Electronic supplementary information:

The supplementary information contains:

1) Details of the spectroscopic and analytical characterisation of 2·Li

2) Experimental details of the line-shape analysis

3) Details of the X-ray structural analysis in .cif format.

1) NMR spectroscopic data of 2·Li

$^{31}$P{¹H} NMR (–80 °C, 161.98 MHz, d⁸-toluene), ABCD spin system, $\delta_A = 120.51$, $\delta_B = 92.81$, $\delta_C = 50.95$, $\delta_D = 41.52$, $^1J_{A,D} = -295.7$ Hz, $^1J_{B,C} = -282.0$ Hz, $^1J_{C,D} = -307.6$ Hz, $^2J_{A,B} = -21.3$ Hz, $^2J_{A,C} = 25.3$ Hz, $^2J_{B,D} = 12.2$ Hz. $^{31}$P{¹H} NMR (+60 °C, 161.98 MHz, thf/d⁸-thf), AA'BB' spin system, $\delta_A = \delta_{A'} = 111.51$, $\delta_B = \delta_{B'} = 48.90$, $^1J_{A,B} = ^1J_{A',B'} = -290.8$ Hz, $^1J_{B,B'} = -314.0$ Hz, $^2J_{A,B'} = 7.2$ Hz, $^2J_{A,A'} = -13.4$ Hz. ¹H NMR (+25 °C, 400.13 MHz, C₆D₆), $\delta = 0.83$ (br s, 1H, CH), 1.32 (m, 10H, CH₂ of thf), 1.52 (d, 18H, CH₃ of tBu at Pₐ,B, $^3J_{P,H} = 10.2$ Hz), 1.70 (dd, 18H, CH₃ of tBu at Pₐ,D, $^3J_{P,H} = \text{ca. 6 Hz}$), 3.52 (m, 10H, CH₂ of thf). ¹³C{¹H} NMR (+25 °C, 100.16 MHz, C₆D₆), $\delta = 25.12$ (s, CH₂ of thf), 25.62 (br m, CH, no P-C coupling observed due to overlap with signal of thf), 29.76 (d, C(CH₃)₃ at Pₐ,B, $^3J_{P,C} = 14.4$ Hz), 31.26 (d, C(CH₃)₃ at Pₐ,D, $^2J_{P,C} = 12.0$ Hz), 31.32 (m, C(CH₃)₃ at P₉,D, no P-C coupling observed due to overlap with signal at 29.76), 32.96 (m, C(CH₃)₃ at P₉,D, no P-C coupling observed due to overlap with signal at 29.76), 68.91 (s, CH₂ of thf). ⁷Li NMR (+25 °C, 155.51 MHz, C₆D₆), $\delta = 1.58$ (s).

M.p. 152–153 °C.
Elemental analysis. Samples of $2\cdot$Li partly lose thf ligands on evacuation and varying elemental analyses were therefore obtained; found C 57.48, H 9.70; calcd. for

$$[\text{Li(thf)}_{1.5}\text{cyclo-}(\text{P}_4\text{Bu}_4\text{CH})] \quad (\text{C}_{23}\text{H}_{49}\text{O}_{1.5}\text{P}_4\text{Li}) \quad \text{C 57.49, H 10.28.}$$

2) Details of the line-shape analysis:

The rate constants $k$ for the exchange between $(R_P,S_P,S_P,R_P,R_C)-2$ and $(S_P,R_P,R_P,S_P,S_C)-2$ (Fig. 1) were obtained by line-shape analysis using the program DNMR as implemented in SPINWORKS 2.3 (Kirk Marat, University of Manitoba, 2004). Simulated and experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectra that were taken into account are displayed in Figs. 2 and 3. $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ were obtained according to the Eyring equation by plotting $T^{-1}$ against $\ln(k/T)$ (Figs. 4 and 5, Eqs. 1 to 3) and linear regression (Microcal Origin v5.0, Microcal Inc., Northampton, USA, 1997). The uncertainties in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were determined by using the error margins for A and B given by Origin and multiplication by the universal gas constant $R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The error in $\Delta G^\ddagger$ at 25 °C was determined by adding the error of $\Delta H^\ddagger$ and the error of $\Delta S^\ddagger$ multiplied by $T = 298 \text{ K}$. 
Figure 1. Assumed equilibrium between the two enantiomers of 2.
Figure 2. Experimental (left) and simulated (right) $^{31}$P-$^1$H NMR spectra in thf/d$^8$-thf: a) $T = 252.3$ K, $k = 95000$ s$^{-1}$; b) $T = 241.1$ K, $k = 58000$ s$^{-1}$; c) $T = 230.7$ K, $k = 22500$ s$^{-1}$; d) $T = 219.2$ K, $k = 9000$ s$^{-1}$; e) $T = 209.9$ K, $k = 4700$ s$^{-1}$; f) $T = 199.5$ K, $k = 1850$ s$^{-1}$; g) $T = 189.8$ K, $k = 1100$ s$^{-1}$. 
Figure 3. Experimental (left) and simulated (right) $^{31}$P($^1$H) NMR spectra in d$_8$-toluene:
a) $T = 293.8$ K, $k = 20000$ s$^{-1}$; b) $T = 288.1$ K, $k = 15000$ s$^{-1}$; c) $T = 274.8$ K, $k = 6400$ s$^{-1}$; d) $T = 264.5$ K, $k = 4000$ s$^{-1}$; e) $T = 248.3$ K, $k = 900$ s$^{-1}$; f) $T = 237.1$ K, $k = 300$ s$^{-1}$; g) $T = 229.9$ K, $k = 150$ s$^{-1}$.

Figure 4. Linear regression of ln($k/T$) plotted against $1/T$ for 2·Li in thf/d$_8$-thf.

$[\text{[(P}_4\text{R}_4\text{CH) Li(thf)}_3\text{] (2·Li)}$ in thf/d$_8$-thf

$\Delta H = 27.95$ kJ/mol; $\Delta S = -37.69$ J/mol;

$\Delta G(298K) = 39.18$ kJ/mol

<table>
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<th>Parameter</th>
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<td>B</td>
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| R         | -0.99445    | <0.0001   |

Linear Regression for Data2_J:
$Y = A + B \cdot X$
Figure 5. Linear regression of ln(k/T) plotted against 1/T for 2·Li in d⁸-toluene.

\[ \Delta H^\ddagger = -B \cdot R \]

Equation 1. Calculation of \( \Delta H^\ddagger \), \( B \): slope from linear regression, \( R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)

\[ \Delta S^\ddagger = (A - 23.76) \cdot R \]

Equation 2. Calculation of \( \Delta S^\ddagger \), \( A \): intercept from linear regression, \( R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)

\[ \Delta G^\ddagger = \Delta H^\ddagger - T \cdot \Delta S^\ddagger \]

Equation 3. Calculation of \( \Delta G^\ddagger \) (Helmholtz equation)
Solvent | $\Delta H^\dagger$ in kJ/mol | $\Delta S^\dagger$ in J/mol | $\Delta G^\dagger$ in kJ/mol at 298 K
---|---|---|---
d\textsuperscript{8}-toluene | 41.0 ± 1.2 | -22.1 ± 4.8 | 47.6 ± 2.6
thf/d\textsuperscript{8}-thf | 27.9 ± 1.3 | -37.7 ± 6.1 | 39.2 ± 3.1

**Figure 5.** Results of the line-shape analysis of 2-Li