C_α,C_{ortho}-Dimetalated phosphazene complexes†‡

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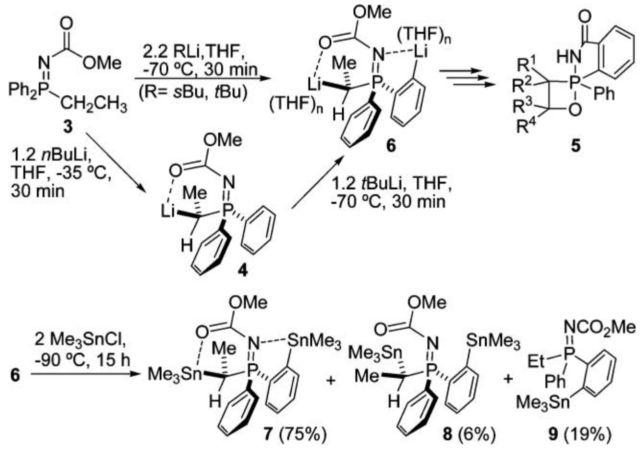
The first C_α,C_{ortho} dilithium complex of a phosphazene has been synthesized as a single stereoisomer and has been structurally characterized in solution; the complex is monomeric, with the dianion acting as an N–C_{ortho} and O–C_α chelate. Transmetallation with Me_3SnCl and PhHgCl afforded the first C_α,C_{ortho} homo- and hetero-bimetallic phosphazene complexes, which contain a desymmetrised Ph_2PN moiety.

Ortho- and α-lithiated phosphazenes have seen widespread use in organic and organometallic chemistry.[1] These monoanions can act as chelating ligands to give four- (**A**),[2] five- (**B**),[3] and six-membered (**C**[4] and **D**[5]) metallocycles (Fig. 1). Double deprotonation of phosphazenes has been achieved exclusively at the position α to the phosphorus of bis(phosphazenyl)methanes.[6] The dianions **E** are valuable precursors for a wide range of metal complexes.[1,7] Access to α,*o*-dilithiated phosphazenes might open new prospects in this area of chemistry. Lappert and co-workers isolated complex **2** through lithiation of $CH_2(SiMe_3)P(Ph)_2{=}NSiMe_3$ (**1**) with *n*BuLi in hexane (Fig. 1).[8] The formation of **2** was assumed to proceed *via* an *ortho*-lithiated species.

We have previously proposed the participation of α,*o*-dianions of phosphazenes **3** as key intermediates in the synthesis of spiro 1,2-oxaphosphetanes **5** (Scheme 1).[9] The process would involve the *ortho* lithiation of the α monoanions **4**.[5] The work described here concerns the first synthesis and structural characterization of a C_α,C_{ortho} dilithium phosphazene **6** in solution and its application in the synthesis of the bimetallic tin(IV) and tin(IV)–mercury(II) complexes **7** and **10**, respectively. The solid-state structure of the compound **7** is also described.

Treatment of **3** with 2.2 equiv. of RLi (R = *s*Bu, *t*Bu) in THF at −70 °C for 30 min afforded an orange solution of **6** (Scheme 1),§ which was investigated by NMR methods.[10] α,*o*-Dilithiation was evidenced in the ^1H NMR spectrum at −90 °C by the broad signal for H1 at δ 0.4 ppm and the four multiplets signal [δ 6.7 (t, H8), 6.72 (q, H9), 7.4 (dd, H10), 7.95 (d, H7) ppm] arising from the *ortho* deprotonated phenyl ring [Fig. 2(a)].[11] The $^{13}C\{^{31}P,^1H\}$ NMR spectrum acquired at −95 °C showed two quartets [δ 1.83, $^1J(^{13}C^7Li)$ 17.0 Hz; 209.27, $^1J(^{13}C^7Li)$ 30.3 Hz, ppm] assigned to C1 and C6, respectively [Fig. 2(b), S5, ESI‡]. The multiplicity of C1 and C6 reveals the binding of each carbon to only one lithium atom. This fact, together with the absence of significant changes in the NMR spectra of a diluted sample of **6** (0.062 M), suggests that the dianion is a monomer. At −100 °C the $^7Li\{^1H\}$ spectrum consists of two doublets [δ 1.2, $^2J(^{31}P^7Li)$ 3.2 Hz; 2.3, $^2J(^{31}P^7Li)$ 7.1 Hz, ppm] [Fig. 2(c)]. The ^{31}P,^7Li coupling of 3.2 Hz is very similar to that found in chelates **D** (Fig. 1).[5] Hence, the high field lithium signal of **6** can be assigned to Li1, which is coordinated to C_α and the oxygen of the CO group of the phosphazenyl moiety. The large deshielding of the carbon C12 [$\Delta\delta_{C12}$(**6**/**3**) = 12.9 ppm]



Scheme 1 Synthesis of dilithium phosphazene **6** and reactivity toward Me_3SnCl.

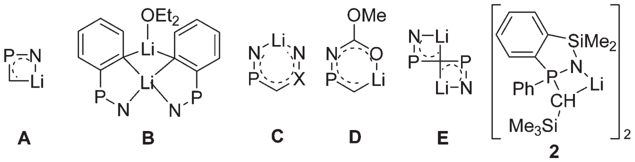


Fig. 1 Different types of lithium phosphazenes.

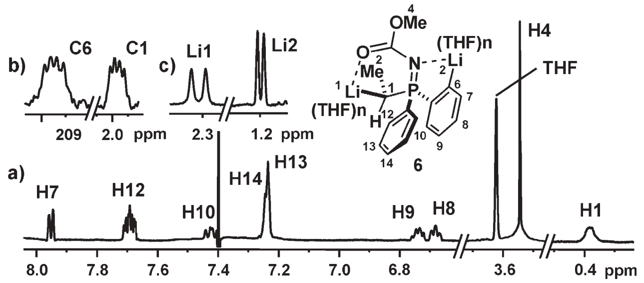


Fig. 2 NMR spectra of **6** in THF-d_8: (a) expansions of the ^1H spectrum (500.13 MHz) measured at −90 °C. (b) Expansions of the C1 and C6 signals of the $^{13}C\{^{31}P,^1H\}$ spectrum (125.76 MHz) measured at −95 °C. (c) $^7Li\{^1H\}$ spectrum (194.37 MHz) measured at −100 °C.

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‡ Electronic supplementary information (ESI) available: Experimental and spectroscopic details. See DOI: 10.1039/b707320h

and the decrease in the ^{31}P,^{13}C coupling [$\Delta^{1}J_{\mathrm{PC12}}$(**6**/**3**) = −17.9 Hz] are consistent with this assignment.[1c,5]

The large magnitude of $^{2}J(^{31}\mathrm{P}^{7}\mathrm{Li}2)$ establishes the existence of PN–Li coordination. The double chelation in **6** will add rigidity to the complex. This hypothesis was verified by 1D gROESY measurements at −90 °C (ESI‡). Selective irradiation of H1 produced NOE on the *ortho* protons H10 and H12 of both aromatic rings, whereas irradiation of H2 gave NOE only on H10. The NOEs observed indicate that complex **6** is configurationally stable, the relative configuration is *l*, and it exists in a conformation in which H1 is *gauche* with respect to both *P*-phenyl rings and *anti* with respect to the nitrogen. These results imply that the initially formed α anion **4** directs the *ortho* deprotonation with excellent diastereoselectivity. To the best of our knowledge, this is the first report on the desymmetrisation of a Ph$_2$PN moiety by directed *ortho* lithiation. α,*o*-Dianions have previously been characterised only for a few alkyl phenyl sulfones[12] and one sulfoximine.[12d] Although the dianions do not showed C$_\alpha$–Li contacts, these systems proved to mimic the reactivity of α,α-dilithiosulfones toward alkylating reagents.[12a,d,13]

Dianion **6** remains unaltered for three days in the temperature range from −90 to −70 °C. Above −70 °C, **6** undergoes cyclocondensation with loss of MeOLi. The process is completed in a few minutes at −35 °C. Subsequent addition of benzaldehyde furnishes **5** (R^1 = H, R^2 = Me, R^3 = H, R^4 = Ph) quantitatively.[9]

The reaction of **6** with 2 equiv. of Me$_3$SnCl at −90 °C during 15 h led, after aqueous workup, to the bis(stannane) **7** in high yield (Scheme 1), together with small amounts of the diastereomer **8** (6%) (ratio **7** : **8** of 12.5 : 1), and the *ortho* monostananne **9** (19%). The three compounds were separated by column chromatography and identified on the basis of the NMR data. Recrystallization of **7** from hexane at −30 °C gave colourless crystals, which were studied by X-ray methods.¶

The solid structure of **7** displays two SnMe$_3$ groups σ-bonded to the phosphazenyl ligand at the C$_\alpha$ and C$_{ortho}$ positions (Fig. 3). The Sn–C distances fall within the expected range for Sn–C$_{(\mathrm{alkyl/aryl})}$ bonds.[14] The C=O and P=N groups are directed toward the tin atoms Sn1 and Sn2, respectively. The Sn1–O1 (284.0 pm) and Sn2–N1 (272.2 pm) distances are shorter than the sum of the corresponding van der Waals radii (Sn/O: 370.0 pm; Sn/N: 372.0 pm), thus indicating the existence of Sn–O and Sn–N contacts.[15] In agreement with this coordination the Sn–C bond distances of the methyl groups *anti* to the O/N donor atoms are slightly larger than the other Sn–CH$_3$ bonds: Sn1–C31 215.9(5) pm; Sn1–C32/33, av. 212.7 pm; Sn2–C42 218.1(5) pm; Sn2–C41/43, av. 213.4 pm. The geometry at the tin atoms can be considered as being located on the tetrahedral-trigonal bipyramidal path.[16] The values $\Delta\sum\theta$(Sn1) = 28° and $\Delta\sum\theta$(Sn2) = 47° indicate that the tin atom Sn2 exists in a five-coordinate geometry best described as a distorted trigonal bipyramid, whereas the Sn1 configuration is closer to a distorted tetrahedron. The Sn2–N1 coordination gives rise to an almost planar five-membered ring [torsion angles N1–P1–C21–C22 of 5.8(4)°, P1–C21–C22–Sn2 of −0.1(5)°]. The Sn2 atom is part of a six-membered ring showing a puckered half-chair conformation with a planar bay defined by the PNCO moiety [torsion angles P1–N1–C53–O1 of 5.7(6)°, C51–P1–N1–C53 of 56.6(4)°, N1–P1–C51–Sn1 of −68.9(3)°]. This is the first time that a α,*o*-bis(stannyl)phosphazene has been characterized.[17] Phosphazenes bearing one tin(II) atom at the α[15b–d,18] or *ortho*[15a] carbon and two tin(II) atoms at the α position[7b] have been described previously. It is worth noting that the solid-state structure of **7** shows the same molecular arrangement as the precursor **6** in solution.

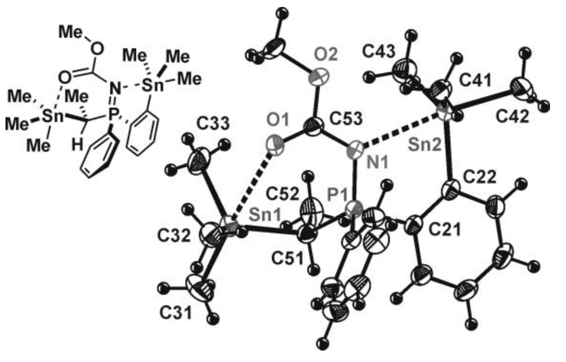
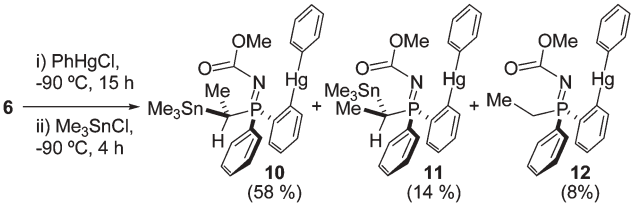


Fig. 3 ORTEP drawing of **7**. Selected bond lengths (pm) and angles (°): P1–N1 160.9(23), P1–C51 177.5(4), N1–C53 134.9(5), C53–O1 122.7(5), Sn1–C51 220.9(4), Sn1–C31 215.9(5), Sn1–C32 212.7(5), Sn1–C33 212.8(5), Sn2–C22 217.0(4), Sn2–C41 213.2(4), Sn2–C42 218.1(5), Sn2–C43 213.6(4); C32–Sn1–C33 113.9(2), C32–Sn1–C31 108.6(2), C33–Sn1–C31 107.1(2), C32–Sn1–C51 118.80(17), C33–Sn1–C51 108.87(18), C31–Sn1–C51 97.88(19), C41–Sn2–C43 119.49(18), C41–Sn2–C22 116.52(17), C41–Sn2–C42 99.3(2), C43–Sn2–C22 113.62(18), C43–Sn2–C42 103.0(2), C22–Sn2–C42 100.19(17).

This success with **7** prompted us to investigate the usefulness of dianion **6** as scaffold for accessing to hetero-bimetallic complexes. To our delight, stepwise addition of PhHgCl and Me$_3$SnCl to **6** at −90 °C afforded α-stannyl-*o*-mercurated phosphazene **10** in good yields (mixture of **10**, **11** and **12** in a ratio of 73 : 17 : 10) (Scheme 2).[19] Purification by column chromatography furnished pure complexes **10–12**. Their structures were assigned based on multinuclear magnetic resonance spectroscopy measurements. Compound **10** is characterised by a ^{31}P signal at δ 35.34 ppm showing ^{119}Sn and ^{199}Hg satellites. The corresponding metallic nuclei appear as doublets at δ (^{119}Sn) 7.55 ppm, $^{2}J(^{119}\mathrm{Sn}^{31}\mathrm{P})$ 32.8 Hz,[20] and δ(^{199}Hg) −701.9 ppm, $^{3}J(^{199}\mathrm{Hg}^{31}\mathrm{P})$ 90.5 Hz. A detailed NMR study will be published elsewhere. Compounds **10** and **11** are the first examples of heterodinuclear Sn,Hg-phosphazene complexes.

In summary, the first α,*o*-dilithium phosphazene **6** has been synthesized as a single stereoisomer. The solution structure shows the characteristic motifs of monolithiated C$_\alpha$ and C$_{ortho}$ phosphazenes. The CO–Li and PN–Li coordination of **6** leads to a rigid monomeric complex that is configurationally stable. The desymmetrisation of the Ph$_2$P=N moiety achieved in the formation of dianion **6** is transferred very efficiently to C$_\alpha$,C$_{ortho}$ homo- and



Scheme 2 Synthesis of heterodinuclear Sn,Hg-phosphazene complexes **10** and **11**.

hetero-dinuclear phosphazene complexes **7** and **10**, respectively. Complexes **6**, **7** and **10** could serve as precursors for a variety of bimetallic complexes *via* transmetallation reactions. This area of chemistry is currently under investigation.

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Notes and references

§ *Synthesis* of **6**: To a solution of 26 mg (91 mmol) of **3** in dry THF-d_8 (0.3 mL) prepared in a dried 5-mm NMR tube at −70 °C were added 132 μL (0.199 mmol) of *s*BuLi (1.3 M solution in *n*-hexane). The sample was transferred to the magnet with the probehead previously cooled to −90 °C. The extra signals shown in the spectra correspond to the solvent of the organolithium base, which was not eliminated. The same procedure was used for the reactions carried out in bulk. NMR data for **6** in THF-d_8: ^{1}H NMR (500.13 MHz, −90 °C) δ 0.4 (br s, H1), 1.34 (dd, H2, J_{PH} = 20.5, J_{HH} = 8.2 Hz), 3.55 (s, H4), 6.70 (br t, H8, J_{PH} = 2.0, J_{HH} = 6.8 Hz), 6.72 (q, H9, J_{PH} = J_{HH} = 6.8 Hz), 7.24 (m, H13), 7.25 (m, H14), 7.4 (dd, H10, J_{PH} = 10.9, J_{HH} = 6.8 Hz), 7.69 (m, H12), 7.95 (d, H7, J_{HH} = 6.8 Hz). ^{13}C NMR (125.76 MHz, −95 °C) δ 1.83 (dq, C1, J_{PC} = 51.9, J_{CLi} = 17.0 Hz), 11.58 (C2), 51.45 (C4), 121.3 (d, C9, J_{PC} = 16.0 Hz), 124.5 (C8), 127.62 (C10), 127.79 (d, C13, J_{PC} = 9.0 Hz), 128.87 (d, C14, J_{PC} = 3.1 Hz), 131.0 (d, C12, J_{PC} = 7.5 Hz), 140.06 (d, C11, J_{PC} = 81.8 Hz), 142.28 (d, C7, J_{PC} = 24.9 Hz), 145.44 (d, C5, J_{PC} = 110.7 Hz), 165.08 (C3), 209.27 (m, C6, J_{CLi} = 30.3 Hz). ^{31}P NMR (202.46, −100 °C) δ 43.81. ^{7}Li NMR (194.37 MHz, −100 °C) δ 1.2 (d, Li2, J_{PLi} = 3.2 Hz), 2.3 (d, Li1, J_{PLi} = 7.1 Hz).

¶ *Crystal data* for **7**: $C_{22}H_{34}NO_2Sn_2$, M_r = 612.85, crystal size: 0.25 × 0.18 × 0.109 mm, triclinic, space group $P\bar{1}$, $a = 9.249(5)$, $b = 11.414(5)$, $c = 13.629(5)$ Å, $\alpha = 77.744(5)$, $\beta = 80.155(5)$, $\gamma = 68.041(5)^\circ$, $V = 1297.3(10)$ Å^3, $Z = 2$, $D_c = 1.569$ g cm^{-3}, $F_{000} = 608$, $T = 150(2)$ K; $\mu = 2.002$ mm^{-1}. 6932 reflections measured, 4449 independent ($R_{int} = 0.0187$), 261 parameters, final R indices R_1 $[I = 2\sigma(I)] = 0.0337$ and wR_2 (all data) = 0.0869, GOF on $F^2 = 1.081$, max./min. residual electron density = 1.150/−0.722 e Å^3. Data were collected on a BRUKER Smart-Apex CCD area-detector diffractometer, using Mo-Kα radiation (λ = 0.71069 Å). The intensities were measured using the ω scan method. Empirical absorption correction was applied. The structure was solved by direct methods SIR97 and refined by full-matrix least-squares on F^2 using SHELXTL97 software package. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. All the diagrams were generated by using the SHELXTL 97 and ORTEP programs. CCDC 621431. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707320h

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20 Complexes **7/10** and **8/11** show similar ^{119}Sn NMR data for the tin atom bonded at the α carbon (see ESI†).