## Electronic Supplementary Information

## Synthesis of 1,2-Diphospholides Using a Main Group 'Superbase'

Lily S. H. Dixon, ${ }^{\dagger}$ Schirin Hanf, ${ }^{\dagger, \ddagger}$ Jessica E. Waters, ${ }^{\dagger}$ Andrew D. Bond ${ }^{\dagger}$ and Dominic S. Wright ${ }^{\dagger}, *$<br>${ }^{\dagger}$ Chemistry Department, Cambridge University, Lensfield Road, Cambridge CB2 1EW (U.K.).<br>${ }^{\dagger}$ Fäkultät für Chemie und Mineralogie, University of Leipzig, Johannisallee 29, D-04103 Leipzig, Germany.

## General Experimental Details.

NMR spectra were recorded at $25^{\circ} \mathrm{C}$ on a Bruker 500 MHz Spectrometer ( ${ }^{1} \mathrm{H}$ at $500.1 \mathrm{MHz},{ }^{31} \mathrm{P} 202.5 \mathrm{MHz},{ }^{13} \mathrm{C} 125.7$ MHz ) or a Bruker 400 MHz AVIII HD Smart Probe spectrometer ( ${ }^{1} \mathrm{H}$ at $400.1 \mathrm{MHz},{ }^{31} \mathrm{P} 162.0 \mathrm{MHz},{ }^{13} \mathrm{C} 100.6 \mathrm{MHz}$ ). Chemical shifts ( $\delta, \mathrm{ppm}$ ) are given relative to residual solvent signals for ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ and to external $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ in $\mathrm{D}_{2} \mathrm{O}$ for ${ }^{31} \mathrm{P}$, with coupling constants reported in Hz . The multiplicities of NMR resonances are denoted by the abbreviations $s$ (singlet), d (doublet), t (triplet) q (quarter), m (multiplet) and combinations thereof for highly coupled systems.

Single crystal X-ray diffraction was carried out at $180(2) \mathrm{K}$ on a Bruker D8-Quest PHOTON-100 diffractometer equipped with an Incoatec $\mathrm{I} \mu \mathrm{S} \mathrm{Cu}$ microsource ( $\lambda_{\text {ave }}=1.5418 \AA$ ). Structures were solved using SHELXT and refined using full-matrix least squares on $\mathrm{F}^{2}$ using SHELXL (ver.2018/1).

Mass spectrometry Low-resolution electrospray mass spectrometry (LR-ESI-MS) was undertaken on a Micromass Quattro LC mass spectrometer (cone voltage 10.30 eV ; desolvation temperature 313 K ; ionisation temperature 313 K ) infused from a Harvard syringe pump at a rate of $10 \mu \mathrm{Lmin}-1$. High-resolution electrospray ionisation mass spectrometry (HR-ESI-MS) was performed on a ThermoFinnigan Orbitrap Classic mass spectrometer incorporating a linear ion trap and an orbit trap analyser. Data collection was conducted by Felix Rizzuto whose assistance is greatly appreciated.

Computational details Geometry optimisations of the diphospholides 1-5 and the indenyl derivative were carried out using the Gaussian-Programme package. ${ }^{6}$ The optimised structures were obtained employing the B3LYP ${ }^{7}$ functional in conjunction with a cc-pVTZ basis set. ${ }^{8}$ Toluene solvent effects were considered during all calculations using a polarisable continuum model (PCM, SMD) ${ }^{9}$ implemented in the Gaussian 09 suite. 16 Frequency calculations of the optimised structures, to proof the absence of imaginary frequencies were carried out. HOMO-LUMO energies and gaps were obtained from single-point calculations, employing the cc-PVQZ basis set. ${ }^{8}$ Wiberg bond indices and natural charges were calculated, using NBO Version $3^{10}$ and molecular orbitals were visualised using the programme GaussView 5.0.8. ${ }^{11}$


Figure $\mathrm{S} 1:{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\mathrm{K}($ PMDETA $) \mathbf{1}$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure $\mathrm{S} 2:{ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{K}($ PMDETA $) \mathbf{1}$ in $\mathrm{d}_{8}$-THF.


Figure $\mathrm{S} 3:{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][2]$ in $\mathrm{d}_{8}$-THF.


Figure $\mathrm{S} 4:{ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][2]$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure $\mathrm{S} 5:{ }^{13} \mathrm{C}$ NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][2]$ in $\mathrm{d}_{8}$-THF.


Figure S6: ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][2]$ in $\mathrm{d}_{8}-\mathrm{THF}$.

| Chemical shift (ppm) | Assignment | Coupling constants | Integration |
| :--- | :--- | :--- | :--- |
| $7.90(\mathrm{~d})$ | Ha | ${ }^{2} J_{\mathrm{PH}}=38 \mathrm{~Hz}$ | 1 H |
| $7.88(\mathrm{t})$ | Hb | ${ }^{3} J_{\mathrm{HHC}}=7.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{PH}}=7.0 \mathrm{~Hz}$ | 1 H |
| $7.57(\mathrm{~d})$ | He | $J_{\mathrm{HHd}}=8.0$ | 1 H |
| $6.64(\mathrm{dd})$ | ${ }^{3} J_{\mathrm{HHe}}=8.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HHc}}=6.6 \mathrm{~Hz}$ | 1 H |  |
| $6.48(\mathrm{dd})$ | ${ }^{3} J_{\mathrm{HHb}}=7.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HHd}}=6.6 \mathrm{~Hz}$ | 3 H |  |
| $2.29(\mathrm{~s})$ | $\mathrm{nd} / \mathrm{a}$ | 8 H |  |
| $2.15(\mathrm{~s})$ | Hc | $\mathrm{n} / \mathrm{a}$ | 36 H |

Table S1: ${ }^{1} \mathrm{H}$ NMR assignments for $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][\mathbf{2}]$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S7: Proton labels for NMR assignment in Table S1.


Figure $\mathrm{SB}:{ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ HSQC NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][2]$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S9: ${ }^{31} \mathrm{P}$ NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S10: ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}$-THF (excess TMEDA present).


Figure $\mathrm{S} 11:{ }^{13} \mathrm{C}$ NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}$-THF.


Figure S12: COSY NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}$-THF.


Figure S13: COSY NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}$-THF, aromatic region.

| Chemical shift (ppm) | Assignment | Coupling constants | Integration |
| :--- | :--- | :--- | :--- |
| $7.70(\mathrm{~d})$ | Ha | ${ }^{2} J_{\mathrm{PH}}=39 \mathrm{~Hz}$ | 1 H |
| $7.69(\mathrm{dd})$ | Hb | ${ }^{3} J_{\mathrm{HHc}}=8.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{PH}}=5.9 \mathrm{~Hz}$ | 1 H |
| $7.06(\mathrm{~s})$ | Hd | $\mathrm{n} / \mathrm{a}$ | 1 H |
| $6.25(\mathrm{~d})$ | $\mathrm{Hc}_{\mathrm{HHb}}=8.5 \mathrm{~Hz}$ | 1 H |  |
| $3.71(\mathrm{~s})$ | $\mathrm{n} / \mathrm{a}$ | 3 H |  |
| $2.29(\mathrm{~s})$ | OCH | 8 H |  |
| $2.15(\mathrm{~s})$ | $\mathrm{CH}_{2}$ TMEDA | $\mathrm{n} / \mathrm{a}$ | 36 H |

Table S2: ${ }^{1} \mathrm{H}$ NMR assignments for $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S14: Proton labels for NMR assignment in Table S2.

Figure S15: HSQC NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}$-THF.


Figure S16: HSQC NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}$-THF, aromatic region.


Figure S17: HMBC NMR spectrum of $\left[\operatorname{Li}(\text { TMEDA })_{2}\right][3]$ in $d_{8}$-THF.


Figure S18: HMBC NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][3]$ in $\mathrm{d}_{8}$-THF, aromatic region.


Figure $\mathrm{S} 19:{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\left[\mathrm{Li}(\text { TMEDA })_{2}\right][4]$ in $\mathrm{d}_{8}$-THF


Figure XXX : ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{Li}(\text { TMEDA })_{2}\right][4]$ in $\mathrm{d}_{8}$-THF


Figure S20 : ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][4]$ in $\mathrm{d}_{8}$-THF


Figure 521 : COSY NMR spectrum of $\left[\operatorname{Li}(\mathrm{TMEDA})_{2}\right][4]$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S 22 : COSY NMR spectrum of $\left[\operatorname{Li}(\text { TMEDA })_{2}\right][4]$ in $d_{8}$-THF, aromatic region


Figure S23: HSQC NMR spectrum of $\left[\operatorname{Li}(\text { TMEDA })_{2}\right][4]$ in $\mathrm{d}_{8}$-THF.


Figure S24 : HSQC NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][4]$ in $\mathrm{d}_{8}$-THF, aromatic region.


Figure S 25 : HMBC NMR spectrum of $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right][4]$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S26 : HMBC NMR spectrum of $\left[\operatorname{Li}(\text { TMEDA })_{2}\right][4]$ in $d_{8}$-THF, aromatic region.


Figure S27: ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right]$ salts of 5 (purple) and 6 (green) in $\mathrm{d}_{8}$-THF.


Figure S28: ${ }^{1} \mathrm{H}$ NMR spectrum of the $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right]$ salts of 5 (purple) and 6 (green) in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure $\mathrm{S} 29:{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right]$ salts of 5 (purple) and 6 (green) in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S30 : COSY NMR spectrum of the $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right]$ salts of $\mathbf{5}$ and $\mathbf{6}$ in $\mathrm{d}_{8}$-THF.


Figure S31: COSY NMR spectrum of the $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right]$ salts of 5 and 6 in $\mathrm{d}_{8}$-THF, aromatic region.


Figure S32: HSQC NMR spectrum of the $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right]$ salts of 5 and 6 in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S 33 : HSQC NMR spectrum of the $\left[\mathrm{Li}(\mathrm{TMEDA})_{2}\right]$ salts of 5 and 6 in $\mathrm{d}_{8}-\mathrm{THF}$, aromatic region.


Figure S34: HMBC NMR spectrum of the $\left[\operatorname{Li}(T M E D A)_{2}\right]$ salts of $\mathbf{5}$ and $\mathbf{6}$ in $\mathrm{d}_{8}-\mathrm{THF}$.


Figure S35: HMBC NMR spectrum of the $\left[\operatorname{Li}(T M E D A)_{2}\right]$ salts of 5 and 6 in $d_{8}-$ THF, aromatic region.

## 2. Computational Details

Geometry optimisation of the diphospholides 1-5 and the indenyl anion were carried out using the Gaussian-Programme package. ${ }^{[1]}$ The optimised structures were obtained employing the B3LYP ${ }^{[2]}$ functional in conjunction with a cc-pVTZ ${ }^{[3]}$ basis set. Toluene solvent effects were considered during all calculations using a polarisable continuum model (PCM, SMD ${ }^{[4]}$ ) implemented in the Gaussian 09 suite. Frequency calculations of the optimised structures, to prove the absence of imaginary frequencies, and natural bond orbital analyses were carried out. HOMO-LUMO energies and gaps were obtained from single-point calculations, employing the cc-PVQZ ${ }^{[3]}$ basis set. Molecular orbitals were visualised using the programme GaussView 5.0.8. ${ }^{[5]}$



Figure S36: Numbering Scheme.

1.33

1
P1-P2-C1 $94.5^{\circ}$
P2-C1-C2 $119{ }^{\circ}$ P1-C3-C2 $115.8^{\circ}$


4

```
P1-P2-C1 96.7 
```

P1-P2-C1 96.7
P2-C1-C2 116.5
P2-C1-C2 116.5
P1-C3-C2 117.1

```
P1-C3-C2 117.1 
```


1.33

2
P1-P2-C1 $95.6^{\circ}$
P2-C1-C2 $116.7^{\circ}$
P1-C3-C2 $114.7^{\circ}$


5

$$
\begin{aligned}
& \text { P1-P2-C1 } 94.9^{\circ} \\
& \text { P2-C1-C2 } 118.0^{\circ} \\
& \text { P1-C3-C2 } 116.1^{\circ}
\end{aligned}
$$

$1.75 \AA$

1.39 A
1.33

3
P1-P2-C1 $95.6^{\circ}$
P2-C1-C2 $116.7^{\circ}$
P1-C3-C2 $114.7^{\circ}$

indenyl
C1-C2-C3 $110.8^{\circ}$
C2-C3-C4 $107.8^{\circ}$
C1-C9-C4 $109.0^{\circ}$

Figure S37: Selected bond lengths and angles from geometry optimisations and Wiberg bond orders in italics.

| Compound | NPA charges P1/C1 | NPA charges P2/C2 |
| :--- | :--- | :--- |
| Indenyl | -0.38 | -0.26 |
| $\mathbf{1}$ | -0.05 | 0.11 |
| $\mathbf{2}$ | -0.04 | 0.11 |
| $\mathbf{3}$ | -0.05 | 0.11 |
| $\mathbf{4}$ | -0.04 | 0.11 |
| $\mathbf{5}$ | -0.01 | 0.10 |

Table S3: Natural charges on P1 and P2 in the benzodiphospholide anions 1-5 and on C1 and C2 in the indenyl derivative.

| Compound | Hartree | eV | $\mathrm{kJ} / \mathrm{mol}$ |
| :--- | :--- | :--- | :--- |
| Indenyl | 0.15649 | 4.26 | 410.86 |
| $\mathbf{1}$ | 0.13740 | 3.74 | 360.74 |
| $\mathbf{2}$ | 0.13765 | 3.75 | 361.40 |
| $\mathbf{3}$ | 0.13187 | 3.59 | 346.22 |
| $\mathbf{4}$ | 0.13308 | 3.62 | 349.40 |
| $\mathbf{5}$ | 0.13841 | 3.77 | 363.40 |

Table S4: HOMO-LUMO energy differences obtained from single-point calculations.
[1] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
[2] Becke, A. D. J. Chem. Phys., 1993, 98, 5648; Lee, R. P. W.C.; Wang, W.; Parr, R. G. Phys. Rev., 1998, B37, 785; Vosko, S. H.; Wilk, L.; Nusair, M. Can. J. Phys., 1980, 58, 1200; Stephens, P. J. F.; Devlin, J.; Chabalowski, C. F.; Frisch, M. J. J. Phys. Chem., 1994, 98, 11623.
[3] Dunning, Jr. T.H.; J. Chem. Phys., 1989, 90, 1007; Woon, D.E.; Dunning, Jr. T.H. J. Chem. Phys., 1993, 98, 1358.
[4] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. J. Phys. Chem. B 2009, 113, 6378.
[5] GaussView, Version 5, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission, KS, 2009.

## 3. X-Ray Crystallography

$\left.[\text { Li(TMEDA) })_{2}\right][\mathbf{2}]$
The structure contains two crystallographically independent benzo-1,2-diphospholide anions on general equivalent positions, two independent $\mathrm{Li}(\text { TMEDA })_{2}$ cations on 2-fold rotation axes and one Li(TMEDA)2 cation on a general position. Both -1,2-diphospholide anions display disorder by which the molecule is flipped over. This necessitates additional atomic sites for P1, P2 and C1 (or the equivalent labels). In each case, the site occupancy factors were refined for the two molecular components as a free variable, constrained to sum to unity. The refined values are 0.912(3):0.088(3) and 0.897(3):0.103(3) for the two independent molecules, respectively. In both cases, all non-H atoms were restrained to lie in a common plane (FLAT restraint) and the $2 \times P$ and $1 \times C$ atom of the minority component were refined with a common isotropic displacement parameter. A SAME restraint was also applied to tie the geometry of the minority component to that of the majority component. In the tables below, only the geometry of the majority component is listed.

The two $\mathrm{Li}(\text { TMEDA })_{2}$ cations on the 2 -fold rotation axes were refined routinely, but the cation on the general position was found to be disordered over two orientations. The two components could be resolved and all non-H atoms could be refined freely with anisotropic ADPs. The site occupancy factors were refined for the two molecular components as a free variable, constrained to sum to unity. The refined value is $0.643(3): 0.357(3)$.
$\left[\mathrm{Li}(12-\mathrm{crown}-4)_{2}\right][4]$
The diffraction pattern for this crystal clearly had contributions from multiple domains. Indexing using CELL_NOW suggested a second domain related to the first domain by a 2 -fold rotation around the real $a$-axis. However, integration and refinement as a two-component twin did not improve the refinement. The published refinement is therefore based on a standard single-component integration and refinement. The data were relatively weak at higher angle (with I/ $\sigma(I)$ falling below 2.0 by ca $0.95 \AA$, so the data were truncated at $0.95 \AA$ for the final refinement. The $R$-factors are high, but the structure is clear.

The displacement ellipsoids of the 12-crown-4 molecules are significantly elongated. This may reflect a systematic problem with the data and/or some degree of disorder of the crown molecules. Refinement of the crowns with one set of atom sites and distorted ellipsoids was considered to be preferable to a split-atom model. All of the O atoms have ADPs elongated along the $\mathrm{C}-\mathrm{O}$ bond, which provides numerous anomalous indicators for the Hirshfeld rigid-bond tests applied within checkCIF. This clearly reflects some deficiency of the data and/or model, but the structure remains clear.

Table S5. Crystallographic details for $\left[\operatorname{Li}(\text { TMEDA })_{2}\right][2]$ and $\left[\mathrm{Li}(12-c r o w n-4)_{2}\right][4]$

|  | [Li(TMEDA) ${ }_{2}$ ][2] | [Li(12-crown-4) ${ }_{2}$ ][4] |
| :---: | :---: | :---: |
| CCDC number | 1852045 | 1852044 |
| Cambridge data number | DW_B1_0030 | DW_B2_0111 |
| Chemical formula | $\mathrm{C}_{19} \mathrm{H}_{37} \mathrm{LiN}_{4} \mathrm{P}_{2}$ | $\mathrm{C}_{24} \mathrm{H}_{39} \mathrm{LiO}_{8} \mathrm{P}_{2}$ |
| Formula weight | 390.40 | 524.43 |
| Temperature / K | 180(2) | 180(2) |
| Crystal system | monoclinic | triclinic |
| Space group | C2/c | P-1 |
| $a /$ angstrom | 32.3894(7) | 8.4645(4) |
| $b /$ angstrom | 17.6315(4) | 12.2344(6) |
| c / angstrom | 16.9036(4) | 14.0658(7) |
| alpha / degrees | 90 | 95.494(3) |
| beta / degrees | 103.1995(11) | 95.567(4) |
| gamma / degrees | 90 | 110.021(3) |
| Unit-cell volume / angstrom ${ }^{3}$ | 9398.2(4) | 1349.13(12) |
| Z | 16 | 2 |
| Calc. density / g cm ${ }^{-3}$ | 1.104 | 1.291 |
| F(000) | 3392 | 560 |
| Radiation type | CuK $\alpha$ | CuK $\alpha$ |
| Absorption coefficient / mm ${ }^{-1}$ | 1.735 | 1.835 |
| Crystal size / mm ${ }^{3}$ | $0.260 \times 0.100 \times 0.050$ | $0.300 \times 0.100 \times 0.050$ |
| 2-Theta range / degrees | 5.60-140.59 | 6.37-108.47 |
| Completeness to max 2-theta | 0.979 | 0.988 |
| No. of reflections measured | 35584 | 16339 |
| No. of independent reflections | 8792 | 3241 |
| $\mathrm{R}_{\text {int }}$ | 0.0461 | 0.0820 |
| No. parameters / restraints | 601 / 38 | 317 / 96 |
| Final R1 values ( $1>2 \sigma(1)$ ) | 0.0723 | 0.1273 |
| Final wR( $F^{2}$ ) values (all data) | 0.1226 | 0.1590 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.022 | 1.040 |
| Largest difference peak \& hole /e angstrom ${ }^{-3}$ | 0.784, -0.366 | 1.189, -0.372 |

Table S6. Bond distances ( A ) and angles ( ${ }^{\circ}$ ) for the benzo-1,2-diphospholide anions in the crystal structures of 1 (Dixon et al., Eur. J. Inorg. Chem., 2015, 2041), [Li(TMEDA) ${ }_{2}$ ][2] and [Li(12-crown4) ${ }_{2}$ [4]


|  | 1 (Mol 1) | 1 (Mol 2) | 1 (Mol 3) | 2 (Mol 1) | 2 (Mol 2) | 4 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| P1-P2 | 2.121(3) | 2.104(3) | $2.133(5)$ | 2.1029(15) | 2.1082(16) | 2.111(4) |
| P1-C3 | 1.752(7) | 1.872(5) | 1.751(9) | 1.800(3) | 1.776(3) | 1.791(9) |
| P2-C1 | 1.699(9) | 1.722(11) | 1.688(13) | 1.711(4) | 1.726(4) | 1.754(10) |
| C1-C2 | 1.420(10) | 1.407(11) | 1.425(13) | 1.390(5) | 1.395(5) | 1.430(13) |
| C2-C3 | 1.435(10) | 1.390* | 1.421(12) | 1.423(4) | 1.413(4) | 1.411(13) |
| C3-C4 | 1.420(10) | 1.390* | 1.423(14) | 1.395(4) | 1.407(4) | 1.407(14) |
| C4-C5 | 1.377(11) | 1.390* | 1.368(13) | 1.362(5) | 1.367(4) | 1.380(15) |
| C5-C6 | 1.418(11) | 1.390* | 1.435(14) | 1.386(5) | 1.398(5) | 1.419(16) |
| C6-C7 | 1.357(11) | 1.390* | 1.369(13) | 1.359(5) | 1.356(5) | 1.354(14) |
| C7-C2 | 1.401(10) | 1.390* | 1.419(13) | 1.458(4) | 1.434(4) | 1.429(13) |
| P1-P2-C1 | 95.1(3) | 98.7(4) | 94.6(4) | 96.99(14) | 95.59(14) | 98.0(4) |
| P2-C1-C2 | 118.6(6) | 117.1(8) | 118.9(7) | 116.1(3) | 116.6(3) | 114.1(8) |
| C1-C2-C3 | 115.5(7) | 116.2(6) | 115.9(9) | 119.2(3) | 118.6(3) | 117.7(8) |
| C2-C3-P1 | 116.2(6) | 117.9(3) | 115.9(9) | 114.1(2) | 114.7(2) | 117.7(7) |
| C3-P1-P2 | 94.6(3) | 90.1(2) | 94.7(4) | 93.58(11) | 94.45(12) | 92.4(3) |
| $\mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 7$ | 125.6(8) | 123.8(6) | 126.3(11) | 123.9(3) | 123.5(3) | 122.8(10) |
| C2-C7-C6 | 122.4(8) | 120* | 123.1(10) | 120.3(3) | 121.4(3) | 119.6(11) |
| C7-C6-C5 | 118.3(8) | 120* | 117.6(9) | 120.8(3) | 120.2(3) | 120.7(10) |
| C6-C5-C4 | 122.5(8) | 120* | 121.9(10) | 121.0(3) | 120.2(3) | 120.9(11) |
| C5-C4-C3 | 118.9(7) | 120* | 119.7(10) | 120.8(3) | 121.3(3) | 119.1(10) |
| C4-C3-C2 | 119.0(7) | 120* | 119.9(9) | 120.2(3) | 119.1(3) | 120.1(8) |
| C4-C3-P1 | 124.8(6) | 122.1(3) | 124.2(9) | 125.8(2) | 126.1(3) | 122.1(8) |

[^0]
[^0]:    * Constrained during refinement

