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[Li{CH(Me)P(Ph)$_2$(NCO$_2$Me)}$_2$(THF)$_2$]: Crystal, Solution, and Calculated Structure of a *N*-Delocalized Lithium Phosphazene

Ignacio Fernández,[†] Julia María Álvarez Gutiérrez,[‡] Nikolaus Kocher,[§] Dirk Leusser,[§]
Dietmar Stalke,[§] Javier González,[‡] and Fernando López Ortiz*,[†]

Área de Química Orgánica, Universidad de Almería, Carretera de Sacramento s/n, 04120, Almería, Spain,
Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, Julián Clavería 8, 33006 Oviedo, Spain,
and Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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Phosphazenyl-stabilized anions are very useful synthons in organic[1] and organometallic chemistry.[2] Their preparative potential is due to the ability to tune the reactivity and coordinating properties of the system through variation of the substituent at the nitrogen atom. Thus, for a given electrophile the course of the reactions with the lithium anions of *P*-alkyl-*P*,*P*-diphenyl(*N*-phenyl)phosphazenes[3] and those having a strongly electron-withdrawing group linked to the nitrogen[4] differ notably. The diversity in chemical behavior may be ascribed a priori to structural differences of the intervening reactive intermediates.

We have previously reported the crystal structure of the lithium *N*-phenylphosphazene [Li{CH$_2$P(Ph$_2$)═NPh}(THF)$_2$] **1**.[5] The monomer displays a lithium cation to be part of a Li−C−P−N four-membered ring. This structural motif proved to be rather general as it was found in all lithium complexes of alkylphosphazenes subsequently characterized [Li{CH$_2$P(Me$_2$)NSiMe$_3$}$_4$] **2**,[6a] [Li{CMe$_2$P(^{i}Pr$_2$)NSiMe$_3$}$_2$] **3**,[6a] [Li{CH(SiMe$_3$){Ph(1,2-C$_6$H$_4$)PNSiMe$_3$}] **4**,[6b] [Li{CH(SiMe$_3$)P(Ph$_2$)NSiMe$_3$}(Et$_2$O)$_2$] **5**,[6c] and [Li{CH(SiMe$_3$)P(Ph$_2$)NSiMe$_3$}]$_2$ **6**,[6c] [Li{CH(Me)P(Et$_2$)NSiMe$_3$}]$_4$ **7**,[6d] as well as in lithium phosphazenyl dianions,[7] all of them bearing a P═N−SiMe$_3$ group. We describe herein the characterization in solution and in the solid state of the lithium (*N*-methoxycarbonyl)-phosphazene **9**, as well as the ab initio study on a model lithium derivative.

Treatment of CH$_3$CH$_2$P(Ph$_2$)NCO$_2$Me **8**[4d] with LiBu^n in THF at −30 °C for 30 min and then layering the orange solution with hexane at −18 °C for 2 days afforded crystals of dimeric **9**, [Li{CH(CH$_3$)P(Ph$_2$)(NCO$_2$Me)}$_2$](THF)$_2$ as an air-sensitive low-melting (mp −15°C) solid[8] (Scheme 1). Unlike all known lithium phosphazenes, the monomeric unit of **9** consists of a six-membered ring formed by coordination of the lithium atom with the carbanionic center and the oxygen atom of the carbonyl group coming in by side-arm donation (Figure 1). In addition, this oxygen atom provides the link between both lithium atoms of the dimer to form central planar Li$_2$O$_2$ four-membered ring. The six-membered ring exhibits a puckered half-chair conformation with a planar bay defined by the phosphazenyl moiety torsion angles P1−N1−C13−O2 of −1.8(5)°, O2−Li1−C15−P1 of 33.4(2)°, N1−P1−C15−Li1 of −47.5(2)°. The lithium atoms are additionally coordinated by a THF molecule in a distorted tetrahedral geometry. This is the first time that a nonsilylated lithium phosphazene with an electron-withdrawing group at the nitrogen is characterized.

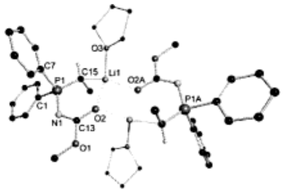

Figure 1. Molecular structure of **9** in the crystal. Selected bond lengths (pm) and angles (deg): P1−N1 163.4(2), P1−C15 169.7(3), C15−Li1 220.1(6), N1−C13 131.3(4), C13−O2 124.5(3), O2−Li1 194.8(5), P1−C1 181.6(3), Li1−O3 197.9(5), N1−P1−C15 118.91(14), C13−N1−P1 123.4(2), O2−C13−N1 131.0(3), O2−Li1−C15 99.2(2), Li1A−O2−Li1A 90.0(2), N1−C13−O1 115.9(3), P1−N1−C13−O2−1.8(5), O2−Li1−C15−P1 33.4(2).

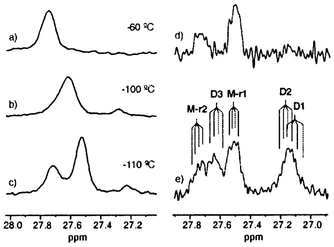

Figure 2. 121.44 MHz ^{31}P NMR spectra of **9** measured in THF-d_8. Sample concentration: (a−d) 0.005 M; (e) 0.057 M. Spectra (d−e) were acquired at −110 °C and processed with resolution enhancement.

Scheme 1

$$\underset{\mathbf{8}}{CH_3CH_2P(Ph)_2{=}NCO_2Me} \xrightarrow[\text{-30 ºC to -18ºC}]{LiBu^n\text{ ,THF}} \underset{\mathbf{9}}{[Li\{CH(CH_3)P(Ph)_2{=}NCO_2Me\}]_2(THF)_2}$$

The C15−Li1 bond distance of 220.1(6) pm is shorter than in monomer **1** 223(1) pm. The P1−N1 bond distance at 163.4(2) pm is slightly longer than the P−N bond length of Ph$_3$P═N(CO)Ph **9** 162.6 pm pm.[9] On the contrary, the N1−C13 distance 131.3(4) pm is shorter than in **9** (135.3 pm), whereas the length of the C13−O2 bond 124.5(3) pm is longer than the average value for the carbonyl group of a α,*β*-unsaturated ester (119.9 pm),[10] although shorter than the C−O distance of an ester enolate (average 131.4 pm).[11] Taking into account that the P1−C15 bond distance of 169.7(3) pm is in the expected range for an ylide group,[12] these data suggest that the negative charge is delocalized through the phosphazenyl fragment. Accordingly, the C15 atom is pyramidal (sum of bond angles of 342.6°), and the carbamate moiety of **9** is essentially planar (torsion angles N1−C13−O1−C14 of −0.3(4)° and O2−C13−O1−C14 of 179.8(2)°).

The solution structure could be unraveled through variable-concentration and -temperature NMR studies. The room temperature NMR spectra of **9** in THF-d_8 show average signals for a single species (Supporting Information) with the expected shielding of the methine group related to **8** ($\Delta\delta_H$(**9**-**8**) = −2.13 ppm, $\Delta\delta_C$(**9**-**8**) = −16.77 ppm).[5] At −60 °C the ^{31}P spectrum of a highly diluted

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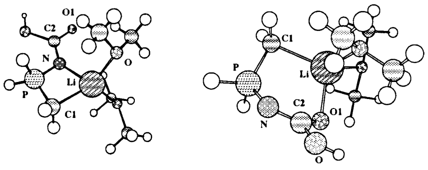
* To whom correspondence should be addressed. E-mail: flortiz@ual.es.
[†] Universidad de Almería.
[‡] Universidad de Oviedo.
[§] Universität Würzburg.



10a **10b**

Figure 3. MP2/6-31+G* optimized geometries of **10a** and **10b**.

sample (0.005 M) shows a single signal, which splits into two broad singlets at −100 °C and is finally resolved in three signals at −110 °C (δ 27.72, 27.54, 27.17, relative ratio 34:57:9) (Figure 2a−c). Resolution enhancement processing revealed the coupling of the two low field phosphorus signals to only one ^{7}Li atom (quartet, $^2J_{P,Li} = 3.2$ Hz Figure 2d).[13] Increasing the concentration to 0.057 M affords a ^{31}P NMR spectrum at −110°C consisting of five quartets at δ 27.15 ($^2J_{P,Li} = 5$ Hz), 27.22 ($^2J_{P,Li} = 3.8$ Hz), 27.54 ($^2J_{P,Li} = 3.2$ Hz), 27.69 ($^2J_{P,Li} = 3.6$ Hz), and 27.75 ($^2J_{P,Li} = 3.2$ Hz) (Figure 2e). Significantly, the relative integral of the overlapped high field signals increased to 34%, and a new quartet appeared at δ 27.69. Additionally, in the concentration range 0.32−0.005 M the variation of the signal integrals correlates reasonably well with an equilibrium monomer−dimer (Supporting Information), provided that the two major signals from the most diluted sample are assigned to the monomer. The fact that the monomer shows two ^{31}P signals may be explained through the presence of two rotamers (**M-r1**/**M-r2**, Figure 2e) due to the restricted rotation of the methoxy group.[14]

On the other hand, a dimer with a structure similar to that found in the solid state (e.g. with trans THF molecules and the cis isomer sterically disfavored) would give rise in solution to a mixture of two diastereoisomers: the (C15*R**,C15A*R**), having two diastereotopic phosphorus atoms, and the (C15*R**,C15A*S**) isomer where the ^{31}P atoms are enantiotopic. Therefore, the ^{31}P spectrum of the dimer would show three signals, as it is experimentally observed (**D1**−**D3**, Figure 2e). The lack of rotamers for the dimer may be assigned to the increase of the bulkiness around the carbonyl group due to the coordination to a second lithium atom.

To understand the reasons of the preference for a six-membered ring chelated lithium structure as compared with the four-membered one, ab initio and *density functional* calculations on the monomeric model compound [$LiCH_2(H)_2P{=}NCO_2H{\cdot}(Me_2O)_2$] were carried out. Two stationary points (**10a** and **10b**, Figure 3), corresponding to the four- and six-membered ring, respectively, were located at the MP2/6-31+G* and Becke3LYP/6-31+G* levels of theory and shown to be energy minima by performing the frequency calculations.[15,16]

According to the calculations, the structure **10b**, with the lithium coordinated to the carbanionic center and to the carbonyl oxygen, in a six-membered ring fashion, is predicted to be stabilized by 2.5 (MP2/6-31+G*) and 3.4 (Becke3LYP/6-31+G*) kcal mol^{-1}, relative to the four-membered ring structure **10a**. This result is in good agreement with the experimental results reported above. The Becke3LYP/6-31+G* calculations predict a higher energetic preference for the six-membered structure than the MP2/6-31+G* level of theory, but there is a close agreement on the geometrical parameters between the two theoretical methods (Table S5, Supporting Information).

The calculated geometrical parameters of **10b** are quite similar to those of **9**, even though the model compound is truncated by the substituents at the carbon and phosphorus atoms. On the other hand, the geometry of **10a** (Table S5) is in good agreement with the X-ray structures previously reported for **1** that show a four-membered ring coordination.[5] The higher stability of **10b** relative to the four-membered ring appears to be due to the distortions present in the geometry of **10a**. Thus, the bond angles around the phosphorus and lithium atoms are far from the ideal values corresponding to the tetrahedral geometry. In addition, the length of the C−Li bond in **10a** is larger than in **10b**, reflecting a weaker bonding interaction between the anionic center and lithium. Finally, the presence of an O−Li bond in **10b**, as compared with the N−Li bond present in **10a**, contributes to an increased stability of the six-membered structure.

Concerning reactivity, the lithium coordination to the CO group in **9** will contribute to increase the electrophilicity of the carbonyl carbon and the phosphorus atom of the phosphazenyl moiety, giving rise to new reaction pathways[4] for the α-lithium *N*-methoxycarbonyl derivatives that are not observed in the *N*-aryl series.[3]

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Supporting Information Available: X-ray data for **9** (CIF). NMR data and spectra of **9**, monomer−dimer equilibrium evaluation of **9**, calculated geometrical parameters (Table S1) and atomic coordinates of **10a** and **10b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Schmidbaur, H.; Jonas, G. *Chem. Ber.* **1967**, *100*, 1120. (b) Johnson, A. W. *Ylides and Imines of Phosphorus*; John Wiley: New York, 1993; Chapter 13, pp 403−483.
(2) (a) Review: Dehnicke, K.; Krieger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19. (b) Wingerter, S.; Pfeiffer, M.; Murso, A.; Lustig, C.; Stey, T.; Chandrasekhar, V.; Stalke, D. *J. Am. Chem. Soc.* **2001**, *123*, 1381.
(3) (a) Álvarez-Gutiérrez, J. M.; López-Ortiz, F. *Chem. Commun.* **1996**, 1583. (b) Álvarez-Gutiérrez, J. M.; López-Ortiz, F.; García-Granda, S.; Rodríguez-González, A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4469.
(4) (a) Álvarez-Gutiérrez, J. M.; López-Ortiz, F. *Tetrahedron Lett.* **1996**, *37*, 2841. (b) Peralta-Pérez, E.; López-Ortiz, F. *Chem. Commun.* **2000**, 2029. (c) Peralta-Pérez, E.; Ahrens, B.; Davidson, M. G.; Raithby, P. R.; Teat, S. J.; Pérez-Álvarez, I.; López-Ortiz, F. *Synlett* **2001**, 275. (d) Álvarez-Gutiérrez, J. M.; Peralta-Pérez, E.; Pérez-Álvarez, I.; López-Ortiz, F. *Tetrahedron* **2001**, *57*, 3075.
(5) López-Ortiz, F.; Peláez-Arango, E.; Tejerina, B.; Pérez-Carreño, E.; García-Granda, S. *J. Am. Chem. Soc.* **1995**, *117*, 9972.
(6) (a) Müller, A.; Neumüller, B.; Dehnicke, K. *Chem. Ber.* **1996**, *129*, 253. (b) Hitchcock, P. B.; Lappert, M. F.; Wang, Z.-X. *Chem. Commun.* **1997**, 1113. (c) Hitchcock, P. B.; Lappert, M. F.; Uiterweerd, P. G. H.; Wang, Z.-X. *J. Chem. Soc., Dalton Trans.* **1999**, 3413. (d) Neumüller, B.; Müller, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2002**, *628*, 100.
(7) (a) Müller, A.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1306. (b) Ong, C. M.; Stephan, D. W. *J. Am. Chem. Soc.* **1999**, *121*, 2939. (c) Kasani, A.; Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1483.
(8) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.
(9) Bar, I.; Bernstein, J. *Acta Crystallogr., Sect. B* **1980**, *36*, 1962.
(10) Allen, F.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
(11) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5403.
(12) Reference 1, p 43−99.
(13) The ^{7}Li NMR spectrum showed two very broad signals apparently resolved in four when strong apodization was applied (Figure S3).
(14) Masamune, S.; Nakamura, N.; Suda, M.; Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481. The slow equilibrium between two conformers of a six-membered ring similar to the one observed in the crystal structure is less probable because this effect is not observed for the dimer.
(15) For a description of the theoretical methods, see: Jensen, F. *Introduction to Computational Chemistry;* John Wiley: New York, 1999.
(16) The calculations were carried out with the Gaussian 98 program: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

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