# Cubane and step-form structures of dilithium bis(aryloxy)phosphines †‡

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The lithium complexes RP(3,5-'Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OLi)<sub>2</sub>(THF)<sub>4</sub>, where R = Ph or 'Pr, (<sup>R</sup>[OPO]Li<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub>, synthesized by reaction of the 2-bromo-4,6-di-*tert*-butylphenol with BuLi and the appropriate dichlorophosphine, possess solid state structures composed of lithium oxide tetragons arranged in a step-form or face sharing half-cubane arrangements. Incorporation of excess lithium aryloxide results in the formation of complexes that display an extended step-form structure, [<sup>Ph</sup>[OPO]Li<sub>2</sub>(ArOLi)]<sub>2</sub>, or a distorted cubane arrangement of tetragons, [<sup>iPr</sup>[OPO]Li<sub>3</sub>Cl(ArOLi)](THF)<sub>3</sub>.

## Introduction

Lithium aryloxide complexes are known to form a variety of aggregate structures,1-5 the majority of which are based on dimeric Li<sub>2</sub>O<sub>2</sub> rings or tetrameric Li<sub>4</sub>O<sub>4</sub> cubanes.<sup>6,7</sup> A measure of control over the aggregation can be conferred through the choice of aryloxide (monodentate vs. bridging), the substitution pattern around the aromatic ring (sterics and electron-donating ability), and the reaction solvent (Lewis basicity). In substituted lithium phenoxide complexes, particularly those substituted at the para position, structures composed of Li2O2 rings and cubanes predominate, whereas bulky substituents at the ortho position lead to steric crowding at the aryloxide oxygen often result in smaller aggregates.8 Ligands containing linked aryloxide units, such as binaphthol, can also give rise to complex structures, including chiral chains and clusters.9 The bidentate aryloxide 2,2'-ethylidenebis(4,6-di-tert-butylphenol) (EDBP) possesses a flexible methyl methyne bridge, and structures of lithium EDBP complexes contain multiple Li<sub>2</sub>O<sub>2</sub> cores that are joined in hexagonal, step-form ladder and distorted sheet skeletons.<sup>1</sup> Alteration of the bridging moiety in linked aryloxides can be used to generate potentially tridentate ligands. The phosphorus substituted ligand bis(3,5-tertbutyl-2-phenoxy)phenylphosphine [OPO], is known,<sup>10</sup> and simple lithium complexes supported by the coordinating solvent 1,2dimethoxyethane (DME) have recently been reported.<sup>11</sup> Herein we report the synthesis of [OPO] lithium complexes in THF and their structural characterization.

# **Results and discussion**

Synthesis of the <sup>R</sup>[OPO]Li<sub>2</sub>(THF)<sub>2</sub> derivatives is achieved through a modification of the published procedure;<sup>10</sup> instead of a hydrolytic workup, the dilithio salts can be isolated directly. Thus, reaction of two equivalents of a 2-bromo-4,6-di-*tert*-butylphenol with RPCl<sub>2</sub> (R = Ph, <sup>i</sup>Pr) in the presence of four equivalents of *n*-BuLi yields the crude product as a cream coloured solid. Addition of excess THF to a hexanes slurry of the crude product affords the dilithio THF adducts ( ${}^{Ph}[OPO]Li_2)_2(THF)_4$  (1) and ( ${}^{Pr}[OPO]Li_2)_2(THF)_4$  (2) as colourless solids, in 70% and 51% yield, respectively (Scheme 1).



X-Ray quality crystals of 1 containing three molecules of cocrystallized solvent were grown by slow evaporation of a saturated benzene solution. The solid-state molecular structure of 1 contains two independent but structurally similar molecular fragments in the asymmetric unit. One of these is presented in Fig. 1, along with its crystallographically related fragment; crystallographic data are given in Table 5, and selected bond distances and angles are collected in Table 1. The structure is dimeric with the two <sup>Ph</sup>[OPO]Li<sub>2</sub> fragments bound via Li–O bonds forming a ladder like structure composed of three Li<sub>2</sub>O<sub>2</sub> rings. The geometry about Li(1) is best described as a highly distorted tetrahedron where the lithium is bound by three [OPO] oxygens and P(1), whereas Li(2) is in a much less distorted tetrahedral geometry with the lithium bound by two [OPO] oxygens and two THF molecules. The structure of 1 stands in stark contrast to the simple monomeric structure of the DME adduct, Ph[OPO]Li2(DME)2,11 with the only chemical difference being the choice of coordinating solvent; the

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 $\begin{array}{ll} \textbf{Table 1} & Selected \ bond \ distances ( \mathring{A} ), bond \ angles ( ^{\circ} ), and \ dihedral \ angles \\ ( ^{\circ} ) \ for \ ( ^{Ph}[OPO]Li_2)_2(THF)_4, 1 \end{array}$ 

Li(1)-P(1) Li(1)-O(1)	2.499(3) 1.948(3)	Li(2)-O(1) Li(2)-O(2)	1.936(3) 2.148(3)
Li(1) = O(2) $Li(1) = O(2^*)$	2.016(3)	Li(2) - O(3) Li(2) - O(4)	1.981(3) 1.994(3)
P(1) = U(1) = O(1)	79 76(10)	O(1) - U(2) = O(2)	93 91(13)
P(1) = Li(1) = O(1) P(1) = Li(1) = O(2) $P(1) = Li(1) = O(2^*)$	81.40(10) 136.55(15)	O(1) $Li(2)$ $O(2)O(1)$ $-Li(2)$ $-O(4)O(1)$ $-Li(2)$ $-O(3)$	113.89(15)
O(1)-Li(1)-O(2) O(1)-Li(1)-O(2) O(1)-Li(1)-O(2*)	97.81(13) 142.18(16)	O(2)-Li(2)-O(3) O(2)-Li(2)-O(4)	105.51(15) 111.82(15) 123.16(15)
O(1) = D(1) = O(2) O(2) = Li(1) = O(2*) Li(1) = O(2) = Li(1*)	98.16(12) 81.84(12)	O(2) = Li(2) = O(4) O(3) = Li(2) = O(4) Li(1) = O(2) = Li(2)	125.10(15) 106.98(15) 76.48(12)
Li(1) - O(1) - Li(2)	83.23(13)	EI(1) O(2) EI(2)	/0.40(12)
Li(1)-O(2)-Li(1*)-O(2*) O(1)-Li(1)-O(2)-Li(2)	0.0 -21.45(12)		

Symmetry operator \*: -x, -y, 1 - z.



Fig. 1 Molecular structure (ORTEP) of  $({}^{Ph}[OPO]Li_2)_2(THF)_4$ , 1. Ellipsoids are drawn at 50% probability.

structure of this DME adduct is shown below. Metrical parameters of the <sup>Ph</sup>[OPO] fragments in 1 agree well with the DME adduct. The monomeric nature of the DME adduct may be rationalized through the chelating nature of the coordinating solvent, which is more strongly donating than the bridging aryloxide unit present in the THF adduct 1.



Mass spectral analysis confirmed the dimeric nature of 1 with the observation of a mass peak corresponding to the dimer with loss of the THF donors. In solution 1 displays  $C_s$  symmetry, with resonances for the *t*-butyl groups appearing as two distinct singlets in the <sup>1</sup>H NMR spectrum.

The isopropyl derivative 2 shows similar symmetry in solution, and a mass spectrum confirms a similar dimeric structure. All

 $\begin{array}{ll} \textbf{Table 2} & \text{Selected bond distances (Å), bond angles (°), and dihedral angles (°) for [{}^{i Pr}[OP(=O)O]Li_2(H_2O)]_2, \textbf{2-O} \end{array}$ 

Li(1)–O(1)	1.854(4)	Li(2)–O(1)	1.916(4)	
Li(1) - O(2)	1.870(4)	$Li(2) - O(2^*)$	1.901(4)	
Li(1) - O(3)	1.975(4)	$Li(2) - O(3^*)$	2.026(5)	
$Li(1) - O(3^*)$	1.991(4)	Li(2) - O(4)	2.033(13)	
P(1)–O(3)	1.5209(17)		. ,	
P(1)–O(3)–Li(1)	119.04(15)	Li(1)-O(1)-Li(2)	85.3(2)	
$P(1) - O(3) - Li(1^*)$	117.66(15)	$O(1) - Li(2) - O(3^*)$	93.3(2)	
P(1)-O(3)-Li(2*)	154.24(17)	$Li(2) - O(3^*) - Li(1)$	79.00(17)	
O(3) - P(1) - C(13)	105.51(11)	$O(3^*)-Li(1)-O(1)$	96.37(19)	
Li(1) - O(3) - Li(1*)	85.79(18)	Li(1)–O(2)–Li(2*)	85.56(19)	
O(3)-Li(1*)-O(3*)	94.21(18)	$O(2) - Li(2^*) - O(3)$	93.4(2)	
Li(1*)-O(3*)-Li(1)	85.79(18)	Li(2*)-O(3)-Li(1)	79.60(17)	
O(3*)–Li(1)–O(3)	94.21(18)	O(3)-Li(1)-O(2)	96.05(19)	
O(1)-Li(1)-O(2)	160.2(3)			
Li(1)-O(3)-Li(1*)-O(3*)	0.0			
$O(1)-Li(1)-O(3^*)-Li(2)$	18.4(2)			
O(2)–Li(1)–O(3)–Li(2*)	17.3(2)			
Symmetry operator *: $1 - x$ , $-y$ , $1 - z$ .				

attempts to crystallize 2 have thus far failed to yield X-ray quality crystals. However, when a  $d_6$ -benzene solution of 2 is allowed to evaporate slowly in the presence of atmospheric oxygen and water, X-ray quality crystals of a related phosphine oxide complex,  $[^{iPr}[OP(=O)O]Li_2(H_2O)]_2$  (2-O), containing four equivalents of co-crystallized benzene, are formed. The solid-state molecular structure of 2-O is presented in Fig. 2; crystallographic data are presented in Table 5, and selected bond distances and angles in Table 2. Structurally, 2-O is a dimer, like 1, with a core composed of Li<sub>2</sub>O<sub>2</sub> rings, arranged not as a ladder but as corners of two half-cubanes that share a face, a structural motif that is rare in the literature.<sup>3,12</sup> Severe disorder in the water molecule O(4) prohibited the location of the attached hydrogens in the difference map; however, the Li(2)–O(4) bond distance is in agreement with other lithium water complexes.<sup>13,14</sup> Each lithium is four-coordinate; with Li(1) bound in a disphenoidal geometry to both phosphine oxides and one oxygen of each [OPO], while Li(2) is bound in a distorted tetrahedral geometry to the oxygens of one [OPO] ligand, the phosphine oxide of the other [OPO] ligand, and the water molecule. Li-O bond distance agree well with those of complex 1, and the phosphorus oxygen double bond is reflected in the



**Fig. 2** Molecular structure (ORTEP) of  $[P^{p_r}[OP(=O)O]Li_2(H_2O)]_2$ , **2-O**. Ellipsoids are drawn at 50% probability.

P–O bond distance of 1.52 Å, which is toward the long end of the literature values.<sup>15,16</sup> The phosphine oxide of **1** has been utilized as an ancillary ligand in early transition metal chemistry;<sup>10,17</sup> however, the solid-state structure of the lithium salt had not been previously reported.

The modest yields for these lithium salt syntheses suggest that other reaction pathways are available in these reactions. For example, during the synthesis of **1**, a different lithium complex can be isolated in low yields from the concentrated toluene solution after the removal of LiCl but before the addition of THF. The isolated material has been structurally characterized as [<sup>Ph</sup>[OPO]Li<sub>2</sub>]<sub>2</sub>(ArOLi)<sub>2</sub> (**3**), where ArOLi is lithium 2,4-di-*tert*butylphenoxide. The solid-state structure is presented in Fig. 3; crystallographic data are given in Table 5 and selected bond distances and angles in Table 3. Complex **3** is dimeric in the sense that it contains two molecules of <sup>Ph</sup>[OPO]Li<sub>2</sub>, but also present are two molecules of ArOLi, and three molecules of cocrystallized toluene are also present in the unit cell. The core of Li<sub>2</sub>O<sub>2</sub> rings is arranged in an open 'S' shape, a very rare



**Fig. 3** Molecular structure (ORTEP) of [<sup>Ph</sup>[OPO]Li<sub>2</sub>]<sub>2</sub>(ArOLi)<sub>2</sub>, **3**. Ellipsoids are drawn at 50% probability.

 $\begin{array}{ll} \textbf{Table 3} & \text{Selected bond distances (Å), bond angles (°), and dihedral angles (°) for [$^h[OPO]Li_2]_2(ArOLi)_2, 3$} \end{array}$ 

Li(1)–P(1*)	2.467(4)	Li(3)–O(1)	1.897(5)
Li(1)–O(1)	1.960(4)	Li(3)–O(2*)	1.826(5)
Li(1)-O(1*)	2.085(5)	Li(3)–O(3*)	2.051(5)
Li(1) - O(3)	1.883(5)	Li(2) - O(3)	1.869(5)
Li(2)–O(2)	1.849(5)		
P(1*)-Li(1)-O(1)	116.6(2)	Li(1)-O(1*)-Li(3*)	79.46(19)
$P(1^*)-Li(1)-O(1^*)$	81.06(14)	$O(1^*)-Li(3^*)-O(3)$	98.7(2)
P(1*)-Li(1)-O(3)	125.1(2)	$Li(3^*)-O(3)-Li(1)$	80.65(19)
$Li(1) - P(1^*) - C(1)$	96.44(13)	$O(3)-Li(1)-O(1^*)$	98.0(2)
O(1)-Li(1)-O(1*)	96.46(18)	Li(2)–O(3)–Li(3*)	79.7(2)
$Li(1) - O(1^*) - Li(1^*)$	83.61(19)	$O(3) - Li(3^*) - O(2)$	93.0(2)
$O(1^*)-Li(1^*)-O(1)$	96.38(14)	$Li(3^*) - O(2) - Li(2)$	86.4(2)
Li(1*) - O(1) - Li(1)	83.62(19)	O(2)–Li(2)–O(3)	98.4(2)
Li(1)-O(1)-Li(1*)-O(1*)	0.0		
$O(3) - Li(1) - O(1^*) - Li(3^*)$	14.0(2)		
Li(2)-O(3)-Li(3*)-O(2)	-11.7(2)		
Symmetry operator $*: -x$ ,	-y, 1-z.		

structural motif for lithium aryloxide complexes;<sup>18</sup> the majority of such complexes composed of greater than three Li<sub>2</sub>O<sub>2</sub> rings form cubanes or hexagonal structures.<sup>19</sup> The complex contains three distinct lithium coordination environments. Li(1) is fourcoordinate, bound in a distorted tetrahedral geometry by two  $^{Ph}[OPO]$  oxygens O(1) and O(1\*), the substituted phenoxide O(3), and a phosphorus P(1\*). Li(3) is three-coordinate, bound in a distorted pyramidal geometry to two <sup>Ph</sup>[OPO] oxygens O(1) and  $O(2^*)$ , and the substituted phenoxide  $O(3^*)$ . In contrast, Li(2) is essentially two-coordinate, bound in a bent configuration to O(2) and O(3), with an O(2)-Li(2)-O(3) angle of 98.4°. The low formal coordination number at lithium is not unusual, however the bent configuration is not often observed.<sup>20-23</sup> The coordination sphere is augmented by close contacts between Li(2) and one of the aromatic rings of the ligand, and a methyl group of the nearest tbutyl moiety. The closest interaction involves the carbon bound to phosphorus Li(2)  $\cdots$  C(1) (2.46 Å) with other interactions greater than 2.7 Å, while the methyl interaction  $Li(2) \cdots C(44)$  (2.57 Å) is intermediate. The interactions are all longer than the sum of the van der Waals radii for lithium and carbon.<sup>21</sup> Close contacts between lithium and saturated and unsaturated carbon fragments are a common characteristic of coordination complexes where the lithium is formally two coordinate and there is no Lewis base.<sup>22-24</sup> Li-O and Li-P distances agree well with complex 1 and with other literature values.25-29

In solution **3** is the only lithium complex of [OPO] to display phosphorus lithium coupling, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is a 1:1:1:1 quartet with a <sup>1</sup>*J*<sub>PLi</sub> coupling of 107.1 Hz. This value is on the large end of the 35–122 Hz range observed for similar lithium phosphide complexes,<sup>30–32</sup> and significantly larger than the value of 33 Hz observed for <sup>Ph</sup>[OPO]Li<sub>2</sub>(DME)<sub>2</sub>.<sup>11</sup>

Synthesis of the isopropyl derivative also yields additional lithium aryloxide complexes, one of which can be obtained in low yield from the hexanes filtrate following the isolation of **2**. Concentration of the hexanes filtrate yields colourless crystals that have been structurally characterized as  $[^{Pr}[OPO]Li_3Cl(ArOLi)](THF)_3$  (**4**). The solid-state structure is shown in Fig. 4, crystallographic data are given in Table 5, and selected bond distances and angles are collected in Table 4. The structure contains one molecule of  $^{Pr}[OPO]Li_2$ , one molecule of ArOLi, and an equivalent of lithium chloride arranged in a distorted cubane of  $Li_2O_2$  rings.



Fig. 4 Molecular structure (ORTEP) of [<sup>#r</sup>[OPO]Li<sub>3</sub>Cl-(ArOLi)](THF)<sub>3</sub>,
4. Ellipsoids are drawn at 50% probability.

Table 4	Selected bond distances (Å) bond angles (°) and dihedral angles

**Table 4** Selected bond distances (A), bond angles (\*), a (°) for  $[^{iPr}[OPO]Li_3Cl(ArOLi)](THF)_3$ , 4

Li(1)–O(1)	2.027(4)	Li(2)–O(1)	2.000(4)
Li(1)–O(4)	1.933(5)	Li(2) - O(2)	1.999(4)
Li(1)-Cl(1)	2.445(5)	Li(2) - O(3)	1.929(4)
Li(3)–O(1)	1.999(3)	Li(2)-Cl(1)	2.445(4)
Li(3)–O(2)	1.810(5)	Li(3) - P(1)	2.340(5)
O(1)-Li(2)-O(2)	96.11(16)	Cl(1)-Li(2)-O(2)	95.80(16)
Li(2) - O(2) - Li(3)	82.83(16)	$Li(2) - O(2) - Li(2^*)$	92.5(2)
O(2)-Li(3)-O(1)	102.61(18)	Li(1) - O(1) - Li(3)	82.99(15)
Li(3) - O(1) - Li(2)	78.28(18)	$O(1)-Li(3)-O(1^*)$	96.8(2)
Li(1)-O(1)-Li(2)	88.50(19)	P(1)-Li(3)-O(1)	86.40(15)
O(1)-Li(2)-Cl(1)	100.15(15)	P(1)-Li(3)-O(2)	166.2(3)
Li(2)-Cl(1)-Li(1)	70.16(12)	O(4)-Li(1)-O(1)	120.79(17)
Cl(1)-Li(1)-O(1)	99.39(17)	O(4)-Li(1)-Cl(1)	116.7(2)
O(3)–Li(2)–O(1)	132.7(2)	O(3)-Li(2)-Cl(1)	114.07(17)
O(3)–Li(2)–O(2)	111.01(19)		
$Li(1) - O(1) - Li(3) - O(1^*)$	11.3(2)		
$Li(3) - O(2) - Li(2^*) - O(1^*)$	3.2(2)		
Cl(1)-Li(2)-O(2)-Li(2*)	15.2(2)		
Symmetry operator *: $x$ , 1	/2 - v, z.		

Each lithium is four-coordinate, bound in a distorted tetrahedral geometry, and Li–O, Li–P and Li–Cl bond distances are in agreement with previously discussed complexes and literature values. Incorporation of a chloride in place of an oxygen in lithium aryloxide cubane structures is very rare, only three examples are known.<sup>33,34</sup> However, lithium chloride adducts, or 'ate' complexes, are very common in early transition metal and lanthanide aryloxide chemistry,<sup>35</sup> where the retention of lithium chloride is at least partially driven by the electron deficient nature of the metal center,<sup>36,37</sup> and the oxophilic nature of lithium.<sup>34,38</sup> Thus, their rarity in lithium aryloxide chemistry could be attributed to the ease of deprotonation reactions for their synthesis and a relative lack of salt metathesis pathways.

Formation of complexes **3** and **4** is capricious in nature and isolated yields can vary from reaction to reaction. However, the low yields of both **3** and **4** suggest that the lithium 2,4-di-*tert*-butylphenoxide impurity is also small, of the order of 1-2%. The most likely source of the phenoxide is from trace amounts of non-brominated phenol in the reaction mixture, although a reaction of adventitious water with a lithium intermediate cannot be ruled out.

# Conclusions

This work illustrates the complexity of lithium–aryloxide structures that can be obtained from very similar materials. Isolation of the dilithium salt of the <sup>Ph</sup>[OPO] ligand from 1,2-dimethoxyethane results in a completely different structural motif as compared to isolation of the same material from tetrahydrofuran: the former is a monomeric dilithio species, whereas the latter is a bridged dimer that has a step-form structure linking the four lithium cations. Oxidation of the <sup>Pr</sup>[OPO] ligand results in a new structural form that now shows a cubane geometry in the solid state. The presence of small impurities can also lead to the isolation of new structure types as indicated by the [<sup>Pr</sup>[OPO]Li<sub>3</sub>Cl(ArOLi)](THF)<sub>3</sub> derivative. While this species and the oxidized <sup>Pr</sup>[OPO] system are not available on synthetic scales, their adventitious isolation does provide further evidence for the range of complex structures available for lithium aryloxide derivatives.

# Experimental

#### General procedures

Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system and a -40 °C freezer). Anhydrous hexanes and toluene were purchased from Aldrich, sparged with dinitrogen, and further dried by passage through a tower of silica followed by passage through a tower of Ridox (or Q-5) catalyst prior to use.<sup>39</sup> Anhydrous pentane, benzene, tetrahydrofuran and diethyl ether were purchased from Aldrich, sparged with dinitrogen, and passed through an Innovative Technologies SPS-PureSolv-400-4 apparatus. All organic solvents were tested with addition of sodium benzophenone prior to use to ensure absence of oxygen and water. Nitrogen gas was dried and deoxygenated by passage through a column containing activated molecular sieves and MnO.

Deuterated benzene was dried by refluxing with molten sodium/potassium alloy in a sealed vessel under partial pressure, then trap-to-trap distilled, and freeze-pump-thaw-degassed three times.  ${}^{1}H$ ,  ${}^{31}P$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{31}P{}^{1}H$ ,  ${}^{7}Li{}^{1}H$  NMR spectra were recorded on either a Bruker AMX-500 instrument operating at 500.13 MHz for <sup>1</sup>H spectra, a Bruker AVA-400 instrument operating at 400.13 MHz for 1H spectra, or a Bruker AVA-300 instrument operating at 300.13 MHz for <sup>1</sup>H spectra. <sup>1</sup>H NMR spectra were referenced to residual protons in deuterated solvent as follows: CDCl<sub>3</sub> ( $\delta$  7.24) and C<sub>6</sub>D<sub>5</sub>H ( $\delta$  7.15) with respect to tetramethylsilane at  $\delta$  0.0. <sup>31</sup>P NMR spectra were referenced to either external or internal P(OMe)<sub>3</sub> ( $\delta$  141.0 with respect to 85% H<sub>3</sub>PO<sub>4</sub> at  $\delta$  0.0). <sup>7</sup>Li{<sup>1</sup>H} NMR spectra were referenced to external LiCl (0.3 M solution in MeOH at  $\delta$  0.0). Elemental analyses were performed by Mr P. Borda and Mr M. Lakha and mass spectrometry (EI/MS on a Kratos MS 50 unless otherwise stated) by Mr M. Lapawa, all at the University of British Columbia, Department of Chemistry.

#### Materials

The compounds 2,4-di-*tert*-butylphenol and *n*-bromosuccinimide were purchased from Aldrich and used as received. Dichlorophenylphosphine (PhPCl<sub>2</sub>) and dichloroispropylphosphine (PrPCl<sub>2</sub>) were purchased from Strem Chemicals and used without further purification.

#### Synthesis of 2-bromo-4,6-di-tert-butylphenol<sup>10</sup>

*n*-Bromosuccinimide (18.21 g, 102.3 mmol) was added in portions to a solution of 2,4-di-*tert*-butylphenol (20.10 g, 97.4 mmol) in CH<sub>3</sub>CN (300 mL) at 0 °C with stirring. The bright yellow solution was then warmed slowly to ambient temperature and the resulting orange solution stirred for 12 h. The reaction was quenched with a saturated solution of sodium bisulfite (10 mL), and the resultant mixture was extracted into petroleum ether (4 × 50 mL) and quickly filtered through a small plug of silica gel. Evaporation of the solvent gave the product as a colourless solid. Yield 23.12 g (83%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.22 (s, 1H, Ph), 7.18 (S, 1H, Ph), 5.58 (s, 1H, OH), 1.31 (s, 9H, *o*-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.21 (s, 9H, *p*-PhC(CH<sub>3</sub>)<sub>3</sub>.

## Synthesis of (Ph[OPO]Li<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub> (1)

To a solution of the bromophenol (20.24 g, 70.96 mmol) in Et<sub>2</sub>O (150 mL) was added a 1.6 M solution of BuLi in hexanes (95.0 mL, 152.0 mmol) dropwise at -78 °C. The solution was warmed to ambient temperature. After stirring for 1 h the solution was cooled to -78 °C and PhPCl<sub>2</sub> (4.8 mL, 35.4 mmol) was added dropwise by syringe. The solution was allowed to warm to ambient temperature slowly, stirred for 8 h, and then the solvent was removed under vacuum. The residue was extracted with toluene (100 mL), the solution filtered through Celite and evaporated to dryness. The pale yellow residue was slurried in hexanes (50 mL), THF was added (10.30 g, 142 mmol) and the solution cooled to -40 °C. The resulting colourless microcrystals were collected, washed with minimal pentane and dried under vacuum. Yield: 16.73 g (70%). Calc. MW: 1349.58 g mol<sup>-1</sup>. X-Ray quality crystals of 1 containing three molecules of co-crystallized solvent were grown by slow evaporation of a saturated benzene solution. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 7.53 (m, 10H, Ph), 7.06 (m, 8H, Ph), 3.29 (16, 8H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 1.60 (s, 36H, o-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.30 (s, 36H, p-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.26 (s, 16H, THF-OCH<sub>2</sub>CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$ 

-37.56 (s). <sup>7</sup>Li{<sup>1</sup>H} NMR (194.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  -1.06 (br s). MS (EI) *m*/*z*, (%): 1060, (100) [M - (THF)<sub>4</sub>]<sup>+</sup>. Anal. calcd for C<sub>84</sub>H<sub>122</sub>Li<sub>4</sub>O<sub>8</sub>P<sub>2</sub>·2C<sub>6</sub>H<sub>6</sub>: C, 76.57; H, 8.97. Found: C, 76.33; H, 9.05%.

## Synthesis of (<sup>iPr</sup>[OPO]Li<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub> (2)

With the same procedure described above for **1**, the bromophenol (7.87 g, 27.59 mmol) was reacted with <sup>*i*</sup>PrPCl<sub>2</sub> (2.00 g, 13.80 mmol). Yield: 8.84 g (51%). Calc. MW: 1281.54 g mol<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.72–7.46 (m, 8H, Ph), 3.06 (s, 16H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 2.92 (m, 2H, P–CH(CH<sub>3</sub>)<sub>2</sub>), 1.64 (s, 36H, *o*-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.36 (s, 36H, *p*-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.39 (d, <sup>3</sup>J = 12.5 Hz, 12H, P–CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (s, 16H, THF-OCH<sub>2</sub>CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –0.72 (s, 2Li), –1.22 (s, 2Li). MS (EI) *m*/*z*, (%): 969, (100) [M – (THF)<sub>4</sub>]<sup>+</sup>. Elemental analysis was not obtained.

## Isolation of [Ph[OPO]Li<sub>2</sub>]<sub>2</sub>(ArOLi)<sub>2</sub> (3)

During the synthesis of **1**, prior to the addition of THF, a concentrated toluene solution was allowed to stand for 24 h during which time a colourless solid crystallized. Several X-ray quality crystals of **3** were removed and the remaining solid was isolated by filtration and dried under vacuum. Yield: 0.8 g (4.5%) based on bromophenol. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  7.63–7.03 (m, 24H, Ph), 1.46 (s, 18H, *o*-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.39 (s, 36H, *o*-PhC(CH<sub>3</sub>)<sub>3</sub>),

 $\begin{array}{l} \textbf{Table 5} \quad Crystallographic and structure refinement data for ($$^{Ph}[OPO]Li_2)_2(THF)_4$ (1), $$$ [$^{iPr}[OP(=O)O]Li_2(H_2O)]_2$ (2-O), $$$ [$^{Ph}[OPO]Li_2]_2(ArOLi)_2$ (3), and $$$ [$^{iPr}[OPO]Li_3Cl(ArOLi)](THF)_3$ (4) $$ \label{eq:constraint} \end{tabular}$ 

	$({}^{Ph}[OPO]Li_2)_2(THF)_4(1)$	$[^{iPr}[OP(=O)O]Li_2 (H_2O)]_2 (2-O)$	$[^{Ph}[OPO]Li_2(ArOLi)]_2 (3)$	$[^{iPr}[OPO]Li_{3}Cl(ArOLi)](THF)_{3}$ (4)
CCDC number	653592	653593	653594	653595
Formula	$C_{84}H_{122}Li_4O_8P_2 \cdot 3C_6H_6$	$C_{62}H_{98}Li_4O_8P_2 \cdot 4C_6H_6$	$C_{96}H_{132}Li_6O_6P_2 \cdot 3C_7H_8$	C <sub>57</sub> H <sub>92</sub> ClLi <sub>4</sub> O <sub>6</sub> P
Μ	1583.84	1369.50	1747.97	968.55
Colour, habit	Colourless, irregular	Colourless, block	Colourless, irregular	Colourless, rod
Crystal size/mm	$0.25 \times 0.15 \times 0.05$	$0.30 \times 0.20 \times 0.20$	$0.50 \times 0.20 \times 0.20$	$0.35 \times 0.25 \times 0.10$
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 1̄ (no. 2)	$P2_1/c$ (no. 14)	<i>P</i> 1 (no. 2)	<i>Pnma</i> (no. 62)
a/	13.4016(13)	10.2530(11)	12.9823(14)	17.7457(3)
b/Å	13.8466(17)	19.8120(16)	15.5897(15)	18.2033(4)
c/Å	27.718(3)	20.8950(19)	16.1226(16)	18.3850(3)
$a/^{\circ}$	77.004(5)	90	103.686(2)	90
β/°	80.257(4)	102.419(3)	101.950(1)	90
y/°	76.333(4)	90	111.550(2)	90
$V/Å^3$	4833.1(9)	4145.1(7)	2788.4(8)	5938.91(19)
Ζ	2	2	1	4
T∕°C	$-100 \pm 1$	$-100 \pm 1$	$-100 \pm 1$	$-100 \pm 1$
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.088	1.097	1.041	1.082
F(000)	1716	1480	946	2104
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	0.097	0.104	0.088	0.135
Transmission factors	0.8956-1.0000	0.8924-1.0000	0.8895-1.0000	0.9013-1.0000
$2\theta_{\rm max}/^{\circ}$	56.0	53.4	55.6	54.1
Total no. of reflns	72152	23709	25238	130426
No. of unique reflns	23119	8047	11572	6708
$R_{ m merge}$	0.0318	0.0421	0.0526	0.0462
No. reflns with $I \ge 2\sigma(I)$	17228	6000	8470	5011
No. of variables	1057	475	653	389
$R(F^2, \text{ all data})$	0.0765	0.1013	0.1102	0.0756
$R_w$ ( $F^2$ , all data)	0.1466	0.2212	0.2190	0.1670
$R(F, I > 2\sigma(I))$	0.0533	0.0765	0.0806	0.0526
$R_w(F, I > 2\sigma(I))$	0.1332	0.1980	0.1942	0.1490
GOF	1.035	1.060	1.047	1.037

1.34 (s, 36H, *p*-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.25 (s, 18H, *p*-PhC(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –31.87 (q, <sup>1</sup>J<sub>PLi</sub> = 107.1 Hz). <sup>7</sup>Li{<sup>1</sup>H} NMR (155.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –1.13 (d, <sup>1</sup>J<sub>PLi</sub> = 107.1 Hz, O–*Li*P–O), –1.34 (s), –1.84 (s). MS (EI) *m*/*z*, (%): 1485, (34) [M]<sup>+</sup>. Elemental analysis was not obtained.

### Isolation of [<sup>iPr</sup>[OPO]Li<sub>3</sub>Cl(ArOLi)](THF)<sub>3</sub> (4)

During the synthesis of **2**, slow evaporation of the hexanes filtrate yielded a colourless crystalline solid. Several X-ray quality crystals of **4** were removed and the remaining solid was collected and dried under vacuum. Yield: 0.5 g (5.6%) based on bromophenol. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.61–7.46 (m, 6H, Ph), 3.01 (s, THF-OCH<sub>2</sub>CH<sub>2</sub>), 2.96 (m, 2H, P–CH(CH<sub>3</sub>)<sub>2</sub>), 1.65 (s, 36H, *o*-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.53 (s, 18H, OPh-(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 1.45 (s, 36H, *p*-PhC(CH<sub>3</sub>)<sub>3</sub>), 1.37 (d, <sup>3</sup>J = 12.5 Hz, 12H, P–CH(CH<sub>3</sub>)<sub>2</sub>), 1.18 (s, THF-OCH<sub>2</sub>CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –36.76 (s). <sup>7</sup>Li{<sup>1</sup>H} NMR (194.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –0.72 (br s), –1.22 (s), –2.13 (br s), –2.45 (s). MS (EI) *m/z*, (%): 751, (55) [M – (THF)<sub>3</sub>]<sup>+</sup>. Elemental analysis was not obtained.

#### X-Ray crystallography

In all cases, suitable crystals were selected and mounted on a glass fibre using Paratone-N oil or an acceptable substitute and frozen to -100 °C.

Measurements for structures 1, 2-O, and 3 were made on a Rigaku/ADSC CCD area detector with graphite monochromated Mo-K $\alpha$  radiation. Data was processed using the d\*TREK<sup>40</sup> module, part of the CrystalClear software package, version 1.3.6 SP0,<sup>41</sup> and corrected for Lorentz and polarization effects and absorption. Neutral atom scattering factors for all non-hydrogen atoms were taken from Cromer and Waber.<sup>42</sup> Anomalous dispersion effects were included in  $F_{calc}$ .<sup>43</sup> Crystallographic and structure refinement data are given in Table 5.

Measurements for structure **4** were made on a Bruker X8 area detector with monochromated Mo-K $\alpha$  radiation. Data were processed and integrated using the Bruker SAINT software package<sup>44</sup> and corrected for absorption effects using the multi-scan technique (SADABS).<sup>45</sup> Neutral atom scattering factors for all non-hydrogen atoms were taken from Cromer and Waber.<sup>42</sup> Anomalous dispersion effects were included in  $F_{calc}$ ;<sup>43</sup> the values for  $\Delta f''$  and  $\Delta f'''$  were those of Creagh and McAuley.<sup>46</sup> The values for the mass attenuation coefficients are those of Creagh and Hubbell.<sup>47</sup>

All structures were solved by direct methods using the programs SIR97<sup>48</sup> or SIR2002.<sup>49</sup> All non-hydrogen atoms were refined anisotropically by least squares procedures on  $F^2$  using SHELXL-97.<sup>50</sup> Hydrogen atoms were included but not refined; their positional parameters were calculated with fixed C–H bond distances of 0.99 Å for sp<sup>2</sup> C, 0.98 Å for sp<sup>3</sup> C, and 0.95 Å for aromatic sp C, with  $U_{iso}$  set to 1.2 times the  $U_{eq}$  of the attached sp or sp<sup>2</sup> C and 1.5 times the  $U_{eq}$  values of the attached sp<sup>3</sup> C atom. Methyl hydrogen torsion angles were determined by electron density. Structure solution and refinements were conducted using the WinGX software package, version 1.64.05.<sup>51</sup> Structural illustrations were created using ORTEP-III for Windows.<sup>52</sup>

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#### References

- 1 B.-H. Huang, B.-T. Ko, T. Athar and C.-C. Lin, *Inorg. Chem.*, 2006, **45**, 7348–7356.
- 2 M. B. Hursthouse, M. A. Hossain, M. Motevalli, M. Sanganee and A. C. Sullivan, J. Organomet. Chem., 1999, 381, 293–297.
- N. A. Khanjin and F. M. Menger, J. Org. Chem., 1997, 62, 8923–8927.
   S. T. Liddle and W. Clegg, J. Chem. Soc., Dalton Trans., 2002, 3923–
- 3924.
  5 S. R. Boss, R. Haigh, D. J. Linton, P. Schooler, G. P. Shields and A. E. H. Wheatley, *Dalton Trans.*, 2003, 1001–1008.
- 6 T. J. Boyle, D. M. Pedrotty, T. M. Alam, S. C. Vick and M. A. Rodriguez, *Inorg. Chem.*, 2000, **39**, 5133–5146.
- 7 D. J. MacDougall, B. C. Noll, A. R. Kennedy and K. W. Henderson, Dalton Trans., 2006, 1875–1884.
- 8 E. M. Arnett and K. D. Moe, J. Am. Chem. Soc., 1991, 113, 7288-7293.
- 9 H. C. Aspinall, J. F. Bickley, J. L. M. Dwyer, N. Greeves and A. Steiner, *Angew. Chem., Int. Ed.*, 2000, **39**, 2858–2860.
- 10 R. Siefert, T. Weyermuller and P. Chaudhuri, J. Chem. Soc., Dalton Trans., 2000, 4656–4663.
- 11 Y.-N. Chang and L.-C. Liang, Inorg. Chim. Acta, 2006, 360, 136-142.
- 12 E. D. Gueneau, K. M. Fromm and H. Goesmann, *Chem.-Eur. J.*, 2003, 9, 509–514.
- 13 A. Oskarsson and I. Ymen, Acta Crystallogr., Sect. C, 1984, 40, 30-32.
- 14 I. Ymen, Acta Crystallogr., Sect. C, 1984, 40, 241-243.
- 15 W. Clegg, R. P. Davies, L. Dunbar, N. Feeder, S. T. Liddle, R. E. Mulvey, R. Snaith and A. E. H. Wheatley, *Chem. Commun.*, 1999, 1401–1403.
- 16 T. Chivers, M. Krahn, G. Schatte and M. Parvez, *Inorg. Chem.*, 2003, 42, 3994–4005.
- 17 T. K. Payne, T. Weyhermueller, L. D. Slep, F. Neese, E. Bill, E. Bothe, K. Wieghardt and P. Chaudhuri, *Inorg. Chem.*, 2004, 43, 7324–7338.
- 18 H. Bock, E. Heigel and N. Nagel, Z. Naturforsch., B: Chem. Sci., 2000, 55, 773–784.
- 19 B. W. F. Gordon and M. J. Scott, Inorg. Chim. Acta, 2000, 297, 206-216.
- 20 H. H. Karsch, K. Zellner, P. Mikulcik, J. Lachmann and G. Muller, Organometallics, 1990, 9, 190–194.
- 21 J. J. Ellison and P. P. Power, Inorg. Chem., 1994, 33, 4231-4234.
- 22 J. S. Vilardo, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1998, 17, 769–771.
- 23 M. B. Dinger and M. J. Scott, Inorg. Chem., 2000, 39, 1238-1254.
- 24 B. Goldfuss, P. v. R. Schleyer and F. Hempel, J. Am. Chem. Soc., 1996, 118, 12183–12189.
- 25 G. D. Smith, P. E. Fanwick and I. P. Rothwell, *Inorg. Chem.*, 1989, 28, 618–620.
- 26 W. Clegg, E. Lamb, S. T. Liddle, R. Snaith and A. E. H. Wheatley, J. Organomet. Chem., 1999, 573, 305–312.
- 27 B.-T. Ko and C.-C. Lin, J. Am. Chem. Soc., 2001, 123, 7973-7977.
- 28 K. Izod, P. O'Shaughnessy and W. Clegg, Organometallics, 2002, 21, 641–646.
- 29 M. D. Fryzuk, J. B. Love and S. J. Rettig, Chem. Commun., 1996, 2783–2784.
- 30 I. J. Colquhoun, H. C. E. McFarlane and W. McFarlane, J. Chem. Soc., Chem. Commun., 1982, 220–221.
- 31 P. B. Hitchcock, M. F. Lappert, P. P. Power and S. J. Smith, J. Chem. Soc., Chem. Commun., 1984, 1669–1670.
- 32 D. Barr, M. J. Doyle, R. E. Mulvey, P. R. Raithby, D. Reed, R. Snaith and D. S. Wright, J. Chem. Soc., Chem. Commun., 1989, 318–319.
- 33 K. Hyvarinen, M. Klinga and M. Leskela, *Polyhedron*, 1996, 15, 2171– 2177.
- 34 J. Pauls and B. Neumuller, Z. Anorg. Allg. Chem., 2000, 626, 270-279.
- 35 E. Ihara, S. Yoshioka, M. Furo, K. Katsura, H. Yasuda, S. Mohri, N. Kanehisa and Y. Kai, *Organometallics*, 2001, 20, 1752–1761.
- 36 G. Boche, M. Schimeczek, J. Cioslowski and P. Piskorz, *Eur. J. Org. Chem.*, 1998, 1851–1860.
- 37 M. Muller, M. Bronstrup, O. Knopff, V. Schulze and R. W. Hoffmann, Organometallics, 2003, 22, 2931–2937.

- 38 W. J. Evans, J. L. Shreeve, R. N. R. Broomhall-Dillard and J. W. Ziller, J. Organomet. Chem., 1995, 501, 7–11.
- 39 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, Organometallics, 1996, 15, 1518–1520.
- 40 J. W. Pflugrath, Acta Crystallogr., Sect. D, 1999, 55, 1718–1725.
- 41 CrystalClear: An Integrated Program for the Collection and Processing of Area Detector Data, Rigaku Corporation, Tokyo, 1997–2004.
- 42 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, UK, 1974.
- 43 J. A. Ibers and W. C. Hamilton, Acta Crystallogr., 1964, 17, 781-782.
- 44 Saint Software User Guide, Version 7.03A, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997–2003.
- 45 G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

- 46 D. C. Creagh and W. J. McAuley, in *International Tables for Crystallog-raphy*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, vol. C, Table 4.2.6.8, pp. 219–222.
- 47 D. C. Creagh and J. H. Hubbell, in *International Tables for Crystallog-raphy*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, vol. C, Table 4.2.4.3, pp. 200–206.
- 48 A. Altomare, M. C. Burla, G. Cammali, M. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and A. Spagna, J. Appl. Crystallogr., 1999, 32, 115–119.
- 49 M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, G. Polidori and R. Spagna, J. Appl. Crystallogr., 2003, 36, 1103.
- 50 G. M. Sheldrick, SHELX97: Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1998.
- 51 L. J. Farrugia, J. Appl. Crystallogr., 1999, 32, 837-838.
- 52 L. J. Farrugia, J. Appl. Crystallogr., 1997, 30, 565.