presence of a bulky phenolate during the addition reaction of a lithiated *N*-phenylphosphazene with an aromatic aldehyde results in a decrease in the reaction yield, but only a slight effect on stereoselectivity. Additionally, the phenolate favors the hydrolysis of the P═N linkage of the hydroxyphosphazenes formed.

**Acknowledgment.** Financial support by the Ministerio de Ciencia y Tecnología (Projects HB1997-0223 and PPQ2001-3266) is gratefully acknowledged. I.F. and G.R.G. thank Junta de Andalucía and Ministerio de Ciencia y Tecnología, respectively, for a doctoral fellowship. M.G.D. and R.D.P. thank the University of Bath for a postdoctoral fellowship.

**Supporting Information Available:** Crystallographic data, 1D gROESY, $^{13}C\{^1H\}$, $^{13}C\{^{31}P,^1H\}$, and 2D $^7Li,^{31}P\{^1H\}$ HMQC NMR spectra of **10**.

OM049608X