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[Li(thf)$_3$*cyclo*-(P$_4{}^t$Bu$_4$CH)] – synthesis, molecular structure and dynamic behaviour†

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[Li(thf)$_3$*cyclo*-(P$_4{}^t$Bu$_4$CH)] (2–Li), containing the first tetraphosphacyclopentanide anion *cyclo*-(P$_4{}^t$Bu$_4$CH)$^-$ (2), was prepared, and its dynamic behaviour in solution analysed by variable-temperature ^{31}P NMR spectroscopy.

While the chemistry of the neutral cyclooligophosphanes *cyclo*-(P$_n$R$_n$) can be considered a mature area, less is known about the chemistry of their anionic counterparts *cyclo*-(P$_n$R$_{n-1}$)$^-$.[1]

Recently, we began to study systematically the chemistry of linear and cyclic alkali metal oligophosphanides and oligophosphanediides and their potential as building blocks for phosphorus-rich metal complexes.[2] Thus, we reported the targeted synthesis and structural characterisation of the anion *cyclo*-(P$_5{}^t$Bu$_4$)$^-$ (**1**),[2a] which shows a fascinating coordination chemistry.[3] In addition, heavier congeners of **1**, *cyclo*-(P$_4$R$_4$E)$^-$ (E = As, Sb; R = Cy), have also been reported.[4] In light of this, and considering that the analogy between phosphorus and carbon has been used to great effect in organometallic chemistry,[5] the synthesis of a carbon analogue of **1** seemed an interesting challenge. In this preliminary account, we report the synthesis and structural characterisation of [Li(thf)$_3$*cyclo*-(P$_4{}^t$Bu$_4$CH)] (**2**–Li) containing the *cyclo*-(P$_4{}^t$Bu$_4$CH)$^-$ anion (**2**).

Initially, the reactions of alkyllithiums (^{n}BuLi, ^{t}BuLi, MeLi) with the tetraphospholane *cyclo*-(P$_4$Ph$_4$CH$_2$)[6] in toluene and thf were studied. However, only intractable mixtures of products were obtained from these reactions, the reaction mixtures turning red immediately on addition of the base even at −78 °C, while the ^{31}P NMR spectra displayed signals for *cyclo*-(P$_n$Ph$_n$) with n = 4–6[1], as well as several other unassignable resonances. Thus, it seems that in this case nucleophilic attack of the lithium alkyl on the P$_4$C backbone of the heterocycle may be favoured over deprotonation, and only the products of ring degradation are observed.[7] Subsequently, the related compound *cyclo*-(P$_4{}^t$Bu$_4$CH$_2$) (**3**)[8] was prepared, the bulky *tert*-butyl substituents of which should prevent this undesired reactivity. Indeed, deprotonation of **3** was achieved cleanly with MeLi or ^{n}BuLi in thf at low temperature to give [Li(thf)$_3$*cyclo*-(P$_4{}^t$Bu$_4$CH)] (**2**–Li) in good yield (63%).‡

A low-temperature X-ray crystallographic study§ revealed that, in the solid state, **2**–Li forms an ion-contact complex in which Li is coordinated by 3 thf molecules and the ring carbon atom of **2** (Fig. 1) in a distorted tetrahedral fashion. While the carbon–lithium distance is similar to that in other (acyclic) lithium phosphanylmethanides [d(C1–Li1) = 2.236(9) Å],[9] a remarkable aspect of the structure is the absence of any significant P–Li interaction, which is probably due to the geometric constraints imposed by the five-membered P$_4$C ring as well as the steric demand of the ^{t}Bu substituents. Although phosphanylmethanides are versatile ligands,[10] exclusive coordination of the carbon atom of the ligand to Li$^+$ has only very rarely been observed.[11] The ^{t}Bu substituents are in an all-*trans* arrangement, and the five-membered P$_4$C ring of **2**–Li has an envelope conformation in which three phosphorus atoms and one carbon atom form an almost planar arrangement (torsion angle between the planes C1–P1–P2 and P1–P2–P3 1.0°), while the fourth phosphorus atom P4 deviates by 0.337 Å from the mean plane of C1–P1–P2–P3. Due to the lack of any symmetry in the molecule, the four phosphorus atoms P1 to P4 must be regarded as chiral centres. Significantly, **2**–Li crystallises in the chiral space group $P2_1$, and the enantiomer (R_P,S_P,S_P,R_P,r_C)-**2**–Li appears to be the major isomer found in the crystal [Flack parameter x = 0.21(17)]. However, most probably both enantiomers are present in solution, and therefore the compound either undergoes deracemisation on crystallisation, or a racemic mixture of crystals is present in the solid.

At 60 °C in thf, the ^{31}P{^{1}H} NMR spectrum of **2**–Li shows two symmetric multiplets of equal intensity at 111.5 and 49.9 ppm that form an AA′BB′ pattern, similar to that in the symmetric parent compound **3**. In contrast, at −100 °C four different multiplets of equal intensity give rise to an ABCD spin system (Fig. 2). Similar behaviour is observed in deuterated toluene. While the appearance of an ABCD spin system in the spectrum is expected for the target compound and indicates the presence of only one diastereomer of **2**–Li in solution (displaying an all-*trans* arrangement of the ^{t}Bu substituents), the appearance of an AA′BB′ spin system seems to be caused by a fluxional process that is fast on the NMR timescale at high temperature and leads to the equivalence of two phosphorus atoms each in the P$_4$C ring of **2**. This surprising observation might

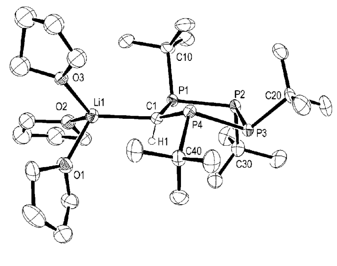

Fig. 1 Molecular structure of **2**–Li. H atoms (except H1) and disorder of coordinated thf molecules have been omitted for clarity. Key bond lengths (Å) and angles (°): C1–Li1 2.236(9), C1–P1 1.778(5), C1–P4 1.794(4), P–P 2.190(2)–2.279(2), Li1–O 1.99(1)–2.04(1), P1–C1–P4 116.9(3), P1–C1–Li1 108.2(3), P4–C1–Li1 126.2(3), C1–Li1–O 114.5(4) to −119.6(5), O–Li1–O 88.3(5) to −113.4(5).

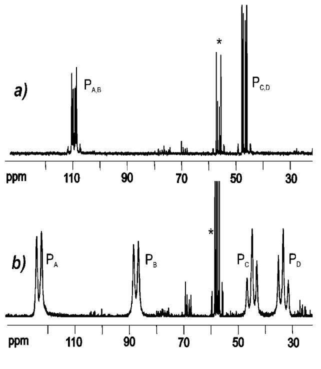

Fig. 2 Variable-temperature ^{31}P{^{1}H} NMR spectrum of **2**–Li in thf/d^8-thf at (a) +60 °C, (b) −100 °C. * denotes signals of **3** present as an impurity.

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† Electronic supplementary information (ESI) available: NMR spectroscopic data of 2–Li and details of the line-shape analysis. See http://www.rsc.org/suppdata/cc/b4/b410617b/

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be explained by assuming that inversion of the phosphorus atoms in the ring is a rapid, concerted process.[12] However, an alternative explanation may be inversion of the ring carbon atom that carries the negative charge. Although there are no studies into the configurational stability of the carbon atoms of phosphanylmethanides, it is well known that inversion barriers in alkali and alkaline earth metal alkyls are rather low and often do not allow their use in stereoselective reactions.[13]

Assuming a first-order process, the activation parameters for conversion between the two enantiomers (R_P,S_P,S_P,R_P,r_C)-**2** and (S_P,R_P,R_P,S_P,s_C)-**2** were determined by line-shape analysis of the variable-temperature $^{31}P\{^1H\}$ NMR spectra.[14] Thus, at +25 °C a free enthalpy of activation $\Delta G^{\ddagger} = 47.6\ (\pm 2.6)\ \mathrm{kJ\ mol^{-1}}$ was found in deuterated toluene. In contrast, the activation barrier is lower in thf [$\Delta G^{\ddagger} = 39.2\ (\pm 3.1)\ \mathrm{kJ\ mol^{-1}}$]. Both of these values are dramatically lower than the inversion barriers observed in tertiary mono- or diphosphanes.[12] However, these values are in the range of those observed in other Li- or Mg-substituted alkyls,[13] and sharp signals are observed in the ^{31}P NMR spectra for the ABCD spin systems of the related carbon-substituted tetraphospholanes *cyclo*-[$P_4R_4CH(CH_2Ph)$] (R = Ph, ^{t}Bu), indicating that no fast equilibria are present in this case.[15] Therefore, it seems likely that the rate-determining process in the equilibrium between the two enantiomers (R_P,S_P,S_P,R_P,r_C)-**2** and (S_P,R_P,R_P,S_P,s_C)-**2** is indeed the inversion of the ring carbon atom.

The lower activation barrier in the donor solvent thf may indicate that an ion-separated structure $[Li(thf)_n]^+$[*cyclo*-(^{t}Bu$_4$P$_4$CH)]$^-$ also plays an important role in this process. Significantly, only a single species is observed in the ^7Li NMR spectrum of **2**–Li in thf (br s at 1.5 ppm) even at −80 °C. Dissociation of the coordinated metal ion is required for inversion of a carbanion, but the full role of the alkali metal may only be elucidated by further investigations.

In summary, the synthesis of the first tetraphosphacyclopentanide anion, *cyclo*-(P$_4$^{t}Bu$_4$CH)$^-$ (**2**), is readily achieved by deprotonation of the tetraphospholane *cyclo*-(P$_4$^{t}Bu$_4$CH$_2$) (**3**). In solution, the two enantiomers (R_P,S_P,S_P,R_P,r_C)-**2** and (S_P,R_P,R_P,S_P,s_C)-**2** are in rapid equilibrium, which is attributed to the inversion of the anionic ring carbon atom. Preliminary studies of the reactivity of **2** show that when **2**–Li is treated with benzyl chloride in C_6D_6 it is converted to the new carbon-substituted species *cyclo*-[P$_4$^{t}Bu$_4$CH(CH$_2$Ph)] (**4**), which displays an ABCD spin system in the $^{31}P\{^1H\}$ NMR spectrum. Furthermore, it will be of interest to explore whether **2** shows a similarly versatile coordination chemistry as its phosphorus analogue *cyclo*-(P$_5$^{t}Bu$_4$)$^-$ (**1**) and thus may indeed be viewed as its "carbon copy". These investigations are presently under way.

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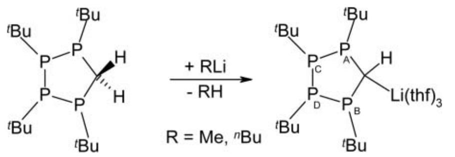
Notes and references

‡ *Synthesis of* **2**–Li: MeLi (0.7 ml; 0.9 mmol; 1.3 M in Et$_2$O) or ^{n}BuLi (0.4 ml; 0.9 mmol; 2.1 M in hexane) was added to *cyclo*-(P$_4$^{t}Bu$_4$CH$_2$) (**3**) which contained *cyclo*-(P$_4$^{t}Bu$_4$) as an impurity (3 : 1, 0.42 g of **3**, 0.87 mmol) in thf (12 ml) at −78 °C. The mixture was stirred for *ca.* 0.5 h and then allowed to warm to room temperature over *ca.* 3 h, and the clear, yellow solution was then stirred overnight. ^{31}P NMR spectra of the reaction mixture showed conversion of **3** of up to 95%. The solvent was reduced to *ca.* 3 ml, and the solution stored at −15 °C for 24 h to give **2**–Li as a crystalline, off-white precipitate. Yield 0.33 g (63%, based on the amount of **3** consumed in the reaction). $^{31}P\{^1H\}$ NMR (+25 °C, 161.98 MHz, C_6D_6), δ = 49.3 (br m, 2P, $P_{C,D}$), 100.0 (br m, 2P, $P_{A,B}$).



3 **2-Li**

§ Crystal data for **2**–Li: $C_{29}H_{61}O_3P_4Li$, M = 588.60, monoclinic, space group $P2_1$, Z = 2, a = 9.996(5), b = 19.104(5), c = 10.290(5) Å, α = 90, β = 113.132(5), γ = 90°, V = 1807.0(13) Å^3, μ(Mo–Kα) = 0.234 mm^{-1}, ρ_{calc} = 1.082 Mg m^{-3}, T = 213(2) K. Data were collected on a Siemens SMART CCD diffractometer. Of a total of 10532 reflections 5286 were unique (R_{int} = 0.0342). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2.[16] Final $R1$ = 0.0628 [$I > 2\sigma(I)$] and $wR2$ = 0.1353 (all data). Absolute structure parameter 0.21(17). Two of the thf molecules exhibit site disorder and were refined over two sites, each of approximately half occupancy. These atoms were refined with isotropic thermal displacement parameters; all other non-hydrogen atoms were refined anisotropically. The hydrogen atom on C1 was located on the difference map and was allowed to refine freely. All other hydrogen atoms were modelled on idealised geometries and were allowed to ride on their parent atom. CCDC 242536. See http://www.rsc.org/suppdata/cc/b4/b410617b/ for crystallographic data in .cif or other electronic format.

1 (*a*) M. Baudler and K. Glinka, *Chem. Rev.*, 1993, **93**, 1623; (*b*) M. Baudler, *Angew. Chem.*, 1987, **99**, 429, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 419; (*c*) M. Baudler, *Angew. Chem.*, 1982, **94**, 520, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 492.

2 (*a*) A. Schisler, U. Huniar, P. Lönnecke, R. Ahlrichs and E. Hey-Hawkins, *Angew. Chem.*, 2001, **113**, 4345, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 4217; (*b*) R. Wolf, A. Schisler, P. Lönnecke, C. Jones and E. Hey-Hawkins, *Eur. J. Inorg. Chem.*, 2004, 3277.

3 A. Schisler, *Dissertation*, University of Leipzig, 2003.

4 A. Bashall, F. Garcia, A. D. Hopkins, J. A. Wood, M. McPartlin, A. D. Woods and D. S. Wright, *Dalton Trans.*, 2003, 1143 and references therein.

5 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998.

6 (*a*) M. Baudler, J. Vesper, P. Junkes and H. Sandmann, *Angew. Chem.*, 1971, **83**, 1019, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 940; (*b*) M. Baudler, J. Vesper, B. Kloth and H. Sandmann, *Z. Anorg. Allg. Chem.*, 1977, **431**, 39.

7 Facile ring fragmentation was observed before in the reaction of the related compound *cyclo*-(P$_5$Ph$_5$) with lithium alkyls: A. Schmidtpeter and K.-H. Zirzow, *Z. Naturforsch.*, 1987, **42b**, 977.

8 M. Baudler, E. Tolls, E. Clef, B. Kloth and D. Koch, *Z. Anorg. Allg. Chem.*, 1977, **435**, 21.

9 Cambridge Crystallographic Database search: C–Li distances in 33 lithium phosphanylmethanides containing trivalent phosphorus atoms range from 2.12 to 2.39 Å.

10 K. Izod, *Adv. Inorg. Chem.*, 2000, **50**, 33.

11 (*a*) H. H. Karsch, K. Zellner, P. Mikulcik, J. Lachmann and G. Müller, *Organometallics*, 1990, **9**, 190; (*b*) A. G. Avent, D. Bonafoux, C. Eaborn, M. S. Hill, P. B. Hitchcock and D. Smith, *J. Chem. Soc., Dalton Trans.*, 2000, 2183.

12 Significantly, related tetraorganodiphosphanes (R′RP)$_2$ cannot be isolated in diastereomerically pure form. J. B. Lambert, G. F. Jackson, III. and D. C. Mueller, *J. Am. Chem. Soc.*, 1970, **92**, 3093 and references therein.

13 J. B. Lambert, in *Topics in Stereochemistry*, ed. N. L. Allinger and E. L. Eliel, Wiley, New York, 1971, **vol. 6**, p. 19.

14 H. Günther, *NMR Spectroscopy*, Wiley, Chichester, 1995; details of the line-shape analysis are given in the electronic supplementary information.

15 R. Wolf and E. Hey-Hawkins, unpublished results.

16 (*a*) *SHELXTL PLUS, Siemens Analyt. X-ray Inst. Inc.*, XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactive Molecular Graphics, 1990; (*b*) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, 1997.