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Key indicators

Single-crystal X-ray study
 T = 100 K
 Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
 H-atom completeness 99%
 Disorder in main residue
 R factor = 0.065
 wR factor = 0.189
 Data-to-parameter ratio = 19.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

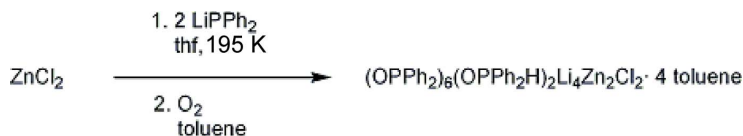
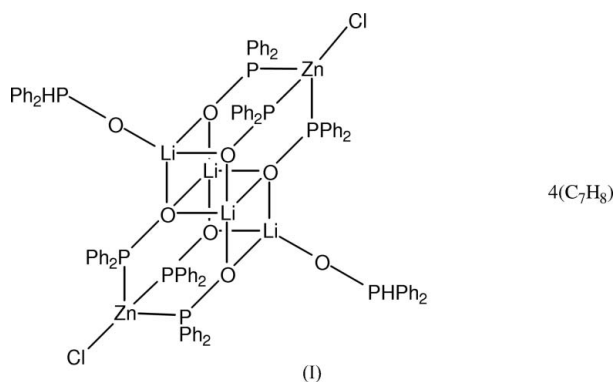
Dichlorohexakis(diphenylphosphinoxy)bis-(hydroxydiphenylphosphine)tetalithium(I)-dizinc(II) toluene tetrasolvate

Molecules of the title compound, $[\text{Li}_4\text{Zn}_2(\text{C}_{12}\text{H}_{10}\text{OP})_6\text{Cl}_2(\text{C}_{12}\text{H}_{11}\text{OP})_2] \cdot 4\text{C}_7\text{H}_8$, are located on crystallographic centres of inversion with one half-molecule in the asymmetric unit.

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Comment

Metal derivatives of secondary phosphine oxides can be obtained by the reaction of tertiary aryl phosphine oxides with alkali metal hydrides (Horner *et al.*, 1961), by metallation of secondary phosphine oxide halides (Horner *et al.*, 1961; Emoto *et al.*, 1974), by deprotonation of secondary phosphine oxides with appropriate bases (Hoskin & Stephan, 1999; Emoto *et al.*, 1974) or by oxidative addition of their P—H bond to appropriate transition metal precursors [Ni: Han *et al.* (2004); Pd: Bedford *et al.* (2003); Pt: Forniés *et al.* (2003); Ru: Torres-Lubián *et al.* (1999)]. The title compound, (I), is a rare example of lithiated diphenylphosphine oxide coordinating lithium with its oxygen lone pairs and a transition metal (Zn^{II}) with its phosphorus lone pair. It was obtained by air oxidation of an unidentified zinc phosphide in toluene solution. The synthesis was accidental but proved to be reproducible.



Molecules of (I) are located on crystallographic centres of inversion with one half-molecule in the asymmetric unit. The central unit is composed of four Li atoms, each of which is bonded to four O atoms. Each of the O atoms is connected to a PPh₂ unit. Whereas the P atoms of three OPPh₂ residues are bonded to a ZnCl unit, one OPPh₂ residue is not further coordinated. In order to achieve a neutral molecule, the P

atoms of the two terminal phosphine oxide units must be protonated, but since none of these H atoms could be found in a difference map, they were omitted from the refinement. The crystal packing reveals that the space between the clusters is filled by toluene molecules.

Experimental

A solution of LiPPh₂ (577 mg, 3.00 mmol) in tetrahydrofuran (THF, 15 ml) was added slowly to a solution of ZnCl₂ (205 mg, 1.50 mmol) in THF (20 ml) at 195 K with stirring. After the reaction mixture had warmed to ambient temperature overnight, a yellow solution and a colourless precipitate had formed. All volatiles were removed *in vacuo* and the resulting yellow residue was extracted with toluene (3 × 15 ml). Air was bubbled through the combined extracts for 10 s and the mixture was subsequently filtered. The filtrate was reduced to 5 ml. A small number of X-ray quality crystals of the title compound separated from the solution upon standing at ambient temperature for two days.

Crystal data

| | |
|--|---|
| [Li ₄ Zn ₂ (C ₁₂ H ₁₀ OP) ₆ Cl ₂ ·(C ₁₂ H ₁₁ OP) ₂] ₂ ·4C ₇ H ₈ | $V = 5623.4 (4) \text{ \AA}^3$ |
| $M_r = 2209.31$ | $Z = 2$ |
| Monoclinic, $P2_1/c$ | $D_x = 1.305 \text{ Mg m}^{-3}$ |
| $a = 13.3526 (7) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 17.1279 (7) \text{ \AA}$ | $\mu = 0.65 \text{ mm}^{-1}$ |
| $c = 24.7049 (10) \text{ \AA}$ | $T = 100 (2) \text{ K}$ |
| $\beta = 95.570 (4)^\circ$ | Block, colourless |
| | $0.44 \times 0.43 \times 0.36 \text{ mm}$ |

Data collection

| | |
|--|--|
| Stoe IPDS-II two-circle diffractometer | 88399 measured reflections |
| ω scans | 13429 independent reflections |
| Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995) | 9360 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.765$, $T_{\max} = 0.801$ | $R_{\text{int}} = 0.072$ |
| | $\theta_{\text{max}} = 27.9^\circ$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | $w = 1/[\sigma^2(F_o^2) + (0.128P)^2]$ |
| $wR(F^2) = 0.189$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.00$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 13429 reflections | $\Delta\rho_{\text{max}} = 1.08 \text{ e \AA}^{-3}$ |
| 677 parameters | $\Delta\rho_{\text{min}} = -0.85 \text{ e \AA}^{-3}$ |

H atoms were refined with fixed individual displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model, with C—H = 0.99 Å. One P atom is disordered over two sites with occupation factors of 0.589 (4) and 0.411 (4). The highest peak is located 1.17 Å from atom C206.

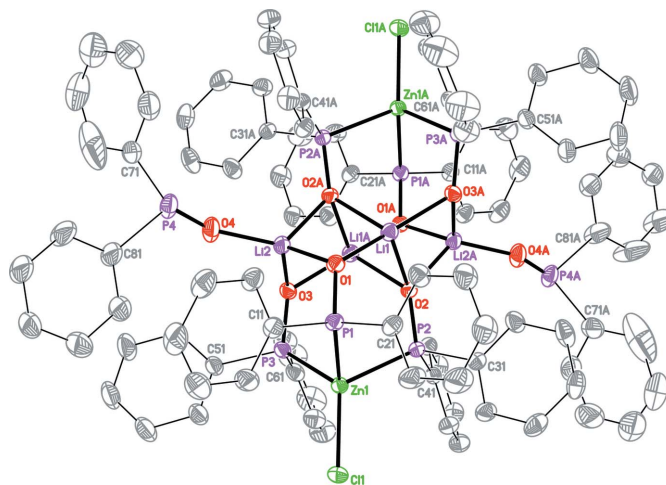


Figure 1

The molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. Only the major occupancy component of the disordered atoms is shown. Atoms with suffix A are generated by the symmetry operator $(1 - x, 1 - y, 1 - z)$.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

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