

Aggregation and Reactivity of Phenyllithium Solutions

Hans J. Reich,* D. Patrick Green, Marco A. Medina, Wayne S. Goldenberg, Birgir Ö. Gudmundsson,

Robert R. Dykstra, and Nancy H. Phillips

Department of Chemistry, University of Wisconsin-Madison,

Madison, WI 53706

Supporting Information**List of Figures.**

- Figure S1.** Lineshape simulations of the *ipso* carbon signal of $(\text{PhLi})_4$ in ether at $-106\text{ }^\circ\text{C}$.
- Figure S2.** Variable concentration study of PhLi in ether (0.01-0.16 M) at $-108\text{ }^\circ\text{C}$.
- Figure S3.** Lineshape simulations of the *meta* and *para* carbon signals of PhLi for a variable temperature ^{13}C NMR study of 0.08 M PhLi in ether.
- Figure S4.** A plot of $\ln(k_1/T)$ vs. $1/T$ for 0.08 M PhLi in ether.
- Figure S5.** ^{13}C and ^6Li NMR spectra of a THF titration of 0.08 M PhLi in ether at $-113\text{ }^\circ\text{C}$.
- Figure S6.** ^{13}C and ^6Li NMR spectra of a dioxolane titration of 0.08 M PhLi in ether at $-115\text{ }^\circ\text{C}$.
- Figure S7.** Variable concentration ^{13}C NMR study of PhLi in THF at $-100\text{ }^\circ\text{C}$.
- Figure S8.** Variable temp. ^6Li NMR study of 0.16 M Ph^6Li in 1:1 THF/ Me_2O with 0.5 equiv of TMEDA.
- Figure S9.** ^{13}C NMR spectra of 0.08 M PhLi in THF at $-105\text{ }^\circ\text{C}$ with the addition of DMPU.

List of Tables.

- Table S1.** Data from variable concentration study of PhLi in ether at $-108\text{ }^\circ\text{C}$ by ^{13}C NMR spectroscopy.
- Table S2.** Data obtained by lineshape analysis of variable temperature ^{13}C NMR spectra of PhLi in ether.
- Table S3.** Data from variable concentration study of PhLi in THF at $-100\text{ }^\circ\text{C}$ by ^{13}C NMR spectroscopy.
- Table S4.** Data obtained by lineshape analysis of variable temperature ^{13}C NMR spectra of PhLi in THF.

Supporting Information Experimental Section.

NMR Study of PhLi in Ether. An oven dried 10 mm NMR tube was fitted with a 9 mm i. d. rubber septum and flushed with N₂. The rubber septum was wrapped with parafilm, 3.58 mL of ether was added and the tube cooled to -78 °C. After 10 min, 416 μL of 0.77 M Ph⁶Li in ether was added, the tube was shaken and the septum was sealed with grease. At all times the NMR tube was stored at -78 °C. Before the experiment was begun, the shim values were checked and adjusted for CDCl₃. The instrument was unlocked and the sweep was turned off. The NMR probe was cooled to -106 °C and the sample was inserted into the probe. After 10 min at -106 °C, optimization of the FID of C-1 of ether was done. Both ¹³C (Fig. 1) and ⁶Li NMR spectra were acquired. Lineshape simulations of the *ipso* carbon signals are presented below in Fig. S1.

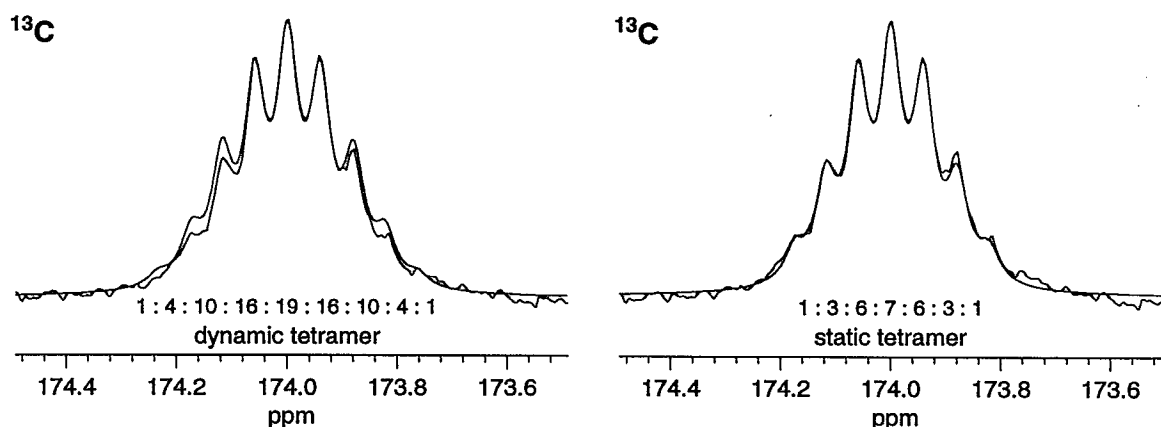


Figure S1. Lineshape simulations of the *ipso* carbon signal of (PhLi)₄ in ether -106 °C.

Variable Concentration NMR Study of PhLi in Ether. An oven dried 10 mm NMR tube was fitted with a 9 mm i. d. rubber septum and flushed with N₂. The rubber septum was wrapped with parafilm, 3.58 mL of ether was added and the tube cooled to -78 °C. After 10 min, 416 μL of 0.77 M Ph⁶Li in ether was added, the tube was shaken and the septum was sealed with grease. At all times the NMR tube was stored at -78 °C. Before the experiment was begun, the shim values were checked and adjusted for CDCl₃. The instrument was unlocked and the sweep was turned off. The NMR probe was cooled to -108 °C and the sample was inserted into the probe. After 10 min at -108 °C, optimization of the FID of C-1 of ether was done. Both ¹³C and ⁶Li NMR spectra were acquired. The sample was removed and stored at -78 °C. The grease from the septum top was removed, 2.0 mL of the Ph⁶Li solution was withdrawn with a syringe, 2.0 mL of ether was added (to make a 0.08 M solution), and the septum greased. The NMR tube was placed in the

probe and after 10 min both ^{13}C and ^6Li NMR spectra were acquired. This procedure was repeated three times to make solutions at 0.04 M, 0.02 M and 0.01 M. The data is presented below in Table S1 and in Fig. S2.

Table S1. Data from variable concentration study of PhLi in ether at $-108\text{ }^\circ\text{C}$ by ^{13}C NMR spectroscopy.

[PhLi] (M)	Area (dim/tet)	[(PhLi) ₂] (M)	[(PhLi) ₄] (M)	K _{eq} (L mol ⁻¹)
0.02	3.00	0.0075	0.0013	23.1
0.04	1.82	0.013	0.0035	20.7
0.08	1.13	0.021	0.0095	21.5
0.16	0.60	0.030	0.025	27.8

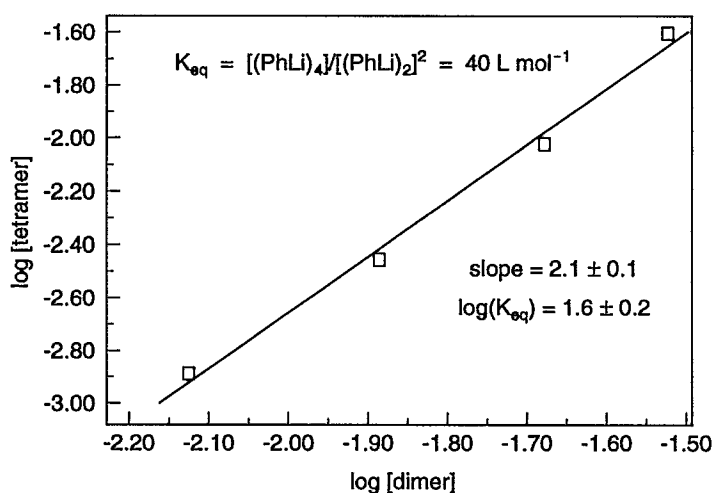
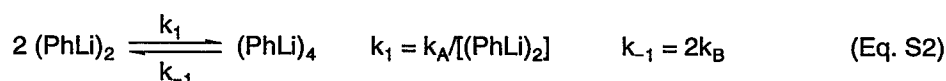


Figure S2. Variable concentration study of PhLi in ether (0.01-0.16 M) at $-108\text{ }^\circ\text{C}$ (integration of ^{13}C NMR spectra).

Variable Temperature NMR Study of 0.08 M PhLi in Ether. An oven dried 10 mm NMR tube was fitted with a 9 mm i. d. rubber septum and flushed with N_2 until the tube was cool. The rubber septum was wrapped with parafilm, 3.58 mL of ether was added and the tube cooled to $-78\text{ }^\circ\text{C}$. After 10 min, 416 μL of 0.77 M Ph^6Li in ether was added, the tube was shaken and the septum was sealed with grease. The NMR tube was stored at $-78\text{ }^\circ\text{C}$. Before the experiment was begun, the shim values were checked and adjusted for CDCl_3 . The instrument was unlocked and the sweep was turned off. The NMR probe was cooled to $-111\text{ }^\circ\text{C}$ and the sample was inserted into the probe. After 10 min at $-111\text{ }^\circ\text{C}$, optimization of the FID of C-1 of ether

was done. Both ^{13}C and ^6Li NMR spectra were acquired. The probe temperature was increased to $-95\text{ }^\circ\text{C}$, and after 10 min both ^{13}C and ^6Li NMR spectra were acquired. This procedure was repeated at $-90\text{ }^\circ\text{C}$, $-84\text{ }^\circ\text{C}$, and $-67\text{ }^\circ\text{C}$. The spectra are shown in Fig. 3. The NMR rate constants k_A and k_B were obtained by lineshape simulation using WinDNMR (Fig S3).^[S1] The spectra used had 2 Hz line broadening to improve the signal to noise. Lineshape fitting without line broadening gave equivalent results. The kinetic constants k_1 and k_{-1} are defined in Eq. S1 and S2. The data obtained is reported in Table S2. A plot of Eq. S3 gave a slope of -4.6 ± 0.4 and an intercept of 27 ± 2 (Fig. S4). The resulting thermodynamic data for the dimer to tetramer interconversion of PhLi is shown below:

[PhLi]	ΔH_1^\ddagger	ΔS_1^\ddagger	ΔH_{-1}^\ddagger	ΔS_{-1}^\ddagger
(M)	(kcal/mol)	(eu)	(kcal/mol)	(eu)
0.08	9.1 ± 0.6	6 ± 4	9.3 ± 0.6	0 ± 4



$$\ln(k/T) = -(\Delta H/RT) + (\Delta S/R) + 23.76 \quad (\text{Eq. S3})$$

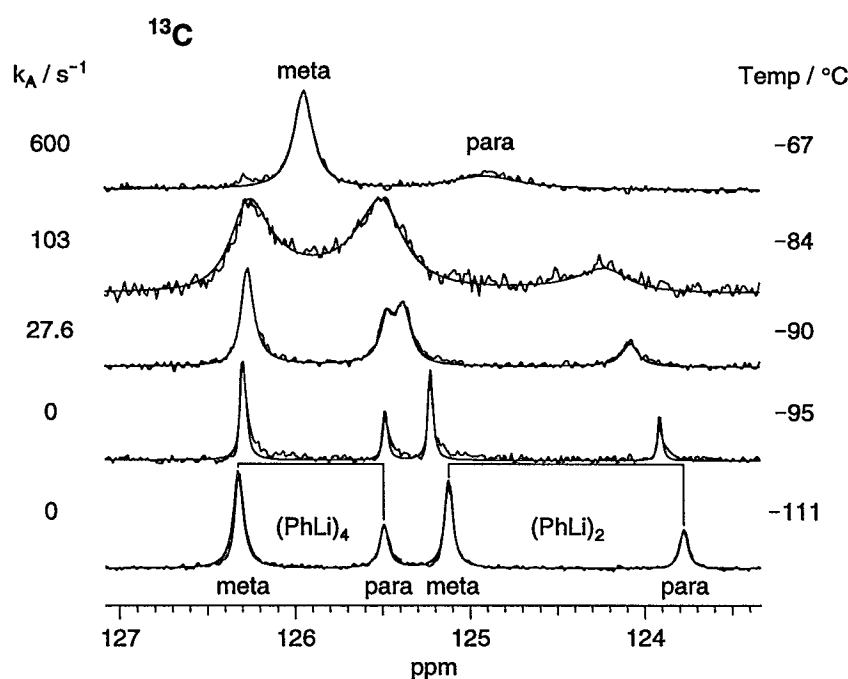


Figure S3. Lineshape simulations of the *meta* and *para* carbon signals of PhLi for a variable temperature ^{13}C NMR study of 0.08 M PhLi in ether.

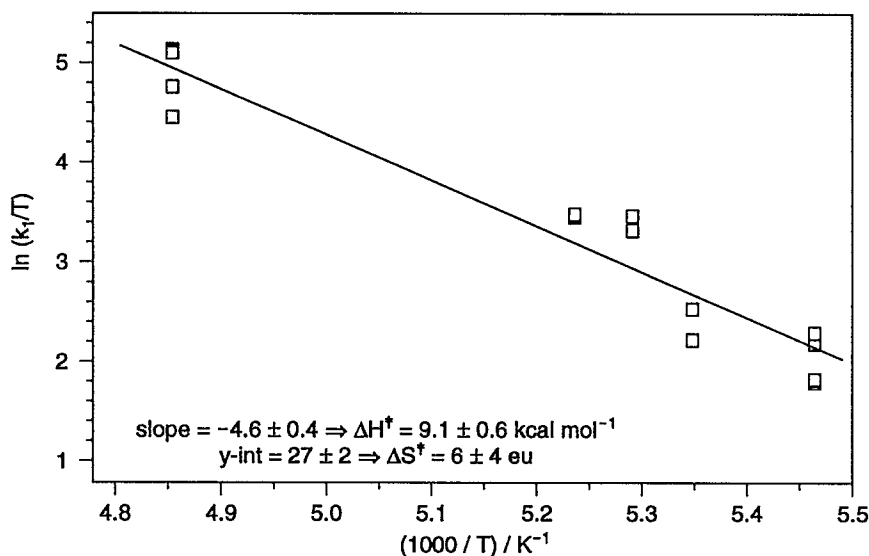


Figure S4. A plot of $\ln(k_f/T)$ vs. $1/T$ for 0.08 M PhLi in ether.

Table S2. Data obtained by lineshape analysis of variable temperature ^{13}C NMR spectra of PhLi in ether (Fig. 2).

T (K)	P(B)/P(A) ^[a]	[dim] (M)	[tet] (M)	k_A (sec ⁻¹)	k_B ^[b] (sec ⁻¹)	k_1 (M ⁻¹ sec ⁻¹)	k_{-1} (sec ⁻¹)	K_{eq} ^[c] (L/mol)
<i>[PhLi] = 0.08 M, ortho carbon signals:</i>								
183	1.36	0.0169	0.0115	30.6	22.4	1810	44.8	40.3
189	1.26	0.0177	0.0111	92.5	73.5	5220	147	35.5
206	1.35	0.0170	0.0115	575	425	33800	850	39.8
<i>[PhLi] = 0.08 M, meta and para carbon signals:</i>								
183	1.35	0.0170	0.0115	27.6	20.4	1620	40.9	39.5
189	1.33	0.0172	0.0114	103	77.2	5990	154	38.8
206	1.33	0.0172	0.0114	600	450	34900	901	38.8

[a] Populations of dimer (A) and tetramer (B), [b] $k_B = (P_A/P_B)k_A$, [c] $K_{eq} = [(\text{PhLi})_4]/[(\text{PhLi})_2]^2$

Solutions of PhLi in Ether Containing Donor Additives Monitored by NMR (e. g., TMEDA). An oven dried 10 mm NMR tube was fitted with a 9 mm i. d. rubber septum and flushed with N_2 until the tube was cool. The rubber septum was wrapped with parafilm, 3.58 mL of ether was added and the tube cooled to $-78\text{ }^\circ\text{C}$. After 10 min, 416 μL of 0.77 M Ph^6Li in ether was added, the tube was shaken and the septum was sealed with grease. The NMR tube was stored at $-78\text{ }^\circ\text{C}$. Before the experiment was begun, the shim values were checked and adjusted for CDCl_3 . The instrument was unlocked and the sweep was turned off. The NMR

probe was cooled to $-111\text{ }^{\circ}\text{C}$ and the sample inserted into the probe. After 10 min at $-111\text{ }^{\circ}\text{C}$, optimization of the FID of C-1 of ether was done. Both ^{13}C and ^6Li NMR spectra were acquired. The sample was removed and stored at $-78\text{ }^{\circ}\text{C}$. The grease from the septum top was removed, 0.25 equiv of TMEDA (12.1 μL , 80.1 μmol) was added and the septum greased. The NMR tube was placed in the probe and after 10 min, both ^{13}C and ^6Li NMR spectra were acquired. This process was repeated for 0.4, 0.5, 0.75, 1.0, 1.25, 1.5 and 2.0 equiv of TMEDA. The spectra are shown in Fig. 7.

The effect of donor additives on PhLi in ether were also performed with 2,5-dimethyltetrahydrofuran (Fig. 5), THF (Fig. 5 and S5), dioxolane (Fig. 5 and S6), DME (Fig. 6), PMDTA (spectra not shown) and HMPA (Fig. 11).

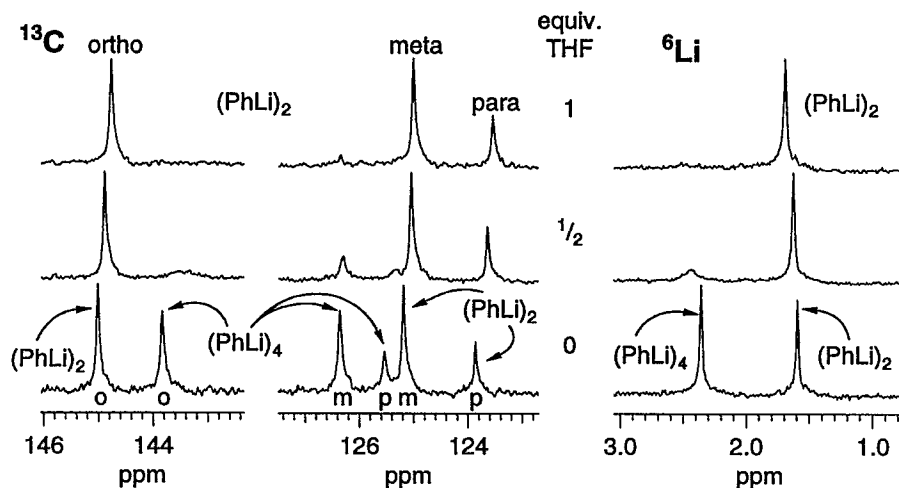


Figure S5. ^{13}C and ^6Li NMR spectra of a THF titration of 0.08 M PhLi in ether at $-113\text{ }^{\circ}\text{C}$.

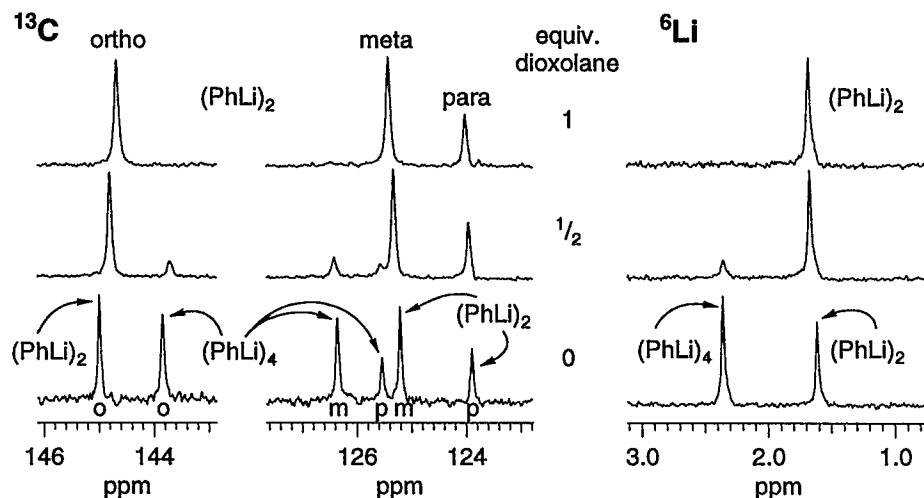


Figure S6. ^{13}C and ^6Li NMR spectra of a dioxolane titration of 0.08 M PhLi in ether at $-115\text{ }^{\circ}\text{C}$.

NMR Study of PhLi in THF. An oven dried 10 mm NMR tube was fitted with a 9 mm i. d. rubber septum and flushed with N₂. The rubber septum was wrapped with parafilm, 3.84 mL of ether was added and the tube cooled to -78 °C. After 10 min, 159 μL of 2.01 M Ph⁶Li in THF was added, the tube was shaken and the septum was sealed with grease. At all times the NMR tube was stored at -78 °C. Before the experiment was begun, the shim values were checked and adjusted for CDCl₃. The instrument was unlocked and the sweep was turned off. The NMR probe was cooled to -111 °C and the sample was inserted into the probe. After 10 min at -111 °C, optimization of the FID of C-3 of THF was done. Both ¹³C and ⁶Li NMR spectra were acquired. The ¹³C spectrum is shown in Fig. 3.

Variable Concentration NMR Study of PhLi in THF. A series of oven dried 10 mm NMR tubes were fitted with 9 mm i. d. rubber septa and flushed with N₂ until the tubes were cool. The desired amount of 2.2 M PhLi in THF was added via syringe and diluted with THF to give a total volume of 3.0 mL. The series of samples contained nominal concentrations of PhLi between 0.01 and 0.13 M. ¹³C and ⁷Li NMR spectra were measured at -100 °C. The relative amounts of dimer and monomer were determined by integration of the ortho carbons. Each sample was quenched with 100 μL of MeSSMe and 10 - 20 μL of n-undecane was accurately weighed into the tube (to serve as a GC standard). Pentane (0.5 mL) and saturated NH₄Cl solution (0.2 mL) were added and the solution was dried over Na₂SO₄. Subsequent analysis by capillary GC gave the absolute concentration of PhLi in the samples. The data is presented in Table S3 and the spectra in Fig. S7.

Table S3. Data from variable concentration study of PhLi in THF at -100 °C by ¹³C NMR spectroscopy.

[PhLi] (M)	Area (mon/dim)	[(PhLi) ₁] (M)	[(PhLi) ₂] (M)	K _{eq} (L mol ⁻¹)
0.008	2.6	0.0057	0.0011	33.9
0.012	2.04	0.0077	0.0019	31.8
0.017	1.48	0.0103	0.0035	33.0
0.018	1.25	0.0098	0.0039	41.0
0.044	0.89	0.0211	0.0119	26.6
0.063	0.54	0.0222	0.0204	41.6
0.075	0.545	0.0265	0.0243	34.6
0.078	0.525	0.027	0.0261	35.3
0.092	0.47	0.029	0.0313	36.7
0.127	0.40	0.0364	0.0453	34.2

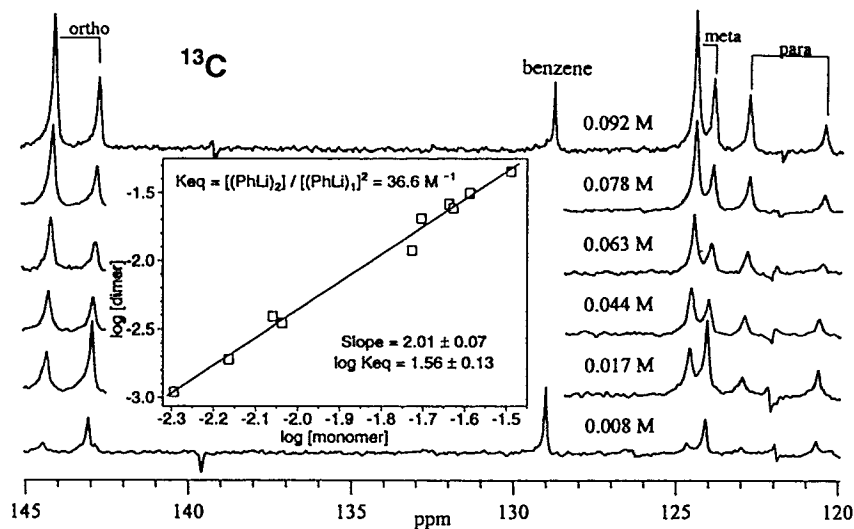


Figure S7. Variable concentration ^{13}C NMR study of PhLi in THF at $-100\text{ }^{\circ}\text{C}$.

Variable Temperature NMR Study of PhLi in THF. Solutions of PhLi (0.075 and 0.127 M) in THF were prepared as above. ^{13}C NMR spectra were measured at 6 temperatures (Fig. 4). The NMR rate constants k_A and k_B were obtained by lineshape simulation using DNMR5.^[S2] The kinetic constants k_1 and k_{-1} are defined in Eq. S4 and S5. The data obtained is reported in Table S4. A plot of Eq. S3 gave a slope of 3.7 ± 0.1 and an intercept of 24.5 ± 0.5 . The resulting thermodynamic data for the monomer to dimer interconversion of PhLi is shown below:

[PhLi] (M)	ΔH_1^\ddagger (kcal/mol)	ΔS_1^\ddagger (eu)	ΔH_{-1}^\ddagger (kcal/mol)	ΔS_{-1}^\ddagger (eu)
0.075	7.5 ± 0.1	3.6 ± 1	7.1 ± 0.1	-7.3 ± 1
0.127	7.4 ± 0.1	1.5 ± 1	6.9 ± 0.1	-8.4 ± 1

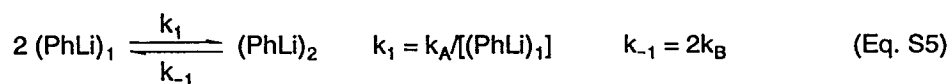
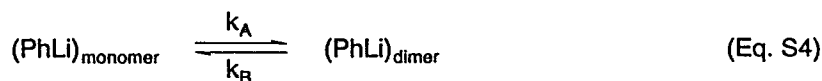


Table S4. Data obtained by lineshape analysis of variable temperature ^{13}C NMR spectra of PhLi in THF (Fig. 4).

T (K)	P(B)/P(A) ^[a]	[mon] (M)	[dim] (M)	k_A (sec ⁻¹)	k_B ^[b] (sec ⁻¹)	k_1 (M ⁻¹ sec ⁻¹)	k_{-1} (sec ⁻¹)	K_{eq} ^[c] (L/mol)
<i>[PhLi] = 0.075 M:</i>								
155.9	1.65	0.028	0.0234	17	10.3	600	20.6	29.3
163.7	1.85	0.0265	0.0243	50	27.3	1890	54.6	34.6
166.4	1.9	0.0257	0.0247	82	42.7	3190	85.4	37.4
170.5	1.9	0.0257	0.0247	187	97.2	7260	194	37.4
175.9	1.95	0.0254	0.0248	253	130	9960	260	38.4
183.8	1.95	0.0254	0.0248	720	369	28300	740	38.4
<i>[PhLi] = 0.127 M:</i>								
160.3	2.35	0.038	0.045	24	10.2	633	20.4	31
168.6	2.45	0.036	0.045	70	28.1	1923	56.2	34
172.5	2.4	0.037	0.045	114	47.1	3070	94.2	32.6
180.4	2.6	0.035	0.046	368	142	10400	284	36.8
188.6	2.75	0.034	0.0465	740	269	21800	538	40.5
197.9	2.75	0.034	0.0465	2102	765	62000	1530	40.5

[a] Populations of monomer (A) and dimer (B), [b] $k_B = (P_A/P_B)k_A$, [c] $K_{eq} = [(\text{PhLi})_2]/[(\text{PhLi})_1]^2$

Solutions of PhLi in THF Containing Donor Additives Monitored by NMR (e. g., TMEDA). An oven dried 10 mm NMR tube was fitted with a 9 mm i. d. rubber septum and flushed with N_2 until the tube was cool. The rubber septum was wrapped with parafilm, 3.84 mL of THF was added and the tube cooled to $-78\text{ }^\circ\text{C}$. After 10 min, 159 μL of 2.01 M Ph^6Li in THF was added, the tube was shaken and the septum was sealed with grease. The NMR tube was stored at $-78\text{ }^\circ\text{C}$. Before the experiment was begun, the shim values were checked and adjusted for CDCl_3 . The instrument was unlocked and the sweep was turned off. The NMR probe was cooled to $-115\text{ }^\circ\text{C}$ and the sample inserted into the probe. After 10 min at $-115\text{ }^\circ\text{C}$, optimization of the FID of C-3 of THF was done. Both ^{13}C and ^6Li NMR spectra were acquired. The sample was removed and stored at $-78\text{ }^\circ\text{C}$. The grease from the septum top was removed, 0.50 equiv of TMEDA (48.3 μL , 320 μmol) was added and the septum greased. The NMR tube was placed in the probe and after 10 min, both ^{13}C and ^6Li NMR spectra were acquired. This process was repeated for 1.0, 2.0, 4.0, 6.0 and 10.0 equiv of TMEDA. The spectra are shown in Fig. 8 and S8.

The effect of donor additives on PhLi in THF were also performed with PMDTA (Fig. 9), HMTTA

(spectra not shown), HMPA (Fig. 10 and 11), DMPU (Fig. S9) and 12-crown-4 (Fig. 12).

Note: Special precautions were needed for the DMPU titration, since PhLi reacts with DMPU at a significant rate at $-78\text{ }^{\circ}\text{C}$. Unlike our other NMR experiments, this experiment required each point in the DMPU titration to be a freshly prepared sample that was immediately placed into the NMR probe at $-105\text{ }^{\circ}\text{C}$.

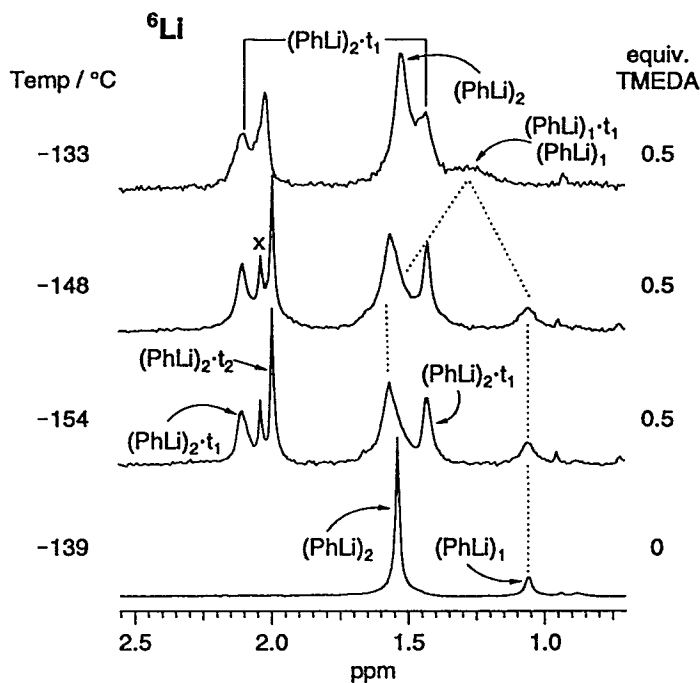


Figure S8. Variable temp. ${}^6\text{Li}$ NMR study of 0.16 M Ph^6Li in 1:1 THF/ Me_2O with 0.5 equiv of TMEDA.

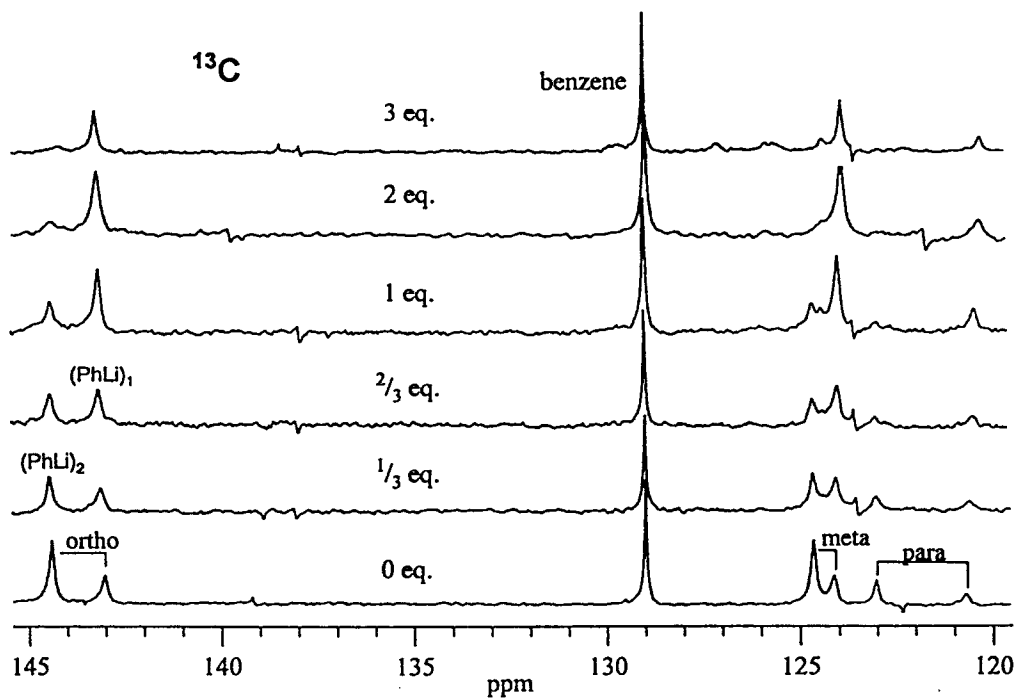


Figure S9. ${}^{13}\text{C}$ NMR spectra of 0.08 M PhLi in THF at $-105\text{ }^{\circ}\text{C}$ with the addition of DMPU.

PhLi Solutions in THF/Dimethyl Ether for NMR Studies. An oven dried 10 mm NMR tube was fitted with a 9 mm i. d. rubber septum and flushed with N₂ until the tube was cool. The rubber septum was wrapped with parafilm, THF was added and the tube cooled to -78 °C. The desired amount of PhLi in THF (stock solution) was slowly added and the tube was shaken briefly. Dry Me₂O was condensed into the NMR tube such that the total volume would be 3.0 mL (assuming volumes to be additive). The appropriate amount of donor additive was syringed into the tube and the resulting solution was gently shaken to insure proper mixing. The sample was transferred to the pre-cooled NMR probe, and the desired spectra were acquired.

Effect of Donor Additives on the Reaction of PhLi with 2-(Methylthio)furan (e. g., HMPA). Six long-necked 5 mL round-bottom flasks were dried, equipped with septa and stir bars, and purged with N₂. HMPA and THF were added in the following amounts: 1) no HMPA added, 2.1 mL; 2) 26.1 μL (0.15 mmol), 2.08 mL; 3) 52.2 μL (0.30 mmol), 2.05 mL; 4) 78.3 μL (0.45 mmol), 2.02 mL; 5) 104.4 μL (0.60 mmol), 2.0 mL; 6) 156.6 μL (0.90 mmol), 1.95 mL. The solutions were cooled to -78 °C while keeping positive N₂ pressure in each flask. Stock PhLi in THF solution (0.90 M, 0.33 mL, 0.30 mmol; 0.11 M n-undecane, 0.0363 mmol) was added down the side of each flask, and the solutions were mixed thoroughly. After 10 min at -78 °C, 33.3 μL of 2-(methylthio)furan (0.30 mmol) was added using a microsyringe. After stirring at -78 °C for 60.0 min, each solution was quenched with 100 μL of MeSSMe (1.1 mmol). The cold bath was removed and the flasks were allowed to warm to room temperature while stirring. Saturated NH₄Cl solution (0.2 mL) and pentane (0.5 mL) were added to each, and the solutions were dried over Na₂SO₄. Subsequent analysis by capillary GC for PhSMe and 2,5-bis(methylthio)furan provided the following results: equiv HMPA, % reaction, % recovery; 0, 0.7, 96; 0.5, 26, 94; 1.0, 54, 91; 1.5, 79, 93; 2.0, 87, 97; 3.0, 93, 98. The data is plotted in Fig. 15.

The Effect of Donor Additives on the Product Ratio Obtained from the Reaction of PhLi with Methyl Isopropyl Disulfide (e. g., HMPA). Three long-necked 5 mL round-bottom flasks were dried, equipped with septa and stir bars, and purged with N₂. Into each was added HMPA and THF in the following amounts: 1) 156.6 μL (0.90 mmol), 2.05 mL; 2) 208.8 μL (1.20 mmol), 2.0 mL; 3) 261 μL (1.5 mmol), 1.95 mL. The solutions were cooled to -78 °C (keeping positive N₂ pressure in each flask) and stock PhLi in THF solution (0.90 M, 0.33 mL, 0.30 mmol; 0.11 M n-undecane, 0.0363 mmol) was added to each solution. After stirring at -78 °C for 10 min, each solution was quenched with 75 μL of isopropyl methyl disulfide (0.6 mmol) and allowed to warm to room temperature. Saturated NH₄Cl solution (0.20 mL) and pentane (0.50 mL) were added to each and the solutions were dried over Na₂SO₄. Analysis by capillary GC gave the

following results: equiv HMPA, % recovery, ratio (5/6); 3.0, 95, 3.1; 4.0, 93, 2.6; 5.0, 95, 3.2. The data is shown in Eq. 3.

Effect of Donor Additives on the Reaction of PhLi with 3-Methylthiophene (e. g., 12-Crown-4).

Eight long-necked 5 mL round-bottom flasks were dried, equipped with septa and stir bars, and purged with N₂. THF (2.1 mL), and the following amounts of 12-crown-4 were added to each flask: 1) no crown added; 2) 2.4 μL (0.015 mmol); 3) 4.9 μL (0.030 mmol); 4) 7.3 μL, (0.045 mmol); 5) 12.1 μL (0.075 mmol); 6) 17.0 μL (0.105 mmol); 7) 24.3 μL (0.150 mmol); 8) 48.5 μL, (0.300 mmol). The flasks were cooled to -78 °C keeping positive N₂ pressure in each. Stock PhLi in THF solution (0.90 M, 0.33 mL, 0.30 mmol; 0.11 M n-undecane, 0.0363 mmol) was added slowly down the side of each flask, and the resulting solutions were mixed thoroughly. After stirring at -78 °C for 10 min, 3-methylthiophene (29 μL, 0.30 mmol) was added to each flask. The solutions were quenched with MeSSMe (100 μL, 1.1 mmol) after the 90 min reaction time, except the reaction without 12-crown-4 which was quenched after 180 min. The flasks were allowed to warm to room temperature, and saturated NH₄Cl solution (0.20 mL) was added to each. The solutions were dried over Na₂SO₄, and analyzed by capillary GC which gave the following results: equiv crown, % reaction, % recovery, ratio (8/9); 0, 4.9, 102, 6.40; 0.05, 4.9, 95, 3.98; 0.10, 7.2, 95, 3.40; 0.15, 10.3, 91, 3.25; 0.25, 15.3; 93, 2.90; 0.35, 20.9, 93, 2.75; 0.50, 28.2, 92, 2.70; 1.0, 58.9, 90, 2.40. The data is shown in Eq. 4 and plotted in Fig. 16.

Supporting Information References.

- S1. Reich, H. J. "WinDNMR: Dynamic NMR Spectra for Windows," *J. Chem. Ed.: Software, Series D.*, **1996**, Vol. 3D, No. 2. WinDNMR requires files to be in the Lybrics file format; the conversion from Bruker to Lybrics format was performed using PCNMR: Bemis, J. M. "PCNMR for Windows," *J. Chem. Ed.: Software*, **1994**, Special Issue 7.
- S2. Stephensen, D. S.; Binsch, G. *Quantum Chem. Prog. Exch.* **1978**, *10*, 365.