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[Li(tmeda)₂][cyclo-(P₅Bu^t₄)]: An unusual ion-separated lithium oligophosphanide

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ABSTRACT

The reaction of lithium with Bu^tPCl₂ and PCl₃ in the ratio 12:4:1 in THF gave a product mixture comprising cyclo-(P₄Bu^t₄), Li₂(P₄Bu^t₄), and lithium tetra-*tert*-butylcyclopentaphosphanide Li[cyclo-(P₅Bu^t₄)] (**1**) among other phosphanides and phosphanes. Optimization of the reaction conditions and recrystallization from THF/TMEDA (TMEDA: Me₂NCH₂CH₂NMe₂) gave [Li(tmeda)₂][cyclo-(P₅Bu^t₄)] (**1b**) which was characterized by multinuclear NMR spectroscopy, mass spectrometry, IR spectroscopy, and elemental analysis. Single-crystal X-ray diffraction studies showed the presence of separated [Li(tmeda)₂]⁺ cations and [cyclo-(P₅Bu^t₄)]⁻ anions. **1b** represents the first structure of a “naked” [cyclo-(P₅Bu^t₄)]⁻ anion.

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1. Introduction

Metal phosphides M_xP_y are an interesting class of compounds which have been successfully used as catalysts and in materials science [1]. One of the possible routes for the preparation of these compounds is the decomposition of phosphorus-rich metal complexes, which can be synthesized by transmetalation reactions of alkali metal oligophosphanides and other metal salts [2]. Thus, the preparation and reactivity of linear alkali metal oligophosphanides has been extensively studied, and many complexes with potential applications as precursors for the preparation of metal phosphides could be obtained [3].

Alternatively, less is known about cyclic oligophosphanide anions than their open-chain counterparts. Although cyclo-(PPh)₅ was described as early as 1877 [4], the first cyclooligophosphanide anions cyclo-(P_nR_{n-1})⁻, were described only ca. 100 years later [5]. Thus, three-membered rings (in M[cyclo-(P₃Bu^t₂)] with M = Li, K), four-membered rings (in M[cyclo-(P₄Bu^t₂R)] with R = SiMe₃,

Bu^t) and five-membered rings (in M[cyclo-(P₅R₄)] with M = Li, R = Bu^t; M = K, R = Ph) have been reported [5,6]. However, these compounds have only been obtained as inseparable mixtures, and some of them have been only detected in solution by ³¹P NMR spectroscopy.

About 15 years after the investigations on these alkali metal cyclooligophosphanides, we reported the high-yield synthesis and full characterization of the sodium salt Na[cyclo-(P₅Bu^t₄)] [7] and the potassium salt [K(pmedta)(thf)][cyclo-(P₅Bu^t₄)] [2 h] (PMEDTA = Me₂NCH₂CH₂NMeCH₂CH₂NMe₂), which were used for the preparation of a wide variety of main group [8] and transition metal complexes [7,9]. However, some of the target compounds were obtained in low yield only, and others were difficult to synthesize, such as as-yet unknown rare-earth metal complexes, which were inaccessible in our hands starting from the highly reactive Na or K salts. In this context, lithium tetra-*tert*-butylcyclopentaphosphanide seemed to be a more promising starting material for the preparation of new cyclic oligophosphanide metal complexes. We now report the synthesis and structural characterization of [Li(tmeda)₂][cyclo-(P₅Bu^t₄)] (**1b**) which has an unusual solid-state structure consisting of separated [Li(tmeda)₂]⁺ cations and “naked” [cyclo-(P₅Bu^t₄)]⁻ anions.

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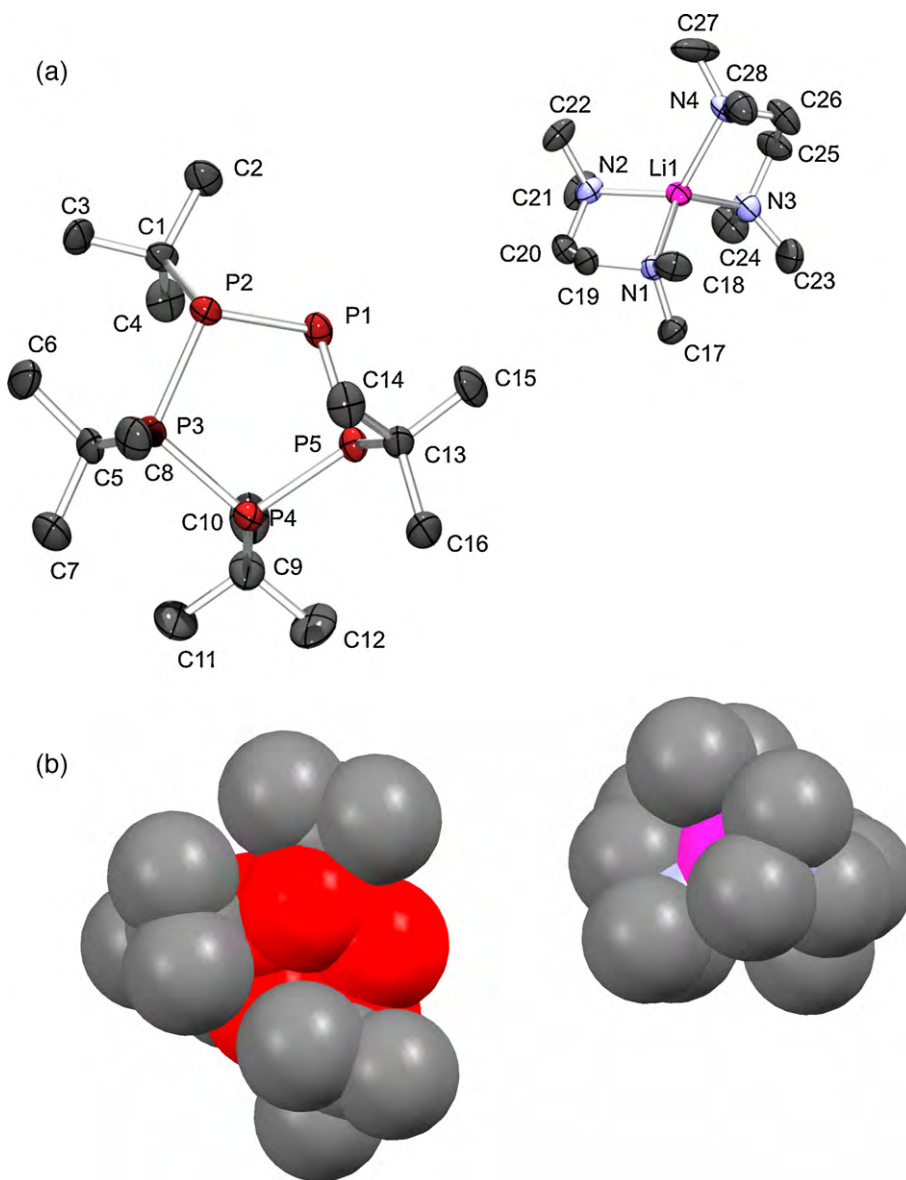


Fig. 1. a) Molecular structure and atom labeling scheme for **1b** with thermal ellipsoids at 50% probability (hydrogen atoms are omitted for clarity) and b) space-filling diagram of **1b** (color code: P red; Li pink; N light blue; C gray).

2. Results and discussion

2.1. Synthesis and spectroscopic studies

We have previously shown that the reaction of sodium with Bu^tPCl_2 and PCl_3 in the ratio 12:4:1 in THF gives a mixture of $\text{Na}[\text{cyclo}-(\text{P}_3\text{Bu}^t_2)]$ [**5a,6b**], $\text{Na}[\text{cyclo}-(\text{P}_4\text{Bu}^t_3)]$ [**6b**], $\text{cyclo}-(\text{P}_4\text{Bu}^t_4)$ [**10**], $\text{Na}_2(\text{P}_4\text{Bu}^t_4)$ [**5a**] and sodium tetra-*tert*-butylcyclopentaphosphanide $\text{Na}[\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]$. The last complex was obtained in reasonable yield after optimization of this reaction [7]. Analogously, $\text{K}[\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]$ was prepared, but it was very difficult to separate from $\text{K}_2(\text{P}_4\text{Bu}^t_4)$ and thus always obtained in low yield [2f]. When lithium is employed, a mixture of $\text{cyclo}-(\text{P}_4\text{Bu}^t_4)$ [**10**], $\text{Li}_2(\text{P}_4\text{Bu}^t_4)$, and lithium tetra-*tert*-butylcyclopentaphosphanide $\text{Li}[\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]$ (**1**) is formed after 6 hours at

80 °C; keeping the reaction mixture at this temperature increased the amount of **1** (to 90% according to $^{31}\text{P}\{^1\text{H}\}$ NMR after 1 d, or 95% after 2 d) (**Scheme 1**). Isolation and recrystallization from THF/TMEDA gave $[\text{Li}(\text{tmeda})_2][\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]$ (**1b**) in good yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1b** shows three sets of signals which correspond to an ABB'CC' spin system. Chemical shifts and coupling constants were successfully calculated by using the program SPINWORKS [11]. The coupling constants are similar to those observed for the analogous Na and K compounds (**Table 1**)¹.

¹ The signs for the coupling constants $^1J(\text{P},\text{P})$ were set as negative, and the remaining signs and all the other coupling constants were obtained with the program SPINWORKS.

Table 1
Comparison of simulated $^{31}\text{P}\{^1\text{H}\}$ NMR data for $\text{M}[\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$).

Compound	δ_A (ppm)	$\delta_{BB'}$ (ppm)	$\delta_{CC'}$ (ppm)	$^1J(\text{P}_A-\text{P}_B) = ^1J(\text{P}_A-\text{P}_{B'})$ (Hz)	$^1J(\text{P}_B-\text{P}_C) = ^1J(\text{P}_{B'}-\text{P}_{C'})$ (Hz)	$^1J(\text{P}_C-\text{P}_C')$ (Hz)	$^2J(\text{P}_A-\text{P}_C) = ^2J(\text{P}_A-\text{P}_{C'})$ (Hz)	Reference
1b	-92.5(1)	86.2(1)	73.8(1)	-394.9(1)	-328.7(1)	-313.4(1)	0.8(1)	This work
$\text{Na}[\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]$	-105.6(1)	82.7(1)	75.0(1)	-379.2(1)	-317.3(1)	-309.4(1)	0.1(1)	7
$\text{K}[\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]$	-104.4(1)	86.9(1)	79.8(1)	-376.9(1)	-319.4(2)	-312.3(1)	0.9(1)	2h

According to the spectroscopic data and based on the steric requirements of the *tert*-butyl groups, only one of the four conformations, the all-*trans* isomer, is preferred as was previously observed for related compounds [7,8,9] and confirmed by X-ray diffraction studies on **1b** (Section 2.2). Additionally, the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1b** showed the expected signals.

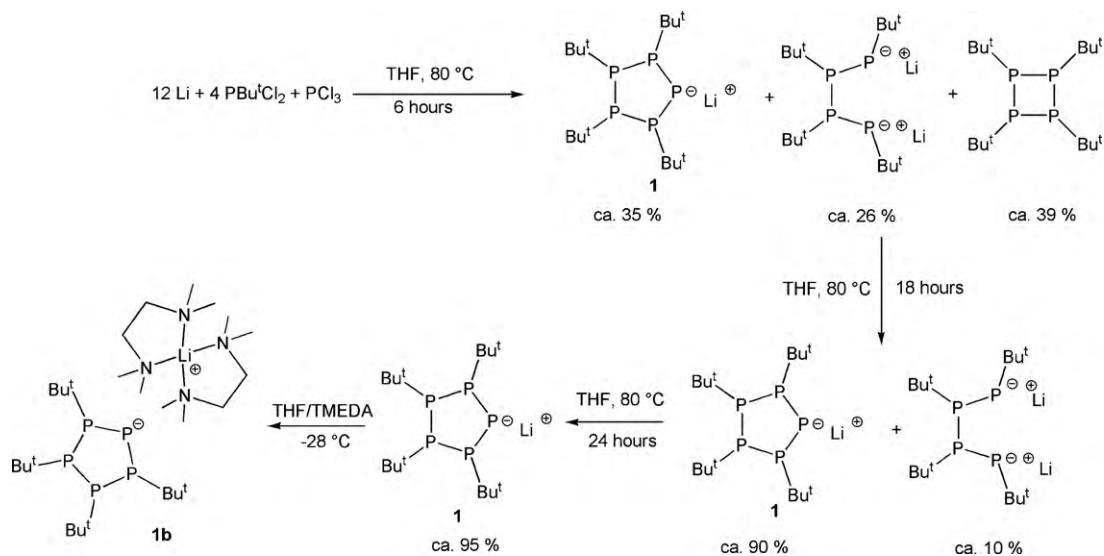
2.2. Structural studies

Orange crystals of **1b** were obtained from THF/TMEDA solution at -28°C . Compound **1b** crystallizes in the noncentrosymmetric monoclinic space group *Cc* with four molecules in the unit cell. Selected bond lengths and angles for **1b** are given in Table 2.

Compound **1b** consists of separated $[\text{Li}(\text{tmEDA})_2]^+$ cations and $[\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]^-$ anions (Fig. 1a). The lithium cation is coordinated in an usual distorted tetrahedral fashion by four nitrogen atoms of two TMEDA molecules ($\text{Li}-\text{N}$ 210.4(8) to 214.4(8) pm, see for example [12]), which prevents interaction of the cation with the anion (Fig. 1b) and thus results in a “naked” $[\text{cyclo}-(\text{P}_5\text{Bu}^t_4)]^-$ anion ($\text{Li}(1)\cdots\text{P}(1)$ 494.0(6) pm). This type of anionic two-coordinate phosphorus atom is typical in metal complexes of white phosphorus (see for example [13] and references therein), but rare for linear or cyclic oligophosphanides [2,3,7,9,14]. Only a few examples display an ion-separated structure, such as $[\text{K}(18\text{-crown-6})(\text{thf})_2][\text{P}_4\text{HMes}_4]$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$), in which the potassium cation is coordinated by 18-crown-6 and two THF molecules [3a],

Table 2
Selected bond lengths (pm) and angles ($^\circ$) for **1b**.

1b	
P(1)–P(2)	220.7 (2)
P(1)–P(5)	212.5 (2)
P(2)–P(3)	222.6 (2)
P(3)–P(4)	221.5 (2)
P(4)–P(5)	221.6 (2)
P(2)–C(1)	191.6 (4)
P(3)–C(5)	190.9 (5)
P(4)–C(9)	189.8 (5)
P(5)–C(13)	188.1 (5)
Li(1)–N(1)	211.3 (8)
Li(1)–N(2)	210.4 (8)
Li(1)–N(3)	214.4 (8)
Li(1)–N(4)	213.3 (8)
P(1)–P(2)–P(3)	102.45 (6)
P(1)–P(5)–P(4)	106.35 (6)
P(2)–P(3)–P(4)	103.16 (6)
P(2)–P(1)–P(5)	104.70 (6)
P(3)–P(4)–P(5)	106.63 (6)
C(1)–P(2)–P(1)	98.5 (2)
C(1)–P(2)–P(3)	100.8 (2)
C(5)–P(3)–P(2)	103.4 (2)
C(5)–P(3)–P(4)	102.0 (2)
C(9)–P(4)–P(3)	101.1 (2)
C(9)–P(4)–P(5)	99.7 (2)
C(13)–P(5)–P(1)	112.0 (2)
C(13)–P(5)–P(4)	102.3 (2)
N(1)–Li(1)–N(3)	122.3 (4)
N(1)–Li(1)–N(4)	121.4 (4)
N(2)–Li(1)–N(3)	118.5 (4)
N(2)–Li(1)–N(4)	121.6 (4)



Scheme 1.

Table 3Comparison of selected structural parameters for alkali and coinage metal complexes of (*cyclo*-P₅Bu^t₄)⁻.

Compound	P(1)–P(5)	Other P–P bonds	M(1)–P(1)	Reference
1b	212.5(2)	220.7(2) 221.5(2) 221.6(2) 222.6(2)	490.4(6)	This work
[Na(thf) ₄][<i>cyclo</i> -(P ₅ Bu ^t ₄)]	213.2(2)	220.4(2) 220.8(1) 221.1(2) 222.9(1)	293.8(2)	[7]
[K(thf)(pmedta)][<i>cyclo</i> -(P ₅ Bu ^t ₄)] ^a	212.9(3)	219.5(4) 220.8(6) 221.4(3) 222.6(5)	325.3(3)	[2h]
[Cu(<i>cyclo</i> -(P ₅ Bu ^t ₄))(PPh ₃) ₂]	214.6(2)	221.0(2) 221.1(2) 221.9(2) 222.2(2)	228.6(2)	[9c]
[Au(<i>cyclo</i> -(P ₅ Bu ^t ₄))(PCyp ₃)] ^b	217.3(2)	220.7(2) 221.6(2) 222.5(2) 223.0(2)	233.3(2)	[9c]

^a Data of only one of the three crystallographically independent molecules of the asymmetric unit are given.^b Cyp = *cyclo*-C₅H₉.

and the lithium phosphanides [Li(12-crown-4)₂][PPh₂] and [Li(12-crown-4)₂][PMes(BMes₂)] [14]. In known lithium oligophosphanides the coordination of only one TMEDA molecule and a phosphorus atom was observed [2i], rather than the coordination of two TMEDA molecules as in **1b**.

The [*cyclo*-(P₅Bu^t₄)]⁻ anions show an all-*trans* arrangement of the *tert*-butyl groups on the phosphorus atoms with an envelope conformation of the chiral anionic P₅ ring (best plane is defined by P(1)–P(3)–P(4)–P(5), deviation of P(2) from this plane is 87.5 pm (P(1) is the anionic phosphorus atom). This conformation is different from those found in [Na(thf)₄][*cyclo*-(P₅Bu^t₄)] [7] and [K(pmedta)(thf)][*cyclo*-(P₅Bu^t₄)] [2g], in which the neutral phosphorus atoms are almost coplanar, while the anionic phosphorus atom lies about 80 pm above this plane. The P(1)–P(5) bond length of 212.5(2) pm in **1b** is about 8 pm shorter than the other P–P bonds, which have values ranging from 220.7(2) to 222.6(2) pm (Table 2), validating the larger coupling constant ¹J(P_A–P_B) = ¹J(P_A–P_B) of –394.9(1) Hz observed in the ³¹P{¹H} NMR spectrum. A comparison of selected structural parameters of alkali and coinage metal complexes containing the *cyclo*-P₅Bu^t₄⁻ ligand is given in Table 3.

3. Conclusions

While the reaction of sodium with Bu^tPCl₂ and PCl₃ in the ratio 12:4:1 in THF gave Na[*cyclo*-(P₅Bu^t₄)] after five days at 80 °C, and the analogous K[*cyclo*-(P₅Bu^t₄)] was obtained only in low yield and with K₂(P₄Bu^t₄) as impurity, the preparation of the corresponding lithium compound Li[*cyclo*-(P₅Bu^t₄)] (**1**) is achieved in two days at 80 °C. Recrystallization of **1** from THF/TMEDA gave crystals of

[Li(tmeda)₂][*cyclo*-(P₅Bu^t₄)] (**1b**), which consists of separated [Li(tmeda)₂]⁺ cations and [*cyclo*-(P₅Bu^t₄)]⁻ anions, representing the first example of a “naked” [*cyclo*-(P₅Bu^t₄)]⁻ anion.

We expect that lithium salts **1** and **1b** may facilitate transmetalation reactions with transition metal or rare-earth metal complexes which were unsuccessful starting from the analogous sodium or potassium salts.

4. Experimental section

4.1. General methods

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. The NMR spectra were recorded at 25 °C on a Bruker AVANCE-DRX-400 spectrometer. ¹H NMR (400.13 MHz) and ¹³C NMR (100.16 MHz): internal standard solvent, external standard TMS; ³¹P NMR (161.9 MHz): external standard 85% H₃PO₄. FAB mass spectra were recorded in a MASPEC II spectrometer with 3-nitrobenzyl alcohol as matrix. IR spectrum: a KBr pellet containing **1b** was prepared in a nitrogen-filled glove box and the spectrum was recorded on a Perkin-Elmer System 2000 FTIR spectrometer in the range 350–4000 cm⁻¹. All solvents were purified by distillation, dried, saturated with argon, and stored over potassium mirror. Elemental analyses were performed on a VARIO EL (Heraeus). The melting point was determined in a sealed capillary under argon and is uncorrected. Bu^tPCl₂ was prepared according to the literature procedure [15].

4.2. Data collection and structure refinement of **1b**

The data of **1b** were collected on a CCD Oxford Xcalibur S (λ(MoK_α) = 71.073 pm) using ω and φ scans mode.

Semi-empirical from equivalents absorption corrections were carried out with SCALE3 ABSPACK [16]. The structures were solved with direct methods [17]. Structure refinement was carried out with SHELXL-97 [17]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined with calculated isotropic displacement parameters. Table 4 lists crystallographic details. CCDC 768441 (**1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.3. Synthesis of [Li(tmEDA)₂][cyclo-(P₅Bu^t)₄] (**1b**)

A solution of PCl₃ (2.89 g, 0.021 mol) and Bu^tPCl₂ (13.35 g, 0.084 mol) in THF (50 mL) was carefully added at 0 °C to lithium sand prepared by trituration of Li (1.75 g, 0.25 mol) in THF (300 mL). The reaction mixture was then warmed to room temperature and heated under reflux for 2 d. After 1 h, the initially colorless solution had turned yellow-green, and it changed to dark brown after one day. THF was then removed under reduced pressure and the brown residue extracted with *n*-hexane (450 mL) to give a green-brown solution. The solvent was removed under reduced pressure to give a brown oily solid (Li[cyclo-(P₅Bu^t)₄] (**1**), 8.20 g, 85%). Recrystallization of this solid from THF/TMEDA (10/1) gave orange needles of [Li(tmEDA)₂][cyclo-(P₅Bu^t)₄] (**1b**; m.p. 139.3–141.6 °C) at –27 °C. Yield of **1b** 7.32 g (56%); IR (KBr): 2951 (s), 2889 (s), 2857 (s), 2368 (w), 2287 (w), 1908 (w), 1648 (w), 1458 (s), 1386 (m), 1359 (s), 1261 (s), 1169 (s), 1046 (s), 897 (m), 806 (s),

667 (w), 559 (m), 500 (w), 481 (m), 440 (w), 406 (w); ¹H NMR (400 MHz, d₈-THF, 25 °C): δ = 1.21 (d, ³J(P,H) = 3.0 Hz, 9H; Bu^t), 1.26 (d, ³J(P,H) = 3.0 Hz, 9H; Bu^t), 1.29 (d, ³J(P,H) = 3.0 Hz, 18H; Bu^t), 2.16 (s, 24H, Me of TMEDA), 2.31 (s, 8H, CH₂ of TMEDA); ¹³C{¹H} NMR (100.6 MHz, d₈-THF, 25 °C): δ = 30.4 (m, C(CH₃)₃), 31.1 (m, C(CH₃)₃), 32.6 (br, C(CH₃)₃), 33.4 (br, C(CH₃)₃), 41.8 (s, Me of TMEDA); 56.7 (s, CH₂ of TMEDA). ³¹P{¹H} NMR (Table 1); FAB MS, matrix: 3-NBA; *m/z* (%): 383.1 (19.7) [M⁺ – Li(tmEDA)₂], 327.1 (100.0) [M⁺ – Li(tmEDA)₂ – Bu^t + H], 270.1 (18.5) [M⁺ – Li(tmEDA)₂ – 2 × Bu^t + H], 239.0 (14.1) [M⁺ – cyclo-(P₅Bu^t)₄]; elemental analysis (%) found (calcd for C₂₈H₆₈LiN₄P₅, *M* = 622.65 g/mol): C 54.01 (53.59); H 11.01 (10.77); N 9.00 (9.25).

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Table 4
Crystallographic data for **1b**.

1b	
Empirical formula	C ₂₈ H ₆₈ LiN ₄ P ₅
Formula mass (g mol ⁻¹)	622.65
Collection <i>T</i> (K)	130(2)
Crystal system	Monoclinic
Space group	Cc
<i>a</i> (pm)	1939.3(2)
<i>b</i> (pm)	1135.45(3)
<i>c</i> (pm)	1982.1(2)
<i>α</i> (deg)	90
<i>β</i> (deg)	115.689(1)
<i>γ</i> (deg)	90
<i>V</i> (nm ³)	3.9332(6)
<i>Z</i>	4
<i>ρ</i> _{calcd} (Mg m ⁻³)	1.052
Absorption coefficient (mm ⁻¹)	0.254
<i>F</i> (000)	1368
Crystal size (mm ³)	0.6 × 0.4 × 0.3
<i>θ</i> range (°)	2.65 to 25.51
Range <i>h, k, l</i>	–23 ≤ <i>h</i> ≤ 23 –13 ≤ <i>k</i> ≤ 13 –24 ≤ <i>l</i> ≤ 24
Data/restraints/parameters	7248/2/363
Goodness-of-fit on <i>F</i> ²	1.069
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0592 <i>wR</i> ₂ = 0.1557
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0666 <i>wR</i> ₂ = 0.1591
Largest diff. peak and hole (e·Å ⁻³)	0.551 and –0.326
Absolute structure parameter (Flack parameter)	0.00(13)

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