

One-step routes for the preparation of MPHMes salts from MesPCl₂ (M = Li, Na, K; Mes = 2,4,6-Me₃C₆H₂)

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Supporting information

This supporting information contains:

1. Synthesis, discussion, data and molecular structure of
[$\{\text{Li}(\text{tmeda})\}_2\text{P}_4\text{Mes}_4\cdot\text{Li}(\text{tmeda})\text{Cl}\cdot\text{LiCl}$]

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Synthesis of [$\{\text{Li}(\text{tmeda})\}_2\text{P}_4\text{Mes}_4\cdot\text{Li}(\text{tmeda})\text{Cl}\cdot\text{LiCl}$]. MesPCl₂ (6.6 g, 30.0 mmol) was dissolved in 150 mL THF and added to freshly prepared lithium sand (0.52 g, 75.0 mmol, prepared using a dispersant machine SilentCrusher M from Heidolph). The mixture was stirred for 30 minutes at room temperature. The red suspension was then analyzed by ³¹P NMR spectroscopy and an AA'XX' spin system in the ³¹P{¹H} NMR spectrum at ca. -12 and -115 ppm was observed. The solvent of the mixture was then removed in vacuo and the deep red solid residue was extracted with Et₂O (3 × 200 mL) and filtered (to remove LiCl). The solvent was evaporated and the oily residue was dissolved in THF (10 mL) and then 1 mL of TMEDA was added. The mixture was stored at -28 °C to give very few crystals of [$\{\text{Li}(\text{tmeda})\}_2\text{P}_4\text{Mes}_4\cdot\text{Li}(\text{tmeda})\text{Cl}\cdot\text{LiCl}$] overnight.

Our efforts to isolate Li₂(P₄Mes₄) were always unsuccessful. Isolation of Li₂(P₄Mes₄) was attempted using short reaction times. However, after evaporation of the solvent, extraction of the residue with Et₂O, filtration and recrystallization from Et₂O/TMEDA or THF/TMEDA, only very small amounts of

[{Li(tmeda)}₂P₄Mes₄]·Li(tmeda)Cl·LiCl crystallized which were always contaminated with *cyclo*-P₄Mes₄ and *cyclo*-P₃Mes₃.

Thus, [{Li(tmeda)}₂P₄Mes₄]·Li(tmeda)Cl·LiCl was only characterized by X-ray crystallography.

In our hands this complex crystallized in very small amounts and the crystals were always very small which led to X-ray structure data of very low quality (with a high disorder degree in one tmeda molecule, one mesityl group and one crystallization THF molecule per asymmetric unit) even though several measurements of different crystals were carried out. However, despite the relatively low quality of the X-ray data, the structural parameters, bond lengths and angles could be determined satisfactorily and without ambiguity.

In this complex, cocrystallization of [{Li(tmeda)}₂P₄Mes₄] and two LiCl units one of them with a coordinated tmeda molecule is observed (see Figure S1), additionally a THF crystallization solvent molecule was also found in the asymmetric unit.

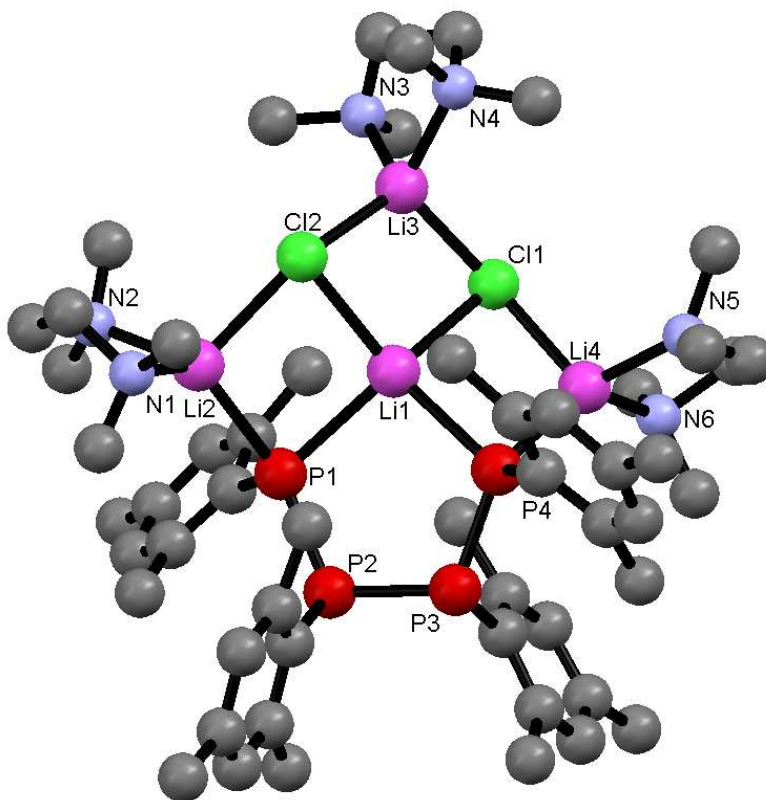


Figure S1. Molecular structure of [{Li(tmeda)}₂P₄Mes₄]·Li(tmeda)Cl·LiCl. Hydrogen atoms have been omitted for clarity

Interestingly, all the phosphorus atoms of the P₄ chain are almost coplanar showing a very small torsion angle of -2.2° (see Figure S2).

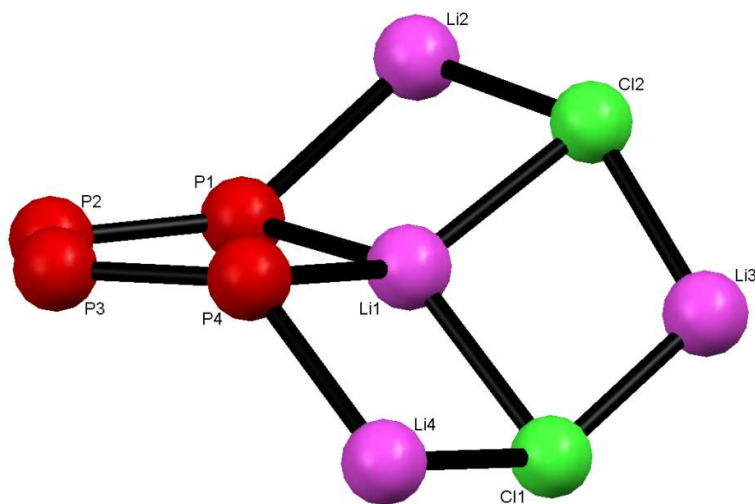


Figure S2. Side view: Planar P₄ chain

The terminal phosphorus atoms of the chain (P1 and P4) are bound to Li2 and Li4, respectively with Li–P bond lengths of 251 to 260 pm similar to other Li–P bonds described in the literature.¹ In addition, the terminal phosphorus atoms of the chain (P1 and P4) are also bound to Li1 in a chelating manner (with Li1–P1 and Li–P4 bond lengths of ca. 259 and 254 pm, respectively) giving rise to a quasi planar five-membered ring (see Figure S3), with the best mean plane defined by Li1–P2–P3–P4 and P1 deviating by ca. 19.9 pm from this plane.

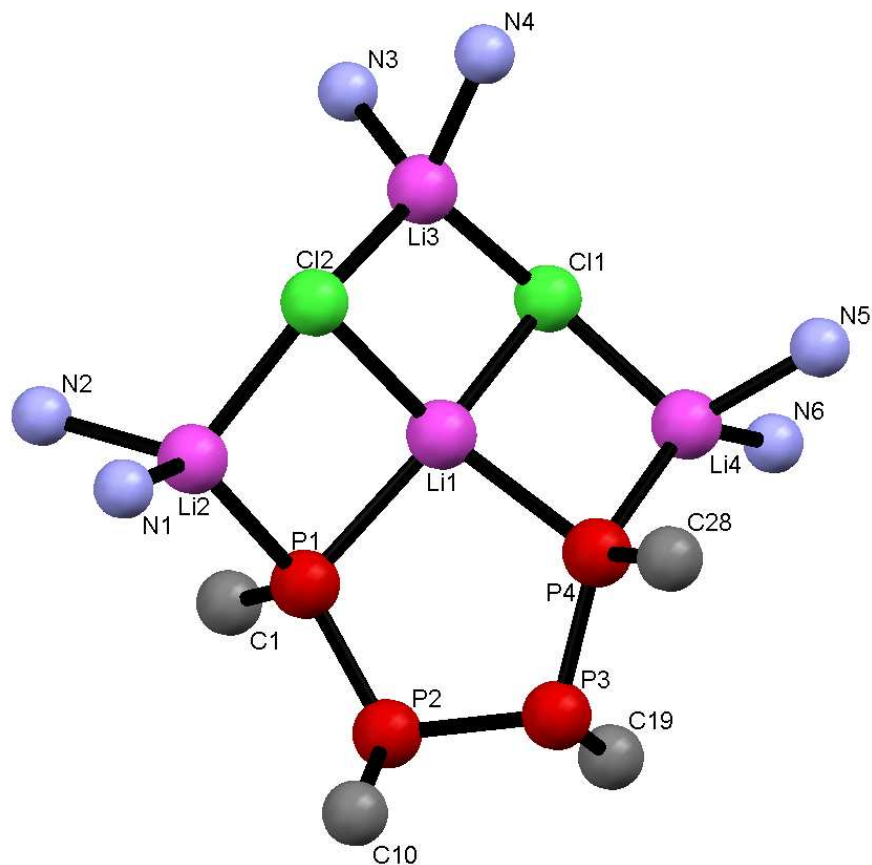


Figure S3. Molecular structure of $[\{Li(tmeda)\}_2P_4Mes_4] \cdot Li(tmeda)Cl \cdot LiCl$. Hydrogen atoms and carbon atoms (except C1, C10, C19 and C28) have been omitted for clarity

Li1 is also bound by two different chlorine atoms (Cl1 and Cl2) which are bridging to another Li atom (Li3) giving rise to a planar four-membered ring (Li1–Cl1–Li3–Cl2 torsion angle of 1.4°) fused with the five-membered ring formed by the P_4 chain and Li1.

Additionally, two different four-membered rings (fused with the one described before) are formed by Li1–Cl1–Li4–P4 (torsion angle of -3.0°) and Li1–Cl2–Li2–P1 (torsion angle of -6.9°). All the lithium atoms of the structure present a typical distorted tetrahedral geometry while the chlorine atoms present the typical distorted T-shape geometry.

Interestingly, short $Li \cdots Li$ contacts of Li1–Li2 341 pm, Li1–Li3 316 pm and Li1–Li4 331 pm are observed.

All the other structural parameters regarding tmeda molecules and mesityl groups are similar to those described in many other similar compounds.¹

Data Collection and Structure Determination of

[{Li(tmeda)}₂P₄Mes₄]·Li(tmeda)Cl·LiCl.

Data for [{Li(tmeda)}₂P₄Mes₄]·Li(tmeda)Cl·LiCl were collected at 130(2) K with an Oxford GEMINI CCD ($\lambda(\text{MoK}\alpha) = 71.073 \text{ pm}$). Semi-empirical from equivalents absorption corrections were carried out with SCALE3 ABSPACK.² The structure was solved by direct methods using SHELXS-97.³ Structure refinement was carried out using full-matrix least-square routines against F^2 with SHELXL-97.³ All non-hydrogen atoms, except some carbon atoms of the disordered mesityl or tmeda moieties, were refined anisotropically; hydrogen atoms were placed in calculated positions and refined with calculated isotropic displacement parameters. A very disordered crystallization THF molecule was removed with SQUEEZE implemented in Platon.⁴ Selected crystallographic data of [{Li(tmeda)}₂P₄Mes₄]·Li(tmeda)Cl·LiCl·THF: empirical formula: C₅₈H₁₀₀Cl₂Li₄N₆OP₄; M: 1119.98; crystal system: orthorhombic; space group: Pbca; a (pm): 19.395(2); b (pm): 24.370(2); c (pm): 27.662(2); α (deg): 90; β (deg): 90; γ (deg): 90; V (nm³): 13.074(2); Z: 8; ρ_{calcd} (Mg m⁻³): 1.138; θ_{max} (deg): 24.71; total data: 124440; unique data (R_{int}): 11129 (0.0591); parameters (restraints): 580 (36); GOF on F^2 : 2.052; R_1 , wR_2 [$I > 2\sigma(I)$]: 0.1640, 0.4538; R_1 , wR_2 (all data): 0.1964, 0.4960; largest diff. peak and hole (e Å⁻³): 5.405 and -1.219.

¹ See for example: (a) Stein, D.; Dransfeld, A.; Flock, M.; Rüegger, H.; Grützmacher, H. *Eur. J. Inorg. Chem.* **2006**, 4157; (b) Niediek, K.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1993**, 619, 885.

² SCALE3 ABSPACK: Empirical absorption correction, CrysAlis – Software package, Oxford Diffraction Ltd. **2006**.

³ SHELX: Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112.

⁴ Platon: Spek, A.L. *Acta Cryst.* **2009**, D65, 148.