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

³¹P {¹H} NMR (-80 °C, 161.98 MHz, d⁸-toluene), ABCD spin system, $\delta_{A} = 120.51$, $\delta_{B} = 92.81$, $\delta_{C} = 50.95$, $\delta_{D} = 41.52$, ${}^{1}J_{AD} = -295.7$ Hz, ${}^{1}J_{BC} = -282.0$ Hz, ${}^{1}J_{CD} = -307.6$ Hz, ${}^{2}J_{AB} = -21.3$ Hz, ${}^{2}J_{AC} = 25.3$ Hz, ${}^{2}J_{BD} = 12.2$ Hz. ${}^{31}P$ {¹H} NMR (+60 °C, 161.98 MHz, thf/d⁸-thf), AA'BB' spin system, $\delta_{A} = \delta_{A'} = 111.51$, $\delta_{B} = \delta_{B'} = 48.90$, ${}^{1}J_{AB} = {}^{1}J_{A'B'} = -290.8$ Hz, ${}^{1}J_{BB'} = -314.0$ Hz, ${}^{2}J_{AB'} = {}^{2}J_{A'B} = 7.2$ Hz, ${}^{2}J_{AA'} = -43.4$ Hz. ${}^{1}H$ 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 'Bu at P_{A,B}, ${}^{3}J_{P,H} = 10.2$ Hz), 1.70 (dd, 18H, CH₃ of 'Bu at P_{C,D}, ${}^{3}J_{P,H} = ca. 6$ Hz), 3.52 (m, 10H, CH₂ of thf). ${}^{13}C$ { $}^{1}H$ } 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, <u>C</u>(CH₃)₃ at P_{A,B}, ${}^{1}J_{P,C} = 14.4$ Hz), 31.26 (d, C(<u>C</u>H₃)₃ at P_{A,B}, ${}^{2}J_{P,C} = 12.0$ Hz), 31.32 (m, C(<u>C</u>H₃)₃ at P_{C,D}, ${}^{2}J_{P,C} = 14.4$ Hz), 68.91 (s, CH₂ of thf). ${}^{7}Li$ NMR (+25 °C, 155.51 MHz, C₆D₆), $\delta = 1.58$ (s). M.p. 152–153 °C.

Elemental analysis. Samples of **2·Li** partly lose thf ligands on evacuation and varying elemental analyses were therefore obtained; found C 57.48, H 9.70; calcd. for $[\text{Li}(\text{thf})_{1.5}cyclo-(P_4^{t}\text{Bu}_4\text{CH})]$ (C₂₃H₄₉O_{1.5}P₄Li) 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 ³¹P{¹H} NMR spectra that were taken into account are displayed in Figs. 2 and 3. ΔH^{\ddagger} , ΔS^{\ddagger} and ΔG^{\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 ΔH^{\ddagger} and ΔS^{\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 ΔG^{\ddagger} at 25 °C was determined by adding the error of ΔH^{\ddagger} and the error of ΔS^{\ddagger} multiplied by T = 298 K.



Figure 1. Assumed equilibrium between the two enantiomers of 2.



Figure 2. Experimental (left) and simulated (right) ³¹P{¹H} NMR spectra in thf/d⁸-thf: *a*) $T = 252.3 \text{ K}, k = 95000 \text{ s}^{-1}; b$) $T = 241.1 \text{ K}, k = 58000 \text{ s}^{-1}; c$) $T = 230.7 \text{ K}, k = 22500 \text{ s}^{-1};$ *d*) $T = 219.2 \text{ K}, k = 9000 \text{ s}^{-1}; e$) $T = 209.9 \text{ K}, k = 4700 \text{ s}^{-1}; f$) $T = 199.5 \text{ K}, k = 1850 \text{ s}^{-1}; g$) $T = 189.8 \text{ K}, k = 1100 \text{ s}^{-1}.$





Figure 3. Experimental (left) and simulated (right) ${}^{31}P{}^{1}H$ NMR spectra in d⁸-toluene:

a) $T = 293.8 \text{ K}, k = 20000 \text{ s}^{-1}; b) T = 288.1 \text{ K}, k = 15000 \text{ s}^{-1}; c) T = 274.8 \text{ K}, k = 6400 \text{ s}^{-1};$ d) $T = 264.5 \text{ K}, k = 4000 \text{ s}^{-1}; e) T = 248.3 \text{ K}, k = 900 \text{ s}^{-1}; f) T = 237.1 \text{ K}, k = 300 \text{ s}^{-1}; g) T$

$$= 229.9 \text{ K}, k = 150 \text{ s}^{-1}.$$



Figure 4. Linear regression of $\ln(k/T)$ plotted against 1/T for **2**·Li in thf/d⁸-thf.

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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 ΔH^{\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 ΔS^{\ddagger} , A: intercept from linear regression, $R = 8.3145 \text{ J} \cdot \text{K}^-$

 $^{1} \cdot mol^{-1}$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \cdot \Delta S^{\ddagger}$$

Equation 3. Calculation of ΔG^{\ddagger} (Helmholtz equation)

Solvent	ΔH^{\ddagger} in kJ/mol	ΔS^{\ddagger} in J/mol	ΔG^{\ddagger} in kJ/mol at 298 K
d ⁸ -toluene	41.0 ± 1.2	-22.1 ± 4.8	47.6 ± 2.6
thf/d 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