SUPPLEMENTARY INFORMATION

Self-Assembly of Benzyl Cyclopentadienyl Lithium

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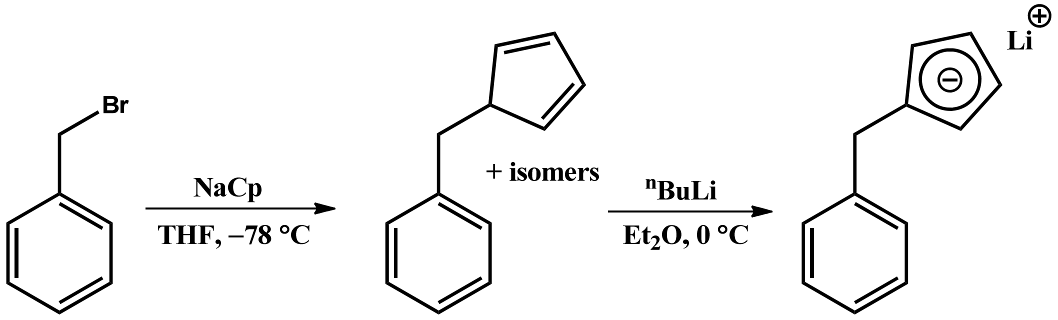
General Methods

All reactions were carried out in flame-dried glassware under nitrogen, using standard Schlenk techniques. Solvents were deoxygenated and dried by passing through activated alumina under nitrogen. The deuterated tetrahydrofuran (THF–d_8) was purchased from Cambridge Isotopes and dried over sodium metal prior to use. ^{n}BuLi (1.6 M in hexanes), sodium cyclopentadienide (2.0 M in THF) and benzyl bromide (98% reagent grade) were purchased from Acros and used without further purification. Silicycle glass backed thin layer chromatography (TLC) plates (extra hard layer, 60 Å, F–254 indicator) were used for all TLC's. Column chromatography was run using Silicycle Ultra Pure Silica Gel (pH 6.5–7.0, 230–400 mesh, 60 Å). NMR spectra were recorded at room temperature (unless otherwise noted) on either a 300 or 500 MHz spectrometer, with working frequencies of 299.9/499.9, 125.7 and 194.3 MHz for the ^{1}H, ^{13}C and ^{7}Li nuclei, respectively. Chemical shifts are reported in ppm relative to tetramethylsilane, using the residual solvent peak as a reference standard. The lithium nucleus was calibrated to the signal of a 0.1 M solution of LiBr in THF–d_8.

Synthesis of Benzyl Cyclopentadienyl Lithium (1)



1

Scheme S1. Synthesis of **1**.

Benzyl cyclopentadiene. This compound was synthesized using a modified literature procedure.[S1] Benzyl bromide (1.00 g, 5.85 mmol) was added to a 250 mL Schlenk flask with a stir bar and dissolved in 30 mL of anhydrous THF. The flask was cooled down to –78 °C and sodium cyclopentadienide (1 equiv., 2.92 mL) was added dropwise to the solution. The mixture was allowed to stir at –78 °C for 5 minutes, and then warmed to 0 °C and stirred for an additional 45 minutes. The mixture was slowly quenched with water at 0 ^{o}C and extracted with dichloromethane (3 x 40 mL). The organic layer was washed three times with water before a final wash with brine. After drying the organic layer over anhydrous Na_2SO_4 and concentrating *in vacuo,* the crude product was purified by flash column chromatography (98:2 hexanes/ethyl acetate) yielding a clear oil (0.152 g, 17%).[S2] The compound was a mixture of 1,3-, 1,4- and 2,4-benzyl cyclopentadiene isomers[S3] and was characterized by comparing its ^{1}H NMR spectrum with that in the literature.[S1] ^{1}H NMR (299.9 MHz, $CDCl_3$, 298 K) δ 7.33–7.19 (m, 10H), 6.42 (m, 3H), 6.28 (m, 1H), 6.17 (m, 1H), 6.02 (m, 1H), 3.75 (s, 2H), 3.72 (s, 2H), 2.99 (d, J = 1.5 Hz, 2H) 2.87 (q, J = 1.5 Hz, 2H) ppm.

Benzyl cyclopentadienyl lithium (1). The benzyl cyclopentadiene mixture (0.151 g, 9.74 mmol) was added to a 100 mL Schlenk flask with a magnetic stir bar and dissolved in dry diethyl ether (3 mL) at 0 ^{o}C. ^{n}BuLi (1.5 equiv., 0.913 mL) was added dropwise to the solution and **1** precipitated out of solution as a white powder. The mixture was allowed to warm gradually to room temperature and **1** was transferred to an air-free filter flask via cannula and rinsed three times with dry diethyl ether, yielding a pure white microcrystalline powder (0.044 g, 28%).[S4] Compound **1** crystallized out of a 1:1 THF/toluene mixture as large colorless needles. ^{1}H NMR (499.9 MHz, THF–d_8) δ 7.20 (d, J = 7.6 Hz, 2H), 7.13 (t, J = 7.3 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 5.55 (t, J = 2.4 Hz, 2H), 5.51 (t, J = 2.7 Hz, 2H), 3.80 (s, 2H) ppm; ^{13}C NMR (125.7 MHz, THF–d_8) δ

147.72, 129.87, 128.93, 125.77, 119.43, 104.45, 103.26, 38.45 ppm; ^{7}Li NMR (194.3 MHz, THF–d_8) δ –8.06 ppm.

NMR Spectra

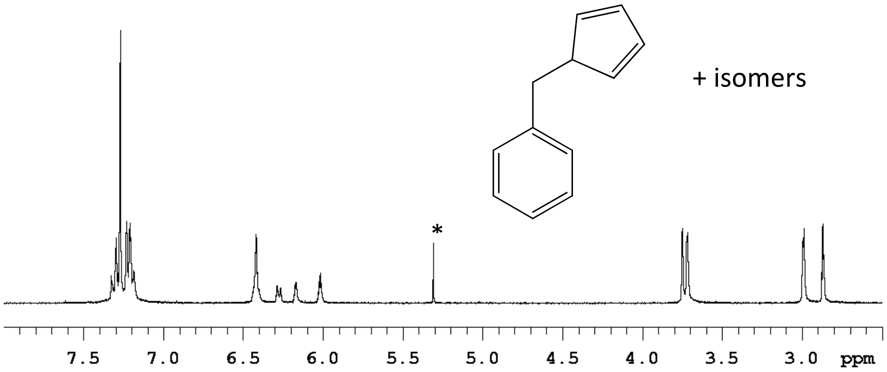


Fig. S1. ^{1}H NMR spectrum (300 MHz, CDCl$_3$, 298 K) of benzyl cyclopentadiene. (* = residual dichloromethane)

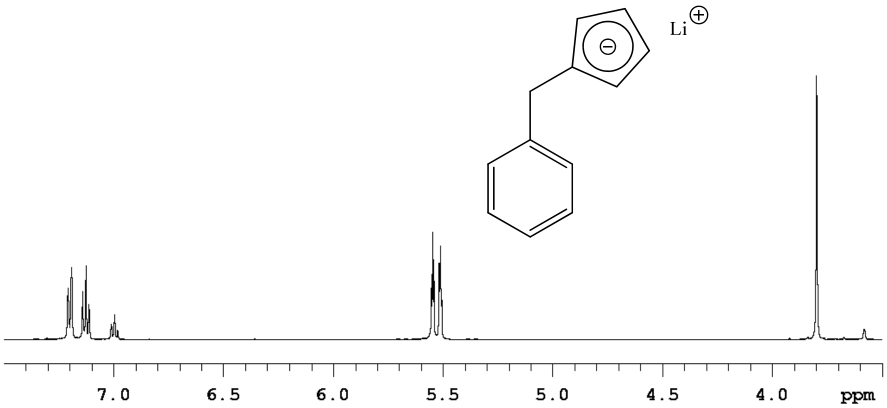


Fig. S2. ^{1}H NMR spectrum (500 MHz, THF–d_8, 298 K) of **1**.

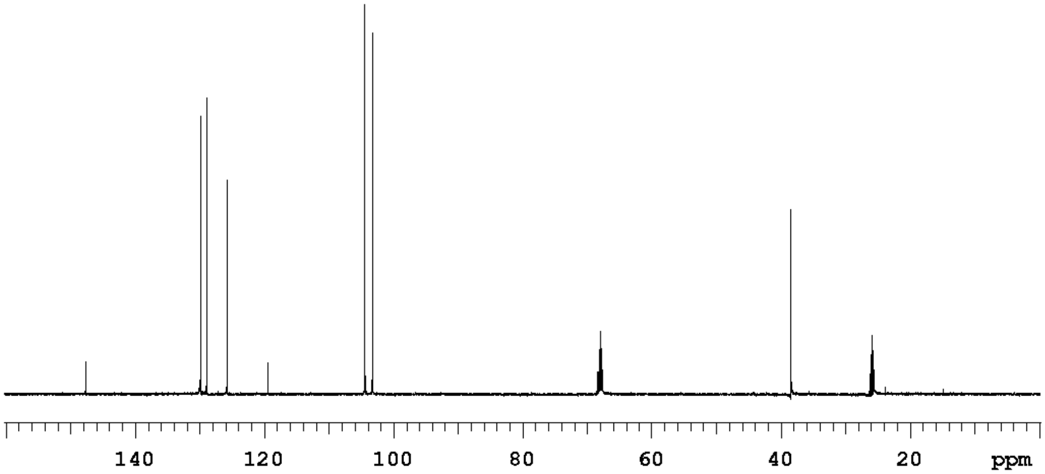


Fig. S3. ^{13}C NMR spectrum (125.7 MHz, THF–d_8, 298 K) of **1**.

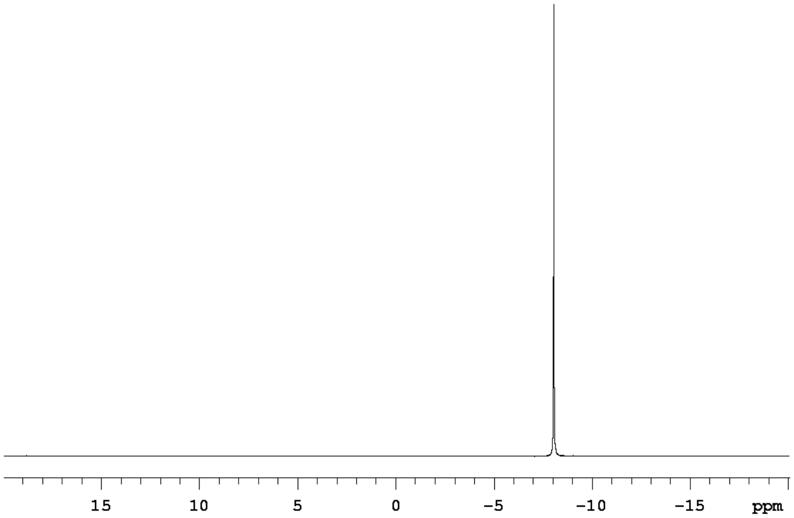


Fig. S4. ^{7}Li NMR spectrum (194.3 MHz, THF–$d_{8,}$ 298 K) of **1**.

Variable Temperature ^{7}Li/^{1}H NMR Spectroscopy

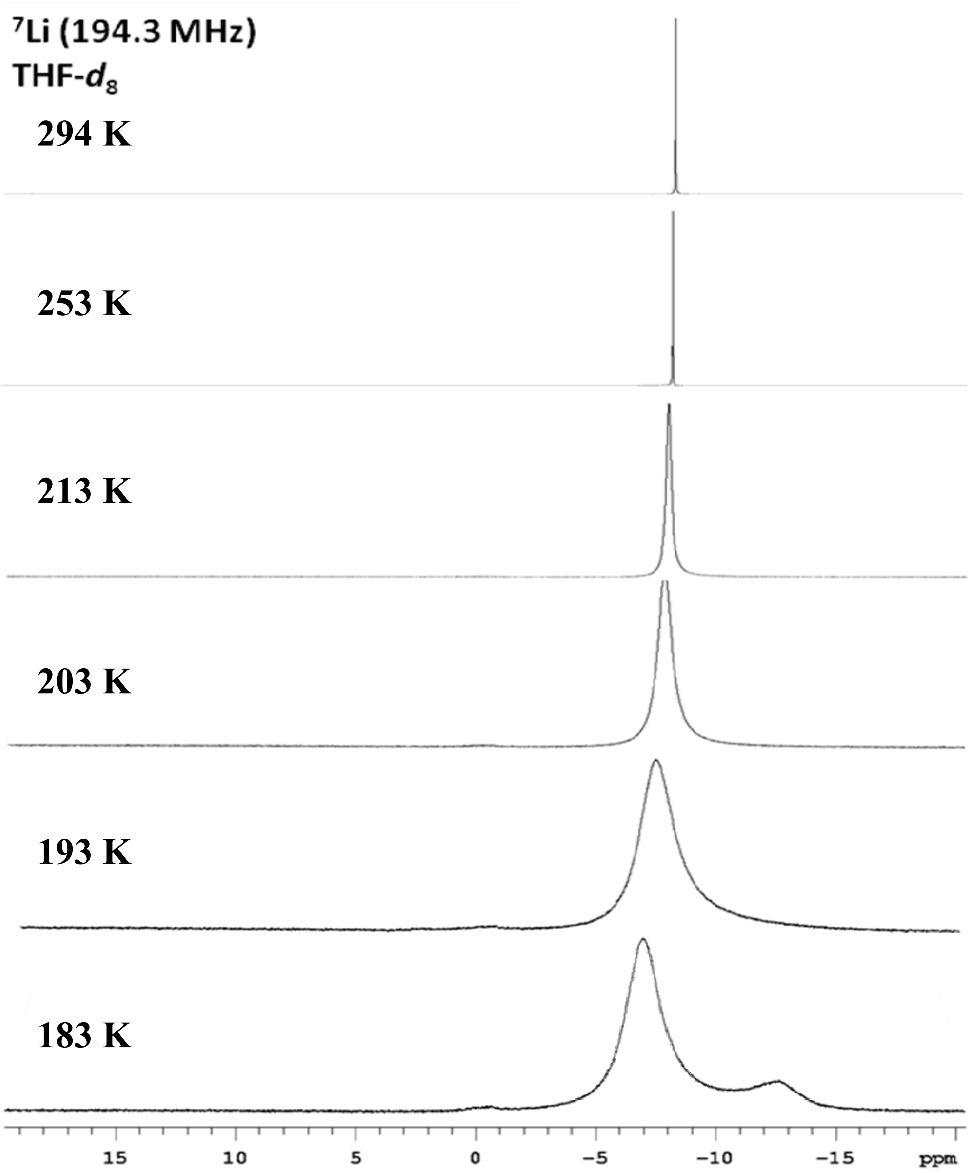


Fig. S5. VT ^{7}Li NMR spectra (194.3 MHz, 0.4 M, THF–d_8) of **1** at incremental temperatures. The signal at ca. 0 ppm (183 K) is from the solvent-separated lithium ion.

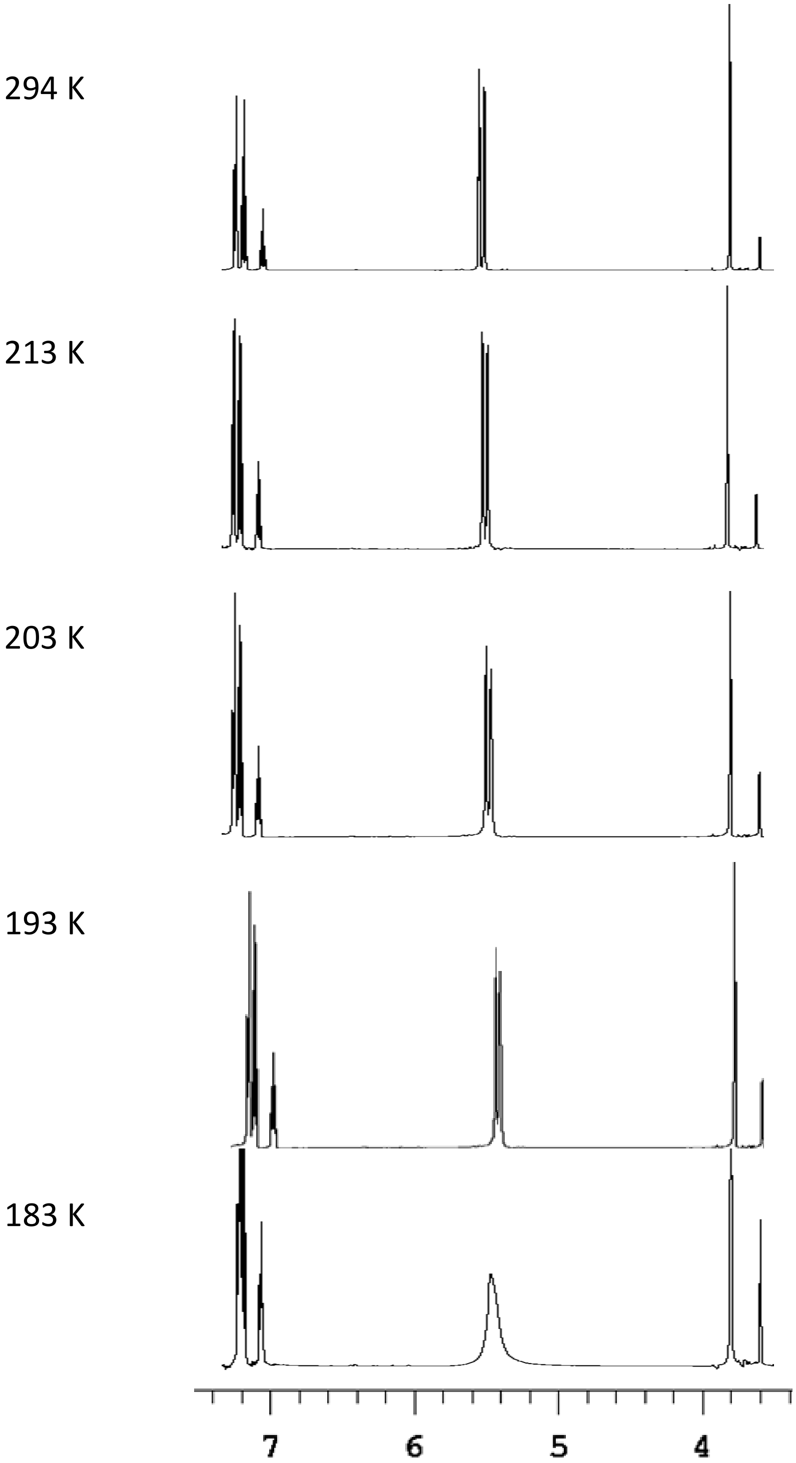


Fig. S6. VT ^{1}H NMR spectra (500 MHz, 0.4 M, THF–d_8) of **1** at incremental temperatures.

X-ray Crystallography Experimental

A colorless needle crystal with dimensions 0.53 x 0.12 x 0.09 mm was mounted on a Nylon loop using very small amount of paratone oil.

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO[S5] where redundancy was expected to be 4.0 and completeness to 0.83 Å to 100%. Cell parameters were retrieved using APEX II software[S6] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[S7] which corrects for Lp. Scaling and absorption corrections were applied using SADABS[S8] multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 and refined by least squares method on F^2, SHELXL- 97, which are incorporated in SHELXTL-PC V 6.10.[S9]

The structure was solved in the space group $P2_12_12_1$ (# 19). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawings are done at 50% ellipsoids.

Table S1. Crystal data and structure refinement for $[^{\mathrm{Bn}}\mathrm{CpLi}]_\infty$ (CCDC 873053).

Empirical formula	C12 H11 Li	
Formula weight	162.15	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.5797(2) Å	α = 90°.
	b = 7.7589(2) Å	β = 90°.
	c = 18.7911(4) Å	γ = 90°.
Volume	959.31(4) Å^3	
Z	4	
Density (calculated)	1.123 Mg/m^3	
Absorption coefficient	0.061 mm^{-1}	
F(000)	344	
Crystal size	0.53 x 0.12 x 0.09 mm^3	
Theta range for data collection	2.17 to 25.37°.	
Index ranges	-5<=h<=7, -9<=k<=9, -22<=l<=22	
Reflections collected	8882	
Independent reflections	1760 [R(int) = 0.0479]	
Completeness to theta = 25.37°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9947 and 0.9680	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1760 / 0 / 118	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0705	
R indices (all data)	R1 = 0.0495, wR2 = 0.0765	
Absolute structure parameter	0(6)	
Largest diff. peak and hole	0.123 and -0.142 e.Å^{-3}	

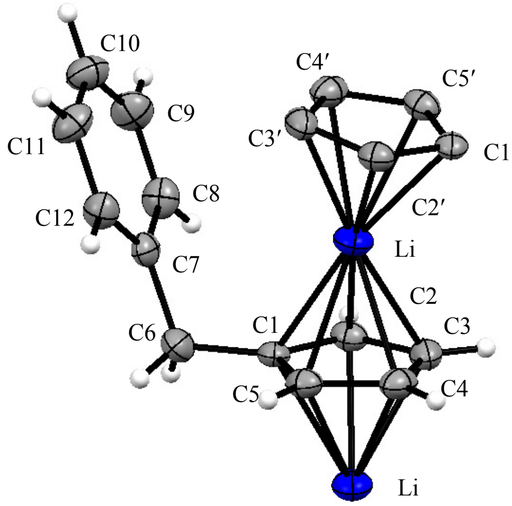


Fig. S7. ORTEP diagram (50% probability ellipsoids) of the repeat unit of the $[^{Bn}CpLi]_\infty$ polymer.

Supporting References

S1. E. H. Licht, H. G. Alt and M. M. Karim, *J. Organomet. Chem.,* 2000, **599**, 275–287.

S2. This reaction was not optimized and the yield is much lower than the reported value in ref. S1. We presume that decomposition is the primary reason for the low yield.

S3. Monosubstituted cyclopentadienes exist in solution as three different structural isomers (1,3-, 1,4- and 2,4-cyclopentadienes) as a result of [1,5]-sigmatropic rearrangements (see ref. H. Jiao, P. v R. Schleyer, *J. Chem. Soc. Perkin Trans.,* 1994, **90**, 1559–1567 and references therein).

S4. The low yield for **1** could be attributed to its slight solubility in diethyl ether, which was used during the washing cycles.

S5. COSMO V1.61, *Software for the CCD Detector Systems for Determining Data Collection Parameters.* Bruker Analytical X-ray Systems, Madison, WI (2009).

S6. APEX2 V2010.11-3. *Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (2010).

S7. SAINT V 7.68A *Software for the Integration of CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (2010).

S8. SADABS V2008/2 *Program for absorption corrections using Bruker-AXS CCD based on the method of Robert Blessing*; R. H Blessing, *Acta Cryst.,* 1995*,* **A51***,* 33-38.

S9. G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112–122.