

# An N,P-disubstituted-2-aminophosphaalkene and lithium and potassium complexes of the deprotonated “phosphaamidinate” anion

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## Supporting Information

### Experimental

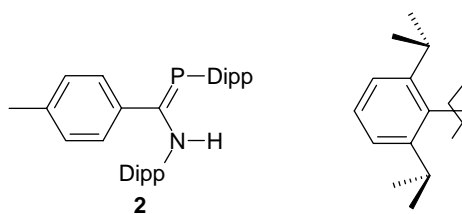
#### General Procedures

All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity dinitrogen in flame-dried glassware. Molybdenum carbonyl (Strem) was used as received. *n*-Butyl lithium (1.6 M in hexane) and potassium bis(trimethylsilyl)amide (0.5M in toluene) were purchased from Aldrich. Solvents were reagent grade, or better, and used as received (methanol, ethanol, hexanes), distilled over LiAlH<sub>4</sub> (*n*-heptane) or distilled over sodium (xylenes). Tetrahydrofuran (THF) and hexane were dried over sodium, freshly distilled from sodium benzophenone ketyl and freeze-thaw degassed prior to use. Infrared spectra were recorded on Bomem MB-100 or Nicolet Avatar 360 and Nexus spectrometers as KBr pellets, as Nujol mulls using sodium chloride plates or in a 0.1 mm NaCl solution cavity cell. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a Bruker AC250/Tecmag Macspect spectrometer operating at 250.13, 101.26 and 62.90 MHz, respectively, a Bruker DPX 300 spectrometer at 300.13, and 75.46 MHz or a Varian Inova 500 operating at 499.3 (<sup>1</sup>H), 202.1 (<sup>31</sup>P), 125.6 (<sup>13</sup>C), and 50.6 (<sup>15</sup>N) MHz. <sup>1</sup>H NMR signals were referenced to tetramethylsilane or THF, <sup>13</sup>C to CDCl<sub>3</sub> or THF <sup>13</sup>P to an external H<sub>3</sub>PO<sub>4</sub> sample and <sup>15</sup>N NMR to an external CH<sub>3</sub>NO<sub>2</sub> sample.

Mass spectra were undertaken in the Department of Chemistry, University of Alberta. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Elemental analyses were run by MHW Laboratories, Phoenix, Az or at the University of Otago, P.O. Box 56, Dunedin, New Zealand..

DippN=C(*p*CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)Cl was prepared as per reference 8a, and DippPH<sub>2</sub> as per reference 9.

#### Preparation of 1,3-bis(2,6-diisopropylphenyl)-2-ptolyl-1-phosphapropene 2



Dipp = 2,6-diisopropylphenyl

38 mL of dry xylenes were freeze-thaw degassed (5×) in a 250 mL side arm flask. Then 5.00 g (15.9 mmol) of DippN=C(*p*CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)Cl and 3.10 g (15.9 mmol) DippPH<sub>2</sub> were added. The flask was fitted with a reflux condenser and heated in a 200-215°C oil bath. The reaction was monitored by <sup>1</sup>H NMR over four days, after which time all starting materials were consumed. Xylenes were removed under high vacuum. The remaining orange solid was dissolved in a minimum of hot 99% ethanol and cooled to –30°C. After four days bright yellow crystals were filtered off and the filtrate was reduced to half the original volume. After harvesting a second crop, a total of 3.06g (6.49 mmol) of crystals were obtained. Analytical crystals were obtained by recrystallization from hot methanol. Yield: 41% Melting Point: 115-119°C.

Elemental Analysis: Calc. for C<sub>32</sub>H<sub>42</sub>NP: C, 81.49; H, 8.98; N, 2.97. Found: C, 81.57; H, 8.48; N, 3.02%.

<sup>1</sup>H NMR (major isomer, CDCl<sub>3</sub>): δ 0.81 (d, J(H-H) 6.7 Hz, 6H), 0.89 (d, J(H-H) 6.7 Hz, 6H), 1.26 (d, J(H-H) 6.7 Hz, 6H), 1.35 (d, J(H-H) 6.9 Hz, 6H), 2.22 (s, 3H), 3.00 (sept., J(H-H) 6.7 Hz, 2H), 3.84 (doublet of septets, J(H-H) 6.8 Hz, <sup>4</sup>J(P-H) 3.4 Hz, 2H), 6.23 (d, J(P-H) 2.4 Hz, 1H), 6.93-7.35 (mult., 10H).

$^{13}\text{C}$  NMR (major isomer,  $\text{CDCl}_3$ ):  $\delta$  21.12 (s, *p*- $\text{CH}_3$ - $\text{C}_6\text{H}_4$ ), 22.30 (s, amino-Dipp- $^i\text{Pr}$ - $\text{CH}_3$ ), 23.05 (s, phosphino-Dipp- $^i\text{Pr}$ - $\text{CH}_3$ ), 25.17 (s, amino-Dipp- $^i\text{Pr}$ - $\text{CH}_3$ ), 26.01 (d,  $^4\text{J}(\text{P-C})$  2.0 Hz, phosphine-Dipp- $^i\text{Pr}$ - $\text{CH}_3$ ), 28.23 (s, amino-Dipp- $^i\text{Pr}$ -CH), 33.03 (d,  $^3\text{J}(\text{P-C})$  7.5 Hz, phosphino-Dipp- $^i\text{Pr}$ -CH), 123.00 (s, phosphino-Dipp-*m*-C), 123.43 (s, amino-Dipp-*m*-C), 126.80 (s, amino-Dipp-*p*-C), 127.24 (d,  $^3\text{J}(\text{P-C})$  15.7 Hz, *o*- $\text{C-C}_6\text{H}_4$ ), 128.35 (s, *m*- $\text{C-C}_6\text{H}_4$ ), 129.50 (s, phosphino-Dipp-*p*-C), 134.38 (d,  $^5\text{J}(\text{P-C})$  29.5, *p*- $\text{C-C}_6\text{H}_4$ ), 135.14 (s, *ipso*- $\text{C-C}_6\text{H}_4$ ), 138.31 (d,  $^3\text{J}(\text{P-C})$  3.0 Hz, *ipso*- $\text{C-N}$ ), 144.53 (d,  $^4\text{J}(\text{P-C})$  2.1 Hz, amino-Dip-*o*-C), 153.79 (d,  $^2\text{J}(\text{P-C})$  4.8 Hz, phosphino-Dipp-*o*-C), 186.21 (d,  $^1\text{J}(\text{P-C})$  61.4 Hz,  $\text{P=C}$ )  
 $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  53.60 (~75%, s),  $\delta$  79.5 (~10%, d, 10 Hz),  $\delta$  -79.6 (5%).

$^{15}\text{N}$  NMR (major isomer,  $\text{CDCl}_3$ ):  $\delta$  -272.2 ppm ( $^1\text{J}(\text{N-H}) = 90.7$  Hz)

MS(70eV): *m/z* 471 ( $\text{M}^+$ , 23%); 428 ( $\text{M} - ^i\text{Pr}$ , 100%); 278 ( $\text{M} - \text{C}_6\text{H}_3^i\text{Pr}_2\text{H}^+$ , 81%); 176 ( $\text{C}_6\text{H}_3^i\text{Pr}_2\text{NH}^+$ ); 105 ( $\text{C}_8\text{H}_9^+$ , 20); 91 ( $\text{C}_6\text{H}_5\text{N}^+$ , 16).

IR ( $\text{CH}_2\text{Cl}_2$ )  $\text{cm}^{-1}$ : 3385(w), 3349(m), 3025(w), 2907(s), 2806(w), 2726(w), 2590(w), 2069(vs), 1942(w), 1905(w), 1873(w), 1803(w), 1709(w), 1666(m), 1659(w), 1641(w), 1607(s), 1586(s), 1565(s), 1510(m), 1501(m), 1493(s), 1484(s), 1468(m), 1383(m), 1345(s), 1203(m), 1180(m), 1111(m), 1056(s), 1007(w), 932(w), 820(w).

IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3350 (w), 2955 (m), 2928 (m), 2866 (m), 1939 (w), 1870 (w), 1666 (w), 1606 (m), 1587 (m), 1565 (m), 1485 (m), 1462 (vs), 1454 (s), 1383 (m), 1345 (vs), 1310 (m), 1264 (w), 1101 (vs), 1002 (s), 889 (w), 866 (w), 833 (w).

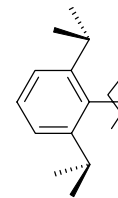
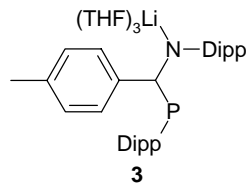
IR (n-heptane)  $\text{cm}^{-1}$ : 3354(vs), 1932(m), 1955(w), 1947(w), 1896(w), 1888(s), 1863(m), 1795(w), 1692(m), 1642(m), 1608(s), 1566(s), 1324(m), 1255(m), 1203(s), 1179(vs), 1111(s), 1055(m), 1038(m), 1007(m), 814(vs), 800(vs), 755(w).

IR (KBr)  $\text{cm}^{-1}$ : 3351(m), 3055(w), 3020(w), 2961(vs), 2925(s), 2867(s), 1588(w), 1563(w), 1492(s), 1466(s), 1385(m), 1349(s), 1308(m), 1278(w), 1254(w), 1204(w), 1183(w), 1110(w), 1056(w), 931(w), 816(m), 802(m), 795(m), 755(m), 746(m), 712(w).

UV (methanol):  $\lambda_{\text{max}}$  203 ( $\epsilon$  74 000), 232 ( $\epsilon$  24 000), 267 ( $\epsilon$  13 000), 347 ( $\epsilon$  9600).

UV (n-hexane):  $\lambda_{\text{max}}$  231 ( $\epsilon$  20 000), 272 ( $\epsilon$  11 000), 356 ( $\epsilon$  14 000).

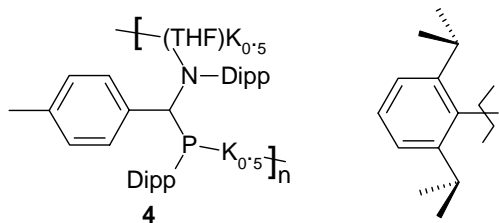
### Preparation of [Li(*E-syn* N,P-Diphosphoamidinate)(THF)<sub>3</sub>], **3**



Dipp = 2,6-diisopropylphenyl

*n*-Butyl lithium (1.6M in hexane, 0.55  $\text{cm}^3$ , 0.88 mmol) was added dropwise to a stirred yellow solution of **2** (0.42 g, 0.89 mmol) in THF (40  $\text{cm}^3$ ) at  $-30$   $^\circ\text{C}$ . The resulting solution, which became deep orange upon addition, was gradually warmed to ambient temperature and stirred overnight. Filtration followed by removal of volatiles under reduced pressure rendered a light orange powder that was washed with cold ( $-10$   $^\circ\text{C}$ ) hexane (3 x 2  $\text{cm}^3$ ) and extracted into fresh THF (10  $\text{cm}^3$ ). Concentration *in vacuo* (ca. 4  $\text{cm}^3$ ) followed by placement at 0  $^\circ\text{C}$  yielded the title compound as light orange plates (0.37 g, 60 %), m.p. 127  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $d_8$ -THF, 303 K):  $\delta$  0.89 (d, 6H,  $\text{CH}(\text{CH}_3)$ ,  $^3J_{\text{HH}}$  6.7 Hz), 0.98 (d, 6H,  $\text{CH}(\text{CH}_3)$ ,  $^3J_{\text{HH}}$  6.9 Hz), 1.15 (d, 6H,  $\text{CH}(\text{CH}_3)$ ,  $^3J_{\text{HH}}$  6.8 Hz), 1.50 (d, 6H,  $\text{CH}(\text{CH}_3)$ ,  $^3J_{\text{HH}}$  6.8 Hz), 1.74 (m, 12H+,  $\text{CH}_2$ , THF), 2.08 (s, 3H,  $\text{CH}_3$ ), 3.56-3.60 (m, 14H,  $\text{CH}_2\text{O}$  and  $\text{CH}(\text{CH}_3)$ ), 4.18 (br s, 2H,  $\text{CH}(\text{CH}_3)$ ), 6.61-6.79 (m, 4H, Ar-*H*), 6.93-7.03 (m, 6H, Ar-*H*).  $^{13}\text{C}$  NMR ( $d_8$ -THF, 303 K):  $\delta$  17.2, 19.2, 21.5, 22.0 (s,  $\text{CH}(\text{CH}_3)$  or  $\text{CH}(\text{CH}_3)$ ), 22.5 (m,  $\text{CH}_2$ ), 24.5, 29.5, 29.6 (s,  $\text{CH}(\text{CH}_3)$  or  $\text{CH}(\text{CH}_3)$ ), 63.9 (m,  $\text{CH}_2\text{O}$ ), 117.6, 120.0, 122.4, 123.8, 124.8 (s, Ar-CH), 149.8 (d, NCP,  $^1J_{\text{CP}}$  6.9 Hz), other signals not observed.  $^{31}\text{P}$  NMR ( $d_8$ -THF, 303 K):  $\delta$  -22.9. IR (Nujol) /  $\text{cm}^{-1}$ : 1917 (sh w), 1901 (sh w), 1850 (sh w), 1789 (sh w), 1507 (sh m), 1460 (s), 1403 (sh m), 1377 (s), 1350 (s), 1306 (m), 1242 (m), 1222 (m), 1174 (sh m), 1098 (sh m), 1043 (s), 978 (sh m), 939 (w), 917 (m), 889(m), 818 (sh m), 801 (sh m), 766 (sh m), 745 (sh m), 668 (w). Anal. Calc. for  $\text{Li}_1\text{C}_{44}\text{H}_{65}\text{N}_1\text{P}_1\text{O}_3$ : C, 76.16; H, 9.44; N, 2.16. Found: C, 75.23; H, 10.00; N, 2.16.

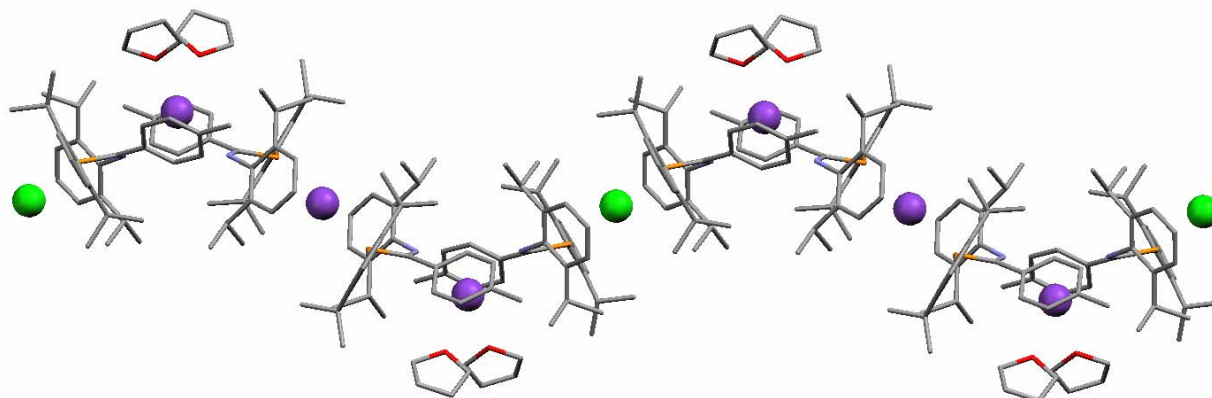
Preparation of [Li(*E*-syn N,P-Dippphosphaamidate)(THF)<sub>n</sub>]<sub>n</sub> THF **4**



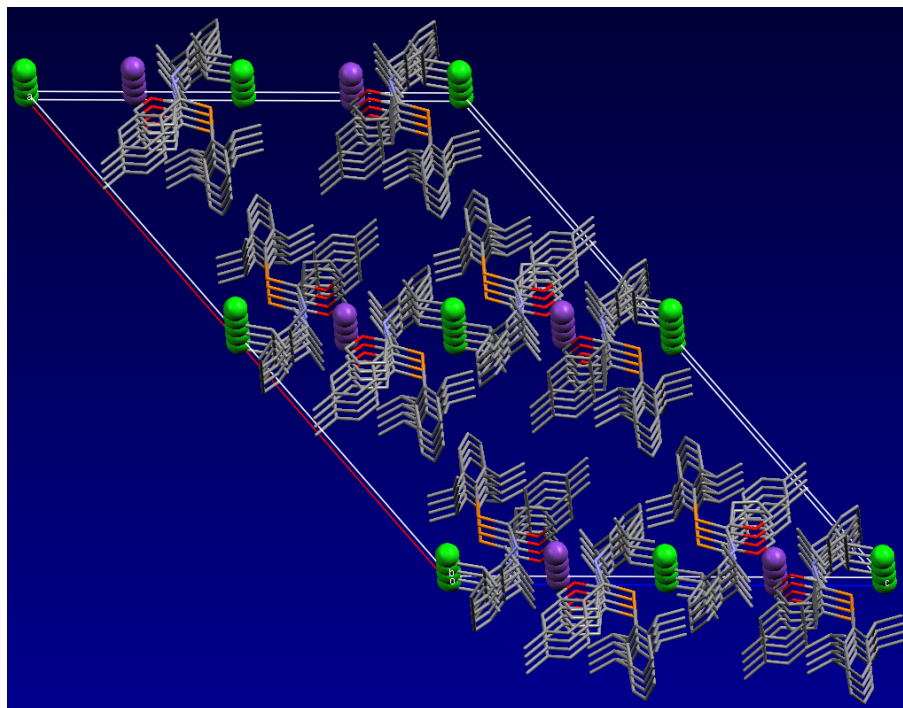
Dipp = 2,6-diisopropylphenyl

Potassium bis(trimethylsilyl)amide (0.5M in toluene, 0.55 cm<sup>3</sup>, 0.88 mmol) was added dropwise to a stirred yellow solution of **2** (0.72 g, 1.53 mmol) in THF (60 cm<sup>3</sup>) at -30 °C. The resulting solution warmed to ambient temperature and stirred for 4 hours, whereupon removal of volatiles *in vacuo* after filtration by canula gave a yellow solid. This was washed with cold (-10 °C) hexane (3 x 5 cm<sup>3</sup>) prior to extraction into fresh THF (20 cm<sup>3</sup>). Placement at 0 °C yielded ultra fine yellow needles of the title compound after

several days (0.63 g, 63%), m.p. 67 °C. <sup>1</sup>H NMR (*d*<sub>8</sub>-THF, 303 K): δ 0.91 (d, 6H, CH(CH<sub>3</sub>), <sup>3</sup>J<sub>HH</sub> 7.0 Hz), 0.96 (d, 6H, CH(CH<sub>3</sub>), <sup>3</sup>J<sub>HH</sub> 6.4 Hz), 1.16 (br s, 6H, CH(CH<sub>3</sub>)), 1.42 (d, 6H, CH(CH<sub>3</sub>), <sup>3</sup>J<sub>HH</sub> 6.3 Hz), 1.72 (m, 8H+, CH<sub>2</sub>, THF), 2.14 (br s, 3H, CH<sub>3</sub>), 3.53-3.58 (m, 10H, CH<sub>2</sub>O and CH(CH<sub>3</sub>)), 4.31 (br s, 2H, CH(CH<sub>3</sub>)), 6.73-7.22 (m, 10H, Ar-H). <sup>13</sup>C NMR (*d*<sub>8</sub>-THF, 303 K): δ 17.3, 19.6, 20.9 (s, CH(CH<sub>3</sub>) or CH(CH<sub>3</sub>)), 21.6 (m, CH<sub>2</sub>), 21.8, 24.7, 29.6, 29.8 (s, CH(CH<sub>3</sub>) or CH(CH<sub>3</sub>)), 63.5 (m, CH<sub>2</sub>O), 118.1, 119.5, 120.0, 123.7, 124.8, 125.5 (s, Ar-CH), 149.5 (d, NCP, <sup>1</sup>J<sub>CP</sub> 7.4 Hz), other signals not observed. <sup>31</sup>P NMR (*d*<sub>8</sub>-THF, 303 K): δ - 15.0. IR (Nujol) / cm<sup>-1</sup>: 1915 (w), 1854 (w), 1799 (w), 1505 (sh m), 1463 (s), 1430 (m), 1410 (sh m), 1377 (sh s), 1356 (m), 1306 (m), 1257 (m), 1228 (w), 1172 (sh m), 1098 (m), 1055 (sh m), 1032 (m), 971 (sh m), 942 (w), 839 (w), 80h (sh m), 772 (sh m), 743 (m), 683 (w). Anal. Calc. for K<sub>1</sub>C<sub>40</sub>H<sub>57</sub>N<sub>1</sub>P<sub>1</sub>O<sub>2</sub>: C, 73.47; H, 8.79; N, 2.14. Found: C, 73.16; H, 8.40; N, 2.45.



**Figure S2** A section of the infinite zigzag chain of ligands and potassium ions of **4** in the basal  $bc$  plane. K ions in green are located at  $0, \frac{1}{2}, -1$ ,  $0, \frac{1}{2}, 0$  and  $0, \frac{1}{2}, 1$  from right to left. These ions and the two half-way between them (the  $0, \frac{1}{2}, \frac{1}{2}$  set) are coordinated by two ligand phosphorus atoms through the in-plane lone pair and by 12 carbon atoms of the Dipp aromatic rings attached to nitrogen (two  $\eta^6$  interactions). The other K ions (the  $0, y, \frac{1}{2}$  set) which form the corners of the zigzags, are coordinated by two out-of-plane nitrogen lone pairs and two THF oxygen lone pairs; additional short contacts to the carbon atoms  $C_2$  and  $C_3$  of the backbone tolyl aromatic rings of two ligand molecules, provide further stabilization for these potassium ions. H atoms and the lattice THF molecule have been omitted for clarity.



**Figure S3.** A packing diagram of **4** showing how the zigzag chains in the  $c$  direction of the lattice, at  $a = 0$  and  $a = \frac{1}{2}$ , combine into infinite ribbons of stacked ligand molecules. The lattice THF molecules fill gaps between the ribbons of ligands and metal ions, and are *not* shown in this diagram.

**Table S1 Crystal data and structure refinement for 2**

Identification code	2
Empirical formula	C <sub>32</sub> H <sub>42</sub> NP
Formula weight	471.64
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 18.2910(17) Å b = 10.0442(5) Å c = 18.1511(16) Å β = 117.179(10)°
Volume	2966.5(4) Å <sup>3</sup>
Z	4
Density (calculated)	1.056 Mg/m <sup>3</sup>
Absorption coefficient	0.111 mm <sup>-1</sup>
F(000)	1024
Crystal size	0.40 x 0.24 x 0.12 mm
Theta range for data collection	2.95 to 25.68°
Index ranges	-22 ≤ h ≤ 22, -12 ≤ k ≤ 12, -22 ≤ l ≤ 22
Reflections collected	24466
Independent reflections	5528 [R(int) = 0.0717]
Completeness to theta	25.68° (98.2%)
Absorption correction	None
Diffractometer	Stoe IPDS
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Refinement software	SHELXTL 5.16 (1998)
Data / restraints / parameters	5528 / 0 / 316
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0460, wR <sub>2</sub> = 0.1056
R indices (all data)	R <sub>1</sub> = 0.0954, wR <sub>2</sub> = 0.1217
Weighting scheme	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) + (0.06400P)] with P = (F <sub>o</sub> <sup>2</sup> + 2F <sub>c</sub> <sup>2</sup> )/3
Goodness-of-fit on F <sup>2</sup>	0.814
Largest diff. peak and hole	0.216 and -0.147 e.Å <sup>-3</sup>

**Table S2 Atomic coordinates (  $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.**

	x	y	z	U(eq)
P(1)	7647(1)	4509(1)	1169(1)	68(1)
N(1)	7493(1)	3132(2)	2377(1)	57(1)
C(1)	7465(1)	3129(2)	1611(1)	52(1)
C(2)	7351(1)	1854(2)	1154(1)	54(1)
C(3)	7730(1)	687(2)	1546(1)	62(1)
C(4)	7692(2)	-445(3)	1095(2)	73(1)
C(5)	7283(2)	-453(3)	240(2)	76(1)
C(6)	7290(2)	-1668(3)	-250(2)	115(1)
C(7)	6881(2)	701(3)	-151(2)	83(1)
C(8)	6906(2)	1842(3)	293(1)	71(1)
C(9)	7288(1)	2135(2)	2815(1)	54(1)
C(10)	6508(2)	1555(2)	2476(1)	60(1)
C(11)	5812(2)	1951(3)	1644(1)	71(1)
C(12)	5159(2)	2731(4)	1769(2)	116(1)
C(13)	5447(2)	761(3)	1065(2)	114(1)
C(14)	6356(2)	629(3)	2962(2)	76(1)
C(15)	6932(2)	333(3)	3751(2)	85(1)
C(16)	7682(2)	930(3)	4076(1)	79(1)
C(17)	7890(2)	1841(2)	3622(1)	62(1)
C(18)	8720(2)	2524(3)	3990(1)	79(1)
C(19)	8675(2)	3878(4)	4371(2)	113(1)
C(20)	9415(2)	1675(5)	4621(2)	136(2)
C(21)	7851(2)	5786(2)	1972(1)	64(1)
C(22)	7208(2)	6445(3)	2041(2)	73(1)
C(23)	6320(2)	6072(3)	1507(2)	89(1)
C(24)	5961(2)	6777(4)	661(2)	145(2)
C(25)	5750(3)	6307(5)	1895(3)	171(2)
C(26)	7405(3)	7485(3)	2610(2)	99(1)
C(27)	8194(3)	7861(3)	3089(2)	116(1)
C(28)	8825(3)	7229(3)	3030(2)	106(1)
C(29)	8674(2)	6174(3)	2476(2)	78(1)
C(30)	9390(2)	5465(4)	2436(2)	107(1)
C(31)	9652(4)	6162(6)	1871(4)	219(3)
C(32)	10106(3)	5192(5)	3281(3)	172(2)

**Table S3 Bond lengths [Å] and angles [°] for 2**

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P(1)-C(1)	1.709(2)	C(4)-C(3)-C(2)	121.0(2)
P(1)-C(21)	1.846(2)	C(5)-C(4)-C(3)	121.6(2)
N(1)-C(1)	1.367(2)	C(4)-C(5)-C(7)	117.4(2)
N(1)-C(9)	1.430(3)	C(4)-C(5)-C(6)	121.3(3)
C(1)-C(2)	1.488(3)	C(7)-C(5)-C(6)	121.3(3)
C(2)-C(3)	1.382(3)	C(5)-C(7)-C(8)	121.6(2)
C(2)-C(8)	1.393(3)	C(7)-C(8)-C(2)	120.4(2)
C(3)-C(4)	1.384(3)	C(10)-C(9)-C(17)	121.85(19)
C(4)-C(5)	1.380(3)	C(10)-C(9)-N(1)	121.40(18)
C(5)-C(7)	1.383(4)	C(17)-C(9)-N(1)	116.6(2)
C(5)-C(6)	1.515(4)	C(14)-C(10)-C(9)	117.3(2)
C(7)-C(8)	1.390(3)	C(14)-C(10)-C(11)	119.0(2)
C(9)-C(10)	1.397(3)	C(9)-C(10)-C(11)	123.57(19)
C(9)-C(17)	1.405(3)	C(10)-C(11)-C(13)	112.5(2)
C(10)-C(14)	1.396(3)	C(10)-C(11)-C(12)	110.1(2)
C(10)-C(11)	1.517(3)	C(13)-C(11)-C(12)	112.1(3)
C(11)-C(13)	1.529(4)	C(15)-C(14)-C(10)	121.8(3)
C(11)-C(12)	1.531(4)	C(16)-C(15)-C(14)	120.0(2)
C(14)-C(15)	1.369(4)	C(15)-C(16)-C(17)	121.8(2)
C(15)-C(16)	1.360(4)	C(16)-C(17)-C(9)	117.3(2)
C(16)-C(17)	1.396(3)	C(16)-C(17)-C(18)	121.7(2)
C(17)-C(18)	1.515(4)	C(9)-C(17)-C(18)	120.9(2)
C(18)-C(20)	1.525(4)	C(17)-C(18)-C(20)	113.7(3)
C(18)-C(19)	1.545(4)	C(17)-C(18)-C(19)	110.4(2)
C(21)-C(22)	1.404(3)	C(20)-C(18)-C(19)	110.6(3)
C(21)-C(29)	1.413(4)	C(22)-C(21)-C(29)	120.0(2)
C(22)-C(26)	1.396(4)	C(22)-C(21)-P(1)	121.5(2)
C(22)-C(23)	1.511(4)	C(29)-C(21)-P(1)	118.29(18)
C(23)-C(25)	1.519(4)	C(26)-C(22)-C(21)	118.4(3)
C(23)-C(24)	1.540(4)	C(26)-C(22)-C(23)	119.9(3)
C(26)-C(27)	1.355(5)	C(21)-C(22)-C(23)	121.7(2)
C(27)-C(28)	1.364(5)	C(22)-C(23)-C(25)	115.4(3)
C(28)-C(29)	1.399(4)	C(22)-C(23)-C(24)	111.6(2)
C(29)-C(30)	1.522(4)	C(25)-C(23)-C(24)	108.7(3)
C(30)-C(31)	1.490(5)	C(27)-C(26)-C(22)	121.5(3)
C(30)-C(32)	1.519(5)	C(26)-C(27)-C(28)	120.7(3)
		C(27)-C(28)-C(29)	120.9(3)
		C(28)-C(29)-C(21)	118.4(3)
		C(28)-C(29)-C(30)	119.8(3)
C(1)-P(1)-C(21)	101.86(9)	C(21)-C(29)-C(30)	121.7(2)
C(1)-N(1)-C(9)	131.69(18)	C(31)-C(30)-C(32)	112.4(4)
N(1)-C(1)-C(2)	120.02(17)	C(31)-C(30)-C(29)	111.6(3)
N(1)-C(1)-P(1)	123.37(16)	C(32)-C(30)-C(29)	113.5(3)
C(2)-C(1)-P(1)	116.34(13)		
C(3)-C(2)-C(8)	117.9(2)		
C(3)-C(2)-C(1)	122.25(18)		
C(8)-C(2)-C(1)	119.6(2)		

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**Table S4 Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$**

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
P(1)	98(1)	58(1)	62(1)	-1(1)	50(1)	-6(1)
N(1)	79(1)	50(1)	49(1)	-1(1)	34(1)	-5(1)
C(1)	57(1)	55(1)	47(1)	1(1)	26(1)	2(1)
C(2)	58(1)	55(1)	56(1)	-6(1)	32(1)	-6(1)
C(3)	69(2)	57(2)	65(1)	-3(1)	35(1)	2(1)
C(4)	84(2)	56(2)	92(2)	-8(1)	52(1)	-4(1)
C(5)	91(2)	64(2)	91(2)	-23(1)	58(2)	-17(2)
C(6)	158(3)	85(2)	137(3)	-48(2)	99(2)	-32(2)
C(7)	98(2)	93(2)	64(1)	-24(1)	41(1)	-22(2)
C(8)	81(2)	73(2)	58(1)	-7(1)	31(1)	-6(1)
C(9)	72(2)	48(1)	50(1)	5(1)	34(1)	6(1)
C(10)	72(2)	56(1)	60(1)	2(1)	38(1)	0(1)
C(11)	63(2)	79(2)	72(1)	5(1)	31(1)	1(1)
C(12)	95(2)	145(3)	128(3)	36(2)	68(2)	37(2)
C(13)	110(3)	106(3)	94(2)	-8(2)	19(2)	-24(2)
C(14)	95(2)	66(2)	86(2)	2(1)	58(2)	-7(1)
C(15)	125(3)	70(2)	79(2)	17(1)	64(2)	4(2)
C(16)	112(2)	77(2)	55(1)	15(1)	44(1)	18(2)
C(17)	77(2)	64(2)	50(1)	3(1)	33(1)	11(1)
C(18)	78(2)	98(2)	57(1)	-3(1)	25(1)	8(2)
C(19)	112(3)	124(3)	102(2)	-48(2)	46(2)	-26(2)
C(20)	98(3)	185(4)	94(2)	27(2)	18(2)	36(3)
C(21)	93(2)	48(1)	62(1)	5(1)	46(1)	2(1)
C(22)	104(2)	55(2)	78(2)	7(1)	57(2)	8(1)
C(23)	106(2)	70(2)	115(2)	17(2)	71(2)	18(2)
C(24)	111(3)	147(4)	158(3)	69(3)	44(3)	16(2)
C(25)	175(4)	167(4)	254(5)	-27(4)	170(4)	-5(3)
C(26)	155(3)	62(2)	107(2)	-5(2)	83(2)	15(2)
C(27)	196(4)	70(2)	93(2)	-21(2)	75(3)	-5(3)
C(28)	137(3)	80(2)	83(2)	-19(2)	36(2)	-19(2)
C(29)	99(2)	61(2)	74(2)	-2(1)	39(2)	-3(2)
C(30)	86(2)	113(3)	114(2)	-18(2)	38(2)	-10(2)
C(31)	245(6)	233(6)	288(7)	82(5)	217(6)	57(5)
C(32)	109(3)	199(5)	180(4)	18(4)	42(3)	19(3)



**Table S5 Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ ) for 2.**

	x	y	z	U(eq)
H(1)	7665	3867	2644	69
H(3)	8014	661	2121	74
H(4)	7947	-1220	1374	88
H(6A)	6800	-1679	-771	172
H(6B)	7310	-2458	56	172
H(6C)	7763	-1639	-348	172
H(7)	6586	715	-726	100
H(8)	6625	2602	15	85
H(11)	6043	2554	1379	85
H(12A)	4893	2151	1994	174
H(12B)	4758	3076	1247	174
H(12C)	5414	3454	2146	174
H(13A)	5875	304	1001	170
H(13B)	5040	1068	535	170
H(13C)	5197	164	1297	170
H(14)	5849	201	2744	91
H(15)	6811	-277	4066	102
H(16)	8066	725	4615	95
H(18)	8852	2706	3533	95
H(19A)	8210	4371	3980	170
H(19B)	9169	4374	4504	170
H(19C)	8619	3732	4865	170
H(20A)	9338	1563	5106	203
H(20B)	9931	2108	4770	203
H(20C)	9414	819	4385	203
H(23)	6308	5114	1398	107
H(24A)	5980	7723	742	218
H(24B)	5401	6502	334	218
H(24C)	6278	6544	379	218
H(25A)	5973	5887	2429	256
H(25B)	5219	5937	1545	256
H(25C)	5697	7246	1957	256
H(26)	6985	7929	2661	119
H(27)	8306	8558	3463	140
H(28)	9362	7502	3362	127
H(30)	9182	4593	2185	128
H(31A)	9188	6268	1336	328
H(31B)	10068	5647	1818	328
H(31C)	9870	7022	2095	328
H(32A)	10496	4622	3220	258
H(32B)	9907	4764	3627	258
H(32C)	10367	6017	3530	258

**Table S11 Crystal data and structure refinement for 3**

Identification code	Compound 3
Empirical formula	C <sub>44</sub> H <sub>65</sub> Li N O <sub>3</sub> P
Formula weight	693.88
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.9877(3) Å    alpha = 90 deg. b = 17.6089(5) Å    beta = 91.2790(10) deg. c = 21.4172(8) Å    gamma = 90 deg.
Volume	4142.8(2) Å <sup>3</sup>
Z, Calculated density	4, 1.113 Mg/m <sup>3</sup>
Absorption coefficient	0.104 mm <sup>-1</sup>
F(000)	1512
Crystal size	0.20 x 0.15 x 0.15 mm
Theta range for data collection	3.56 to 27.87 deg.
Limiting indices	-14<=h<=11, -23<=k<=20, -23<=l<=28
Reflections collected / unique	40099 / 9780 [R(int) = 0.1370]
Completeness to theta = 27.87	99.1 %
Absorption correction	None
Max. and min. transmission	0.9846 and 0.9795
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	9780 / 0 / 460
Goodness-of-fit on F <sup>2</sup>	0.967
Final R indices [I>2sigma(I)]	R1 = 0.0599, wR2 = 0.1098
R indices (all data)	R1 = 0.1945, wR2 = 0.1425
Largest diff. peak and hole	0.610 and -0.371 e.Å <sup>-3</sup>
Note:	All hydrogen atoms placed in calculated positions (riding model).

**Table S12. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for [Li(N,P-Dipamidine)(THF)<sub>3</sub>].  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.**

	x	y	z	$U(\text{eq})$
P(1)	2565(1)	8273(1)	1801(1)	22(1)
O(1)	2604(2)	7924(1)	-923(1)	36(1)
N(1)	2084(2)	7722(1)	629(1)	18(1)
C(1)	2336(2)	8333(1)	984(1)	18(1)
Li(1)	1712(3)	7399(2)	-280(2)	29(1)
O(2)	0(1)	7439(1)	-630(1)	33(1)
C(2)	2452(2)	9061(1)	632(1)	18(1)
O(3)	2023(1)	6295(1)	-527(1)	32(1)
C(3)	1529(2)	9320(1)	233(1)	24(1)
C(4)	1659(2)	9987(1)	-113(1)	30(1)
C(5)	2718(2)	10414(1)	-71(1)	28(1)
C(6)	2897(3)	11120(1)	-461(1)	43(1)
C(7)	3633(2)	10160(1)	335(1)	27(1)
C(8)	3509(2)	9500(1)	679(1)	22(1)
C(9)	2082(2)	7020(1)	965(1)	20(1)
C(10)	983(2)	6717(1)	1184(1)	22(1)
C(11)	-202(2)	7155(1)	1129(1)	27(1)
C(12)	-1152(2)	6734(2)	732(1)	41(1)
C(13)	-708(2)	7340(2)	1770(1)	39(1)
C(14)	1006(2)	6001(1)	1457(1)	29(1)
C(15)	2073(2)	5588(1)	1520(1)	31(1)
C(16)	3156(2)	5904(1)	1319(1)	28(1)
C(17)	3187(2)	6620(1)	1048(1)	23(1)
C(18)	4396(2)	6975(1)	860(1)	25(1)
C(19)	4881(2)	6620(2)	265(1)	39(1)
C(20)	5353(2)	6933(2)	1387(1)	38(1)
C(21)	2773(2)	9280(1)	2037(1)	21(1)
C(22)	1769(2)	9785(1)	2076(1)	23(1)
C(23)	470(2)	9514(1)	1950(1)	24(1)
C(24)	8(2)	9135(1)	2541(1)	30(1)
C(25)	-408(2)	10139(2)	1737(1)	38(1)
C(26)	1970(2)	10528(1)	2269(1)	29(1)
C(27)	3112(2)	10786(1)	2439(1)	32(1)
C(28)	4087(2)	10293(1)	2426(1)	28(1)
C(29)	3946(2)	9547(1)	2227(1)	23(1)
C(30)	5042(2)	9019(1)	2209(1)	28(1)

C(31)	5165(2)	8558(2)	2813(1)	43(1)
C(32)	6242(2)	9424(2)	2076(1)	44(1)
C(33)	3680(2)	8370(2)	-805(1)	42(1)
C(34)	4314(3)	8376(2)	-1398(1)	62(1)
C(35)	3292(2)	8402(2)	-1885(1)	44(1)
C(36)	2273(2)	7984(2)	-1578(1)	35(1)
C(37)	-502(2)	6896(2)	-1063(1)	52(1)
C(38)	-1480(3)	7327(2)	-1433(2)	78(1)
C(39)	-1944(3)	7862(2)	-968(2)	60(1)
C(40)	-802(2)	8083(2)	-601(1)	40(1)
C(41)	1625(2)	5608(1)	-230(1)	38(1)
C(42)	2707(3)	5080(2)	-260(1)	44(1)
C(43)	3242(3)	5273(2)	-890(1)	55(1)
C(44)	2728(2)	6051(2)	-1055(1)	38(1)

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**Table S13. Bond lengths [Å] and angles [deg] for [Li(N,P-Dipamide)(THF) 3].**

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P(1)-C(1)	1.765(2)
P(1)-C(21)	1.855(2)
O(1)-C(33)	1.437(3)
O(1)-C(36)	1.445(3)
O(1)-Li(1)	1.941(4)
N(1)-C(1)	1.343(3)
N(1)-C(9)	1.430(3)
N(1)-Li(1)	2.059(4)
C(1)-C(2)	1.494(3)
Li(1)-O(2)	2.010(4)
Li(1)-O(3)	2.046(4)
Li(1)-C(9)	2.771(5)
O(2)-C(37)	1.435(3)
O(2)-C(40)	1.438(3)
C(2)-C(3)	1.390(3)
C(2)-C(8)	1.398(3)
O(3)-C(41)	1.440(3)
O(3)-C(44)	1.451(3)
C(3)-C(4)	1.397(3)
C(4)-C(5)	1.386(3)
C(5)-C(7)	1.388(3)
C(5)-C(6)	1.513(3)
C(7)-C(8)	1.385(3)
C(9)-C(10)	1.410(3)
C(9)-C(17)	1.412(3)
C(10)-C(14)	1.389(3)
C(10)-C(11)	1.515(3)
C(11)-C(12)	1.525(3)
C(11)-C(13)	1.526(3)
C(14)-C(15)	1.383(3)
C(15)-C(16)	1.390(3)
C(16)-C(17)	1.388(3)
C(17)-C(18)	1.530(3)
C(18)-C(19)	1.526(3)
C(18)-C(20)	1.528(3)
C(21)-C(22)	1.421(3)
C(21)-C(29)	1.423(3)
C(22)-C(26)	1.390(3)
C(22)-C(23)	1.523(3)

C(23)-C(25)	1.527(3)
C(23)-C(24)	1.527(3)
C(26)-C(27)	1.375(3)
C(27)-C(28)	1.380(3)
C(28)-C(29)	1.389(3)
C(29)-C(30)	1.523(3)
C(30)-C(31)	1.530(3)
C(30)-C(32)	1.531(3)
C(33)-C(34)	1.462(4)
C(34)-C(35)	1.516(4)
C(35)-C(36)	1.505(3)
C(37)-C(38)	1.523(4)
C(38)-C(39)	1.471(4)
C(39)-C(40)	1.516(4)
C(41)-C(42)	1.513(3)
C(42)-C(43)	1.523(4)
C(43)-C(44)	1.520(4)
C(1)-P(1)-C(21)	103.11(10)
C(33)-O(1)-C(36)	108.56(18)
C(33)-O(1)-Li(1)	124.20(19)
C(36)-O(1)-Li(1)	127.10(18)
C(1)-N(1)-C(9)	114.10(19)
C(1)-N(1)-Li(1)	142.23(19)
C(9)-N(1)-Li(1)	103.65(18)
N(1)-C(1)-C(2)	114.8(2)
N(1)-C(1)-P(1)	122.50(17)
C(2)-C(1)-P(1)	122.64(17)
O(1)-Li(1)-O(2)	101.6(2)
O(1)-Li(1)-O(3)	100.30(18)
O(2)-Li(1)-O(3)	95.58(18)
O(1)-Li(1)-N(1)	116.5(2)
O(2)-Li(1)-N(1)	120.48(19)
O(3)-Li(1)-N(1)	118.4(2)
O(1)-Li(1)-C(9)	137.1(2)
O(2)-Li(1)-C(9)	118.90(17)
O(3)-Li(1)-C(9)	89.90(16)
N(1)-Li(1)-C(9)	30.11(9)
C(37)-O(2)-C(40)	109.04(19)
C(37)-O(2)-Li(1)	124.11(19)
C(40)-O(2)-Li(1)	125.52(19)
C(3)-C(2)-C(8)	117.1(2)
C(3)-C(2)-C(1)	121.6(2)

C(8)-C(2)-C(1)	121.2(2)
C(41)-O(3)-C(44)	105.51(18)
C(41)-O(3)-Li(1)	129.09(17)
C(44)-O(3)-Li(1)	125.39(18)
C(2)-C(3)-C(4)	121.4(2)
C(5)-C(4)-C(3)	121.2(2)
C(4)-C(5)-C(7)	117.4(2)
C(4)-C(5)-C(6)	122.0(2)
C(7)-C(5)-C(6)	120.5(2)
C(8)-C(7)-C(5)	121.7(2)
C(7)-C(8)-C(2)	121.2(2)
C(10)-C(9)-C(17)	120.6(2)
C(10)-C(9)-N(1)	120.4(2)
C(17)-C(9)-N(1)	118.91(18)
C(10)-C(9)-Li(1)	107.63(17)
C(17)-C(9)-Li(1)	110.40(16)
N(1)-C(9)-Li(1)	46.24(13)
C(14)-C(10)-C(9)	118.4(2)
C(14)-C(10)-C(11)	120.1(2)
C(9)-C(10)-C(11)	121.5(2)
C(10)-C(11)-C(12)	111.9(2)
C(10)-C(11)-C(13)	111.6(2)
C(12)-C(11)-C(13)	110.24(19)
C(15)-C(14)-C(10)	121.7(2)
C(14)-C(15)-C(16)	119.3(2)
C(17)-C(16)-C(15)	121.5(2)
C(16)-C(17)-C(9)	118.5(2)
C(16)-C(17)-C(18)	120.8(2)
C(9)-C(17)-C(18)	120.7(2)
C(19)-C(18)-C(20)	110.43(19)
C(19)-C(18)-C(17)	112.0(2)
C(20)-C(18)-C(17)	111.8(2)
C(22)-C(21)-C(29)	118.4(2)
C(22)-C(21)-P(1)	121.53(17)
C(29)-C(21)-P(1)	119.92(17)
C(26)-C(22)-C(21)	119.3(2)
C(26)-C(22)-C(23)	119.3(2)
C(21)-C(22)-C(23)	121.3(2)
C(22)-C(23)-C(25)	114.3(2)
C(22)-C(23)-C(24)	108.5(2)
C(25)-C(23)-C(24)	110.06(18)
C(27)-C(26)-C(22)	121.8(2)
C(26)-C(27)-C(28)	119.5(2)

C(27)-C(28)-C(29)	121.3(2)
C(28)-C(29)-C(21)	119.7(2)
C(28)-C(29)-C(30)	120.1(2)
C(21)-C(29)-C(30)	120.2(2)
C(29)-C(30)-C(31)	110.94(18)
C(29)-C(30)-C(32)	113.9(2)
C(31)-C(30)-C(32)	110.1(2)
O(1)-C(33)-C(34)	104.9(2)
C(33)-C(34)-C(35)	103.8(2)
C(36)-C(35)-C(34)	103.3(2)
O(1)-C(36)-C(35)	106.7(2)
O(2)-C(37)-C(38)	105.1(2)
C(39)-C(38)-C(37)	102.7(3)
C(38)-C(39)-C(40)	102.6(2)
O(2)-C(40)-C(39)	106.1(2)
O(3)-C(41)-C(42)	104.56(19)
C(41)-C(42)-C(43)	102.7(2)
C(44)-C(43)-C(42)	105.0(2)
O(3)-C(44)-C(43)	106.7(2)



**Table S14. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for [Li(N,P-Dipamide)(THF)<sub>3</sub>]. The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$**

	U11	U22	U33	U23	U13	U12
P(1)	26(1)	23(1)	18(1)	-1(1)	-1(1)	-2(1)
O(1)	44(1)	42(1)	21(1)	1(1)	0(1)	-18(1)
N(1)	20(1)	18(1)	17(1)	0(1)	1(1)	-1(1)
C(1)	14(1)	20(1)	19(1)	0(1)	2(1)	1(1)
Li(1)	30(2)	32(3)	25(3)	-3(2)	0(2)	-2(2)
O(2)	28(1)	39(1)	33(1)	-13(1)	-3(1)	1(1)
C(2)	18(1)	18(1)	18(1)	-4(1)	4(1)	1(1)
O(3)	38(1)	30(1)	29(1)	-3(1)	7(1)	1(1)
C(3)	21(1)	27(2)	25(2)	2(1)	-1(1)	2(1)
C(4)	31(2)	31(2)	28(2)	5(1)	0(1)	9(1)
C(5)	40(2)	19(2)	26(2)	1(1)	10(1)	4(1)
C(6)	62(2)	26(2)	43(2)	11(1)	17(2)	6(1)
C(7)	34(2)	22(2)	26(2)	-3(1)	10(1)	-8(1)
C(8)	25(1)	24(2)	17(1)	-1(1)	-1(1)	-2(1)
C(9)	28(1)	20(1)	14(1)	-1(1)	0(1)	-2(1)
C(10)	28(1)	25(2)	14(1)	-1(1)	2(1)	-3(1)
C(11)	23(1)	27(2)	31(2)	5(1)	3(1)	-6(1)
C(12)	29(2)	58(2)	36(2)	-1(2)	0(1)	-3(1)
C(13)	35(2)	38(2)	46(2)	-7(1)	10(1)	0(1)
C(14)	31(2)	27(2)	28(2)	6(1)	3(1)	-4(1)
C(15)	45(2)	21(2)	28(2)	9(1)	2(1)	-3(1)
C(16)	34(2)	27(2)	24(2)	2(1)	1(1)	7(1)
C(17)	29(1)	22(2)	19(1)	-1(1)	2(1)	2(1)
C(18)	21(1)	26(2)	28(2)	2(1)	1(1)	5(1)
C(19)	36(2)	46(2)	36(2)	-4(1)	6(1)	-2(1)
C(20)	29(1)	45(2)	38(2)	-2(1)	-3(1)	2(1)
C(21)	26(1)	25(2)	12(1)	2(1)	1(1)	-2(1)
C(22)	27(1)	28(2)	13(1)	-2(1)	2(1)	-1(1)
C(23)	24(1)	25(2)	24(2)	-1(1)	1(1)	1(1)
C(24)	29(1)	30(2)	29(2)	0(1)	4(1)	0(1)
C(25)	33(2)	41(2)	38(2)	4(1)	-7(1)	1(1)
C(26)	33(2)	27(2)	27(2)	-8(1)	-2(1)	3(1)
C(27)	44(2)	21(2)	32(2)	-8(1)	-3(1)	-6(1)
C(28)	30(1)	33(2)	22(2)	-4(1)	-3(1)	-11(1)
C(29)	26(1)	28(2)	13(1)	-3(1)	0(1)	-5(1)
C(30)	24(1)	35(2)	24(2)	-7(1)	-2(1)	-2(1)

C(31)	38(2)	56(2)	36(2)	3(2)	-5(1)	11(1)
C(32)	31(2)	52(2)	49(2)	-16(2)	6(1)	-5(1)
C(33)	41(2)	52(2)	34(2)	-5(2)	2(1)	-18(1)
C(34)	61(2)	75(3)	50(2)	-1(2)	10(2)	-26(2)
C(35)	57(2)	47(2)	29(2)	4(1)	5(2)	-14(2)
C(36)	43(2)	39(2)	23(2)	4(1)	-1(1)	1(1)
C(37)	43(2)	61(2)	52(2)	-34(2)	-18(2)	7(2)
C(38)	60(2)	119(3)	55(2)	-33(2)	-23(2)	22(2)
C(39)	48(2)	77(2)	55(2)	-12(2)	-16(2)	19(2)
C(40)	36(2)	37(2)	47(2)	-2(1)	-6(1)	7(1)
C(41)	49(2)	31(2)	35(2)	-4(1)	6(1)	-9(1)
C(42)	64(2)	25(2)	43(2)	-6(1)	2(2)	-1(1)
C(43)	84(2)	34(2)	48(2)	-2(2)	18(2)	14(2)
C(44)	47(2)	42(2)	24(2)	-5(1)	4(1)	9(1)

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**Table S15. Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for [Li(N,P-Dipamide)(THF)<sub>3</sub>]<sub>3</sub>**

	x	y	z	U(eq)
H(3)	794	9038	193	29
H(4)	1011	10151	-381	36
H(6A)	2163	11216	-716	65
H(6B)	3593	11047	-733	65
H(6C)	3053	11555	-185	65
H(7)	4362	10447	378	33
H(8)	4155	9342	951	27
H(11)	-27	7647	916	32
H(12A)	-820	6624	321	61
H(12B)	-1881	7051	681	61
H(12C)	-1367	6257	938	61
H(13A)	-962	6869	1974	59
H(13B)	-1411	7679	1719	59
H(13C)	-78	7590	2027	59
H(14)	270	5790	1603	34
H(15)	2065	5094	1698	38
H(16)	3890	5624	1369	34
H(18)	4239	7524	771	30
H(19A)	5642	6871	154	59
H(19B)	4280	6682	-76	59
H(19C)	5033	6077	335	59
H(20A)	5600	6403	1451	56
H(20B)	5009	7132	1772	56
H(20C)	6064	7236	1276	56
H(23)	491	9121	1614	29
H(24A)	528	8700	2648	44
H(24B)	-830	8961	2467	44
H(24C)	30	9501	2885	44
H(25A)	-526	10498	2080	56
H(25B)	-1192	9913	1614	56
H(25C)	-70	10408	1380	56
H(26)	1300	10868	2284	35
H(27)	3228	11299	2564	39

H(28)	4871	10467	2556	34
H(30)	4889	8649	1862	33
H(31A)	5331	8902	3165	65
H(31B)	5837	8196	2778	65
H(31C)	4407	8282	2883	65
H(32A)	6144	9731	1696	66
H(32B)	6884	9047	2018	66
H(32C)	6463	9754	2429	66
H(33A)	4194	8137	-472	51
H(33B)	3463	8892	-678	51
H(34A)	4813	7912	-1445	74
H(34B)	4846	8827	-1430	74
H(35A)	3057	8932	-1983	53
H(35B)	3532	8145	-2275	53
H(36A)	1499	8266	-1632	42
H(36B)	2169	7473	-1764	42
H(37A)	-860	6461	-840	63
H(37B)	133	6704	-1344	63
H(38A)	-1130	7599	-1791	94
H(38B)	-2130	6981	-1587	94
H(39A)	-2544	7615	-696	72
H(39B)	-2327	8310	-1172	72
H(40A)	-419	8535	-789	48
H(40B)	-997	8200	-163	48
H(41A)	911	5390	-456	46
H(41B)	1405	5706	208	46
H(42A)	2450	4541	-243	53
H(42B)	3299	5180	85	53
H(43A)	4142	5290	-860	66
H(43B)	2995	4893	-1209	66
H(44A)	3395	6414	-1133	45
H(44B)	2203	6019	-1436	45

**Table S16 Crystal data and structure refinement for 4**

Identification code	Compound 4
Empirical formula	C <sub>40</sub> H <sub>57</sub> K N O <sub>2</sub> P
Formula weight	653.94
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 35.6979(5) Å    alpha = 90 deg. b = 12.2579(4) Å    beta = 131.306(2) deg. c = 24.1180(5) Å    gamma = 90 deg.
Volume	7927.8(3) Å <sup>3</sup>
Z, Calculated density	8, 1.096 Mg/m <sup>3</sup>
Absorption coefficient	0.206 mm <sup>-1</sup>
F(000)	2832
Crystal size	0.20 x 0.10 x 0.05 mm
Theta range for data collection	2.82 to 27.85 deg.
Limiting indices	-46<=h<=41, -16<=k<=15, -29<=l<=31
Reflections collected / unique	43531 / 9321 [R(int) = 0.2154]
Completeness to theta = 27.85	98.8 %
Absorption correction	None
Max. and min. transmission	0.9898 and 0.9600
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	9321 / 0 / 418
Goodness-of-fit on F <sup>2</sup>	0.975
Final R indices [I>2sigma(I)]	R1 = 0.0892, wR2 = 0.1638
R indices (all data)	R1 = 0.2776, wR2 = 0.2221
Largest diff. peak and hole	0.273 and -0.298 e.Å <sup>-3</sup>

Note: All hydrogen atoms placed in calculated positions (riding model).  
Both lattice and coordinated THF experience moderate thermal motion.  
Attempted modelling of disorder for the lattice THF failed to yield  
satisfactory thermal parameters. Hence, it was left as is.

**Table S17. Atomic coordinates ( x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for [K(\*\*\*\*\*)(THF)]<sub>n</sub>.nTHF 4. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.**

	x	y	z	U(eq)	
K(1)	0	8006(1)	2500	68(1)	Wyckoff 4(e)
K(2)	0	5000	0	77(1)	Wyckoff 4(b)
P(1)	776(1)	6397(1)	1471(1)	54(1)	
O(1)	476(2)	9838(4)	2548(5)	167(2)	
O(2)	2661(6)	11099(14)	3756(9)	359(7)	
N(1)	145(1)	6552(2)	1737(2)	45(1)	
C(1)	608(1)	6636(3)	2004(2)	42(1)	
C(2)	968(1)	6956(3)	2804(2)	45(1)	
C(3)	936(1)	6464(3)	3294(2)	52(1)	
C(4)	1258(2)	6749(4)	4035(3)	68(1)	
C(5)	1616(2)	7541(4)	4311(3)	70(1)	
C(6)	1968(2)	7870(5)	5121(3)	109(2)	
C(7)	1653(2)	8027(4)	3833(3)	71(1)	
C(8)	1336(2)	7733(3)	3090(3)	60(1)	
C(9)	-239(1)	6198(3)	995(2)	45(1)	
C(10)	-476(2)	6954(4)	403(3)	59(1)	
C(11)	-315(2)	8125(4)	537(3)	80(2)	
C(12)	-233(2)	8522(5)	22(3)	119(2)	
C(13)	-698(2)	8858(4)	460(3)	108(2)	
C(14)	-883(2)	6594(5)	-308(3)	74(1)	
C(15)	-1054(2)	5538(5)	-445(2)	73(1)	
C(16)	-822(2)	4820(4)	134(2)	61(1)	
C(17)	-418(1)	5135(3)	854(2)	47(1)	
C(18)	-175(2)	4311(3)	1473(2)	59(1)	
C(19)	199(2)	3607(5)	1524(3)	105(2)	
C(20)	-545(2)	3584(4)	1415(3)	78(1)	
C(21)	1458(1)	6553(3)	2083(2)	50(1)	
C(22)	1797(2)	5773(4)	2615(2)	55(1)	
C(23)	1627(2)	4796(4)	2776(2)	65(1)	
C(24)	1665(2)	3755(4)	2480(3)	102(2)	
C(25)	1901(2)	4667(5)	3598(3)	99(2)	
C(26)	2306(2)	5894(4)	3007(2)	73(1)	
C(27)	2485(2)	6772(5)	2893(3)	87(2)	
C(28)	2162(2)	7554(4)	2387(3)	77(1)	
C(29)	1651(2)	7471(4)	1979(3)	63(1)	

C(30)	1317(2)	8388(4)	1447(3)	80(2)
C(31)	1165(3)	8207(5)	707(3)	132(2)
C(32)	1533(2)	9514(5)	1732(4)	117(2)
C(33)	573(3)	10194(6)	2088(5)	158(3)
C(34)	1037(3)	10847(6)	2585(5)	154(3)
C(35)	1061(3)	11201(6)	3182(6)	162(3)
C(36)	739(5)	10476(8)	3186(8)	249(7)
C(37)	2819(6)	11809(11)	4442(14)	351(13)
C(38)	2759(8)	10680(20)	4680(7)	368(12)
C(39)	2343(6)	10840(30)	4163(16)	409(16)
C(40)	2571(6)	10096(9)	3928(7)	242(6)

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**Table S18. Bond lengths [Å] and angles [deg] for  $[\{K(\text{THF})\}_n]_n \cdot \text{THF} \cdot 4$ .**

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K(1)-O(1)	2.772(5)
K(1)-O(1)#1	2.772(5)
K(1)-N(1)	2.844(3)
K(1)-N(1)#1	2.844(3)
K(1)-C(3)#1	3.154(4)
K(1)-C(3)	3.154(4)
K(1)-C(2)	3.284(3)
K(1)-C(2)#1	3.284(3)
K(1)-C(1)	3.519(4)
K(1)-C(1)#1	3.519(4)
K(2)-C(16)#2	3.166(4)
K(2)-C(16)	3.166(4)
K(2)-P(1)#2	3.1965(12)
K(2)-P(1)	3.1965(12)
K(2)-C(15)#2	3.225(4)
K(2)-C(15)	3.225(4)
K(2)-C(17)#2	3.248(3)
K(2)-C(17)	3.248(3)
K(2)-C(14)#2	3.348(5)
K(2)-C(14)	3.348(5)
K(2)-C(9)#2	3.368(4)
K(2)-C(9)	3.368(4)
P(1)-C(1)	1.767(4)
P(1)-C(21)	1.841(4)
O(1)-C(36)	1.397(11)
O(1)-C(33)	1.432(8)
O(2)-C(40)	1.399(13)
O(2)-C(37)	1.606(19)
N(1)-C(1)	1.324(4)
N(1)-C(9)	1.424(5)
C(1)-C(2)	1.501(5)
C(2)-C(8)	1.383(5)
C(2)-C(3)	1.397(5)
C(3)-C(4)	1.387(6)
C(4)-C(5)	1.379(6)
C(5)-C(7)	1.379(6)
C(5)-C(6)	1.523(6)
C(7)-C(8)	1.394(6)
C(9)-C(17)	1.392(5)
C(9)-C(10)	1.420(5)



C(10)-C(14)	1.398(6)
C(10)-C(11)	1.501(6)
C(11)-C(12)	1.531(6)
C(11)-C(13)	1.542(7)
C(14)-C(15)	1.375(6)
C(15)-C(16)	1.374(6)
C(16)-C(17)	1.391(5)
C(17)-C(18)	1.514(5)
C(18)-C(20)	1.522(5)
C(18)-C(19)	1.525(6)
C(21)-C(22)	1.406(5)
C(21)-C(29)	1.427(5)
C(22)-C(26)	1.393(6)
C(22)-C(23)	1.508(6)
C(23)-C(24)	1.514(6)
C(23)-C(25)	1.531(6)
C(26)-C(27)	1.369(6)
C(27)-C(28)	1.372(6)
C(28)-C(29)	1.391(6)
C(29)-C(30)	1.520(6)
C(30)-C(31)	1.501(7)
C(30)-C(32)	1.508(7)
C(33)-C(34)	1.484(9)
C(34)-C(35)	1.452(9)
C(35)-C(36)	1.461(10)
C(37)-C(38)	1.56(2)
C(38)-C(39)	1.16(2)
C(39)-C(40)	1.56(2)
O(1)-K(1)-O(1)#1	71.7(2)
O(1)-K(1)-N(1)	99.59(15)
O(1)#1-K(1)-N(1)	148.07(19)
O(1)-K(1)-N(1)#1	148.07(19)
O(1)#1-K(1)-N(1)#1	99.59(15)
N(1)-K(1)-N(1)#1	102.42(12)
O(1)-K(1)-C(3)#1	152.24(17)
O(1)#1-K(1)-C(3)#1	94.94(12)
N(1)-K(1)-C(3)#1	78.68(10)
N(1)#1-K(1)-C(3)#1	56.33(10)
O(1)-K(1)-C(3)	94.94(12)
O(1)#1-K(1)-C(3)	152.24(17)
N(1)-K(1)-C(3)	56.33(10)
N(1)#1-K(1)-C(3)	78.68(10)

C(3)#1-K(1)-C(3)	106.38(15)
O(1)-K(1)-C(2)	77.47(11)
O(1)#1-K(1)-C(2)	148.45(12)
N(1)-K(1)-C(2)	44.36(9)
N(1)#1-K(1)-C(2)	102.93(9)
C(3)#1-K(1)-C(2)	115.91(11)
C(3)-K(1)-C(2)	24.96(9)
O(1)-K(1)-C(2)#1	148.45(12)
O(1)#1-K(1)-C(2)#1	77.47(11)
N(1)-K(1)-C(2)#1	102.93(9)
N(1)#1-K(1)-C(2)#1	44.36(9)
C(3)#1-K(1)-C(2)#1	24.96(9)
C(3)-K(1)-C(2)#1	115.91(11)
C(2)-K(1)-C(2)#1	133.84(14)
O(1)-K(1)-C(1)	84.41(13)
O(1)#1-K(1)-C(1)	150.53(16)
N(1)-K(1)-C(1)	20.74(8)
N(1)#1-K(1)-C(1)	109.73(9)
C(3)#1-K(1)-C(1)	98.70(10)
C(3)-K(1)-C(1)	43.70(9)
C(2)-K(1)-C(1)	25.19(9)
C(2)#1-K(1)-C(1)	122.07(9)
O(1)-K(1)-C(1)#1	150.53(16)
O(1)#1-K(1)-C(1)#1	84.41(13)
N(1)-K(1)-C(1)#1	109.73(9)
N(1)#1-K(1)-C(1)#1	20.74(8)
C(3)#1-K(1)-C(1)#1	43.70(9)
C(3)-K(1)-C(1)#1	98.70(10)
C(2)-K(1)-C(1)#1	122.07(9)
C(2)#1-K(1)-C(1)#1	25.19(9)
C(1)-K(1)-C(1)#1	123.02(12)
C(16)#2-K(2)-C(16)	180.00(12)
C(16)#2-K(2)-P(1)#2	96.14(8)
C(16)-K(2)-P(1)#2	83.86(8)
C(16)#2-K(2)-P(1)	83.86(8)
C(16)-K(2)-P(1)	96.14(8)
P(1)#2-K(2)-P(1)	180.00(4)
C(16)#2-K(2)-C(15)#2	24.80(10)
C(16)-K(2)-C(15)#2	155.20(10)
P(1)#2-K(2)-C(15)#2	103.08(10)
P(1)-K(2)-C(15)#2	76.92(10)
C(16)#2-K(2)-C(15)	155.20(10)
C(16)-K(2)-C(15)	24.80(10)

P(1)#2-K(2)-C(15)	76.92(10)
P(1)-K(2)-C(15)	103.07(10)
C(15)#2-K(2)-C(15)	180.00(15)
C(16)#2-K(2)-C(17)#2	25.01(9)
C(16)-K(2)-C(17)#2	154.99(9)
P(1)#2-K(2)-C(17)#2	72.17(7)
P(1)-K(2)-C(17)#2	107.83(7)
C(15)#2-K(2)-C(17)#2	43.77(10)
C(15)-K(2)-C(17)#2	136.23(10)
C(16)#2-K(2)-C(17)	154.99(9)
C(16)-K(2)-C(17)	25.01(9)
P(1)#2-K(2)-C(17)	107.83(7)
P(1)-K(2)-C(17)	72.17(7)
C(15)#2-K(2)-C(17)	136.23(10)
C(15)-K(2)-C(17)	43.77(10)
C(17)#2-K(2)-C(17)	180.00(17)
C(16)#2-K(2)-C(14)#2	42.53(11)
C(16)-K(2)-C(14)#2	137.47(11)
P(1)#2-K(2)-C(14)#2	86.16(10)
P(1)-K(2)-C(14)#2	93.84(10)
C(15)#2-K(2)-C(14)#2	24.06(11)
C(15)-K(2)-C(14)#2	155.94(11)
C(17)#2-K(2)-C(14)#2	49.60(10)
C(17)-K(2)-C(14)#2	130.40(10)
C(16)#2-K(2)-C(14)	137.47(11)
C(16)-K(2)-C(14)	42.53(11)
P(1)#2-K(2)-C(14)	93.84(10)
P(1)-K(2)-C(14)	86.16(10)
C(15)#2-K(2)-C(14)	155.94(11)
C(15)-K(2)-C(14)	24.06(11)
C(17)#2-K(2)-C(14)	130.40(10)
C(17)-K(2)-C(14)	49.60(10)
C(14)#2-K(2)-C(14)	180.00(14)
C(16)#2-K(2)-C(9)#2	43.10(10)
C(16)-K(2)-C(9)#2	136.90(10)
P(1)#2-K(2)-C(9)#2	54.36(7)
P(1)-K(2)-C(9)#2	125.64(7)
C(15)#2-K(2)-C(9)#2	50.22(11)
C(15)-K(2)-C(9)#2	129.78(11)
C(17)#2-K(2)-C(9)#2	24.20(9)
C(17)-K(2)-C(9)#2	155.80(9)
C(14)#2-K(2)-C(9)#2	42.25(10)
C(14)-K(2)-C(9)#2	137.75(10)

C(16)#2-K(2)-C(9)	136.90(10)
C(16)-K(2)-C(9)	43.10(10)
P(1)#2-K(2)-C(9)	125.64(7)
P(1)-K(2)-C(9)	54.36(7)
C(15)#2-K(2)-C(9)	129.78(11)
C(15)-K(2)-C(9)	50.22(11)
C(17)#2-K(2)-C(9)	155.80(9)
C(17)-K(2)-C(9)	24.20(9)
C(14)#2-K(2)-C(9)	137.75(10)
C(14)-K(2)-C(9)	42.25(10)
C(9)#2-K(2)-C(9)	180.00(15)
C(1)-P(1)-C(21)	107.59(17)
C(1)-P(1)-K(2)	115.75(13)
C(21)-P(1)-K(2)	131.66(12)
C(36)-O(1)-C(33)	110.7(6)
C(36)-O(1)-K(1)	116.5(6)
C(33)-O(1)-K(1)	132.0(5)
C(40)-O(2)-C(37)	99.5(11)
C(1)-N(1)-C(9)	119.5(3)
C(1)-N(1)-K(1)	109.8(2)
C(9)-N(1)-K(1)	124.7(2)
N(1)-C(1)-C(2)	112.4(3)
N(1)-C(1)-P(1)	123.2(3)
C(2)-C(1)-P(1)	124.4(3)
N(1)-C(1)-K(1)	49.51(19)
C(2)-C(1)-K(1)	68.61(18)
P(1)-C(1)-K(1)	155.35(17)
C(8)-C(2)-C(3)	117.2(4)
C(8)-C(2)-C(1)	123.0(3)
C(3)-C(2)-C(1)	119.7(3)
C(8)-C(2)-K(1)	110.8(2)
C(3)-C(2)-K(1)	72.3(2)
C(1)-C(2)-K(1)	86.2(2)
C(4)-C(3)-C(2)	121.3(4)
C(4)-C(3)-K(1)	106.0(3)
C(2)-C(3)-K(1)	82.7(2)
C(5)-C(4)-C(3)	121.0(4)
C(4)-C(5)-C(7)	118.1(4)
C(4)-C(5)-C(6)	121.5(5)
C(7)-C(5)-C(6)	120.3(5)
C(5)-C(7)-C(8)	121.2(4)
C(2)-C(8)-C(7)	121.1(4)
C(17)-C(9)-C(10)	119.4(4)

C(17)-C(9)-N(1)	119.9(3)
C(10)-C(9)-N(1)	120.3(4)
C(17)-C(9)-K(2)	73.1(2)
C(10)-C(9)-K(2)	80.3(2)
N(1)-C(9)-K(2)	122.8(2)
C(14)-C(10)-C(9)	118.4(4)
C(14)-C(10)-C(11)	120.4(4)
C(9)-C(10)-C(11)	121.2(4)
C(14)-C(10)-K(2)	74.9(3)
C(9)-C(10)-K(2)	75.6(2)
C(11)-C(10)-K(2)	122.5(3)
C(10)-C(11)-C(12)	112.5(5)
C(10)-C(11)-C(13)	110.3(4)
C(12)-C(11)-C(13)	110.3(4)
C(15)-C(14)-C(10)	121.9(4)
C(15)-C(14)-K(2)	73.0(3)
C(10)-C(14)-K(2)	81.4(3)
C(16)-C(15)-C(14)	119.0(4)
C(16)-C(15)-K(2)	75.2(2)
C(14)-C(15)-K(2)	83.0(3)
C(15)-C(16)-C(17)	121.5(4)
C(15)-C(16)-K(2)	80.0(2)
C(17)-C(16)-K(2)	80.8(2)
C(16)-C(17)-C(9)	119.8(4)
C(16)-C(17)-C(18)	119.5(4)
C(9)-C(17)-C(18)	120.8(4)
C(16)-C(17)-K(2)	74.2(2)
C(9)-C(17)-K(2)	82.7(2)
C(18)-C(17)-K(2)	112.8(2)
C(17)-C(18)-C(20)	113.7(4)
C(17)-C(18)-C(19)	111.0(3)
C(20)-C(18)-C(19)	109.7(4)
C(22)-C(21)-C(29)	118.1(4)
C(22)-C(21)-P(1)	123.3(3)
C(29)-C(21)-P(1)	118.5(3)
C(26)-C(22)-C(21)	120.0(4)
C(26)-C(22)-C(23)	118.5(4)
C(21)-C(22)-C(23)	121.5(4)
C(22)-C(23)-C(24)	111.6(4)
C(22)-C(23)-C(25)	113.1(4)
C(24)-C(23)-C(25)	110.1(4)
C(27)-C(26)-C(22)	121.2(5)
C(26)-C(27)-C(28)	119.9(4)

C(27)-C(28)-C(29)	121.2(5)
C(28)-C(29)-C(21)	119.6(4)
C(28)-C(29)-C(30)	118.3(4)
C(21)-C(29)-C(30)	122.1(4)
C(31)-C(30)-C(32)	110.6(4)
C(31)-C(30)-C(29)	111.1(4)
C(32)-C(30)-C(29)	114.3(5)
O(1)-C(33)-C(34)	104.5(7)
C(35)-C(34)-C(33)	105.4(6)
C(34)-C(35)-C(36)	107.1(8)
O(1)-C(36)-C(35)	107.0(8)
C(38)-C(37)-O(2)	81.8(9)
C(39)-C(38)-C(37)	81(2)
C(38)-C(39)-C(40)	71.7(16)
O(2)-C(40)-C(39)	82.5(13)

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Symmetry transformations used to generate equivalent atoms:

#1  $-x, y, -z+1/2$     #2  $-x, -y+1, -z$

**Table S19 Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\{\text{K}(\text{THF})\}_n]_n \cdot n\text{THF}$  4. The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [h^2 a^*{}^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$**

	U11	U22	U33	U23	U13	U12
K(1)	72(1)	47(1)	102(1)	0	65(1)	0
K(2)	56(1)	123(1)	58(1)	-13(1)	40(1)	-15(1)
P(1)	43(1)	68(1)	53(1)	7(1)	33(1)	-1(1)
O(1)	178(5)	74(3)	356(9)	-8(4)	221(6)	-14(3)
O(2)	550(20)	289(14)	453(19)	98(13)	422(19)	33(14)
N(1)	36(2)	42(2)	51(2)	5(2)	27(2)	-3(2)
C(1)	36(2)	33(2)	51(3)	10(2)	26(2)	3(2)
C(2)	37(2)	39(2)	59(3)	1(2)	32(2)	2(2)
C(3)	39(2)	58(3)	53(3)	-2(2)	28(2)	-6(2)
C(4)	51(3)	92(4)	59(3)	-6(3)	36(3)	-3(3)
C(5)	36(3)	98(4)	68(3)	-23(3)	31(3)	-8(3)
C(6)	63(4)	168(6)	71(4)	-54(4)	34(3)	-27(4)
C(7)	45(3)	75(3)	87(4)	-29(3)	41(3)	-20(2)
C(8)	56(3)	55(3)	85(4)	-13(3)	53(3)	-10(2)
C(9)	31(2)	55(3)	50(3)	11(2)	28(2)	3(2)
C(10)	44(3)	69(3)	59(3)	24(3)	31(3)	4(2)
C(11)	63(3)	68(4)	94(4)	36(3)	45(3)	9(3)
C(12)	103(5)	114(5)	143(5)	68(4)	83(4)	6(4)
C(13)	99(5)	69(4)	143(5)	43(4)	74(4)	21(3)
C(14)	50(3)	95(4)	64(3)	34(3)	32(3)	8(3)
C(15)	43(3)	117(5)	43(3)	13(3)	21(2)	-7(3)
C(16)	48(3)	79(3)	47(3)	-4(2)	28(3)	-18(2)
C(17)	41(2)	56(3)	43(2)	3(2)	27(2)	-6(2)
C(18)	65(3)	50(3)	50(3)	4(2)	33(3)	-9(2)
C(19)	97(4)	97(4)	120(5)	47(4)	71(4)	29(4)
C(20)	89(4)	77(4)	74(3)	3(3)	56(3)	-24(3)
C(21)	49(3)	57(3)	56(3)	3(2)	40(2)	1(2)
C(22)	47(3)	70(3)	51(3)	8(2)	34(2)	11(2)
C(23)	58(3)	72(3)	63(3)	16(3)	38(3)	10(2)
C(24)	132(5)	89(4)	81(4)	-5(3)	69(4)	-14(4)
C(25)	123(5)	109(5)	87(4)	22(3)	78(4)	21(4)
C(26)	52(3)	102(4)	64(3)	12(3)	38(3)	15(3)
C(27)	47(3)	126(5)	92(4)	10(4)	48(3)	0(3)
C(28)	59(4)	88(4)	96(4)	8(3)	57(3)	-6(3)
C(29)	47(3)	74(3)	75(3)	8(3)	43(3)	0(2)

C(30)	61(3)	80(4)	91(4)	17(3)	47(3)	-10(3)
C(31)	170(7)	107(5)	96(5)	30(4)	77(5)	25(5)
C(32)	118(5)	79(4)	158(6)	8(4)	92(5)	-7(4)
C(33)	127(7)	104(6)	257(10)	-1(6)	132(7)	-18(5)
C(34)	161(7)	80(5)	289(11)	-29(6)	178(8)	-31(5)
C(35)	156(7)	113(6)	273(11)	-20(6)	166(8)	-4(5)
C(36)	401(18)	115(8)	460(20)	-102(10)	384(18)	-91(10)
C(37)	238(16)	158(12)	470(30)	-149(16)	157(19)	-64(11)
C(38)	390(30)	580(40)	105(9)	70(16)	153(14)	100(30)
C(39)	188(15)	570(40)	560(40)	130(30)	290(20)	50(20)
C(40)	286(17)	153(11)	195(12)	-22(8)	119(12)	-60(11)

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**Table S20. Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\{\text{K}(\text{THF})\}_n]\text{nTHF 4}$ .**

	x	y	z	U(eq)
H(3)	691	5929	3118	63
H(4)	1231	6396	4353	81
H(6A)	1889	7456	5375	163
H(6B)	1931	8643	5160	163
H(6C)	2310	7722	5345	163
H(7)	1897	8565	4011	85
H(8)	1372	8069	2777	72
H(11)	6	8188	1051	97
H(12A)	33	8102	111	178
H(12B)	-142	9288	115	178
H(12C)	-537	8427	-487	178
H(13A)	-1007	8865	-51	163
H(13B)	-568	9594	614	163
H(13C)	-760	8574	768	163
H(14)	-1043	7088	-703	89
H(15)	-1325	5311	-929	88
H(16)	-940	4099	43	73
H(18)	13	4724	1941	71
H(19A)	23	3143	1091	158
H(19B)	382	3156	1963	158
H(19C)	430	4072	1550	158
H(20A)	-793	4034	1356	117
H(20B)	-370	3149	1859	117
H(20C)	-709	3106	991	117
H(23)	1269	4907	2514	79
H(24A)	1463	3818	1950	152
H(24B)	1548	3146	2586	152
H(24C)	2010	3633	2713	152
H(25A)	2253	4545	3872	149
H(25B)	1765	4050	3665	149
H(25C)	1860	5325	3776	149
H(26)	2530	5364	3357	88
H(27)	2828	6837	3160	104
H(28)	2288	8158	2315	92
H(30)	1008	8361	1371	96

H(31A)	1457	8245	756	198
H(31B)	928	8766	366	198
H(31C)	1011	7495	521	198
H(32A)	1636	9612	2215	176
H(32B)	1284	10056	1394	176
H(32C)	1820	9599	1771	176
H(33A)	297	10641	1678	190
H(33B)	620	9569	1886	190
H(34A)	1329	10402	2775	184
H(34B)	1025	11476	2323	184
H(35A)	947	11957	3104	194
H(35B)	1405	11158	3655	194
H(36A)	938	10011	3626	299
H(36B)	507	10902	3187	299
H(37A)	3160	12095	4766	422
H(37B)	2577	12366	4318	422
H(38A)	2913	10062	4637	441
H(38B)	2836	10682	5152	441
H(39A)	2257	11586	3968	491
H(39B)	2094	10502	4164	491
H(40A)	2872	9697	4333	291
H(40B)	2332	9624	3503	291

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**END**