TMP (2,2,6,6-Tetramethylpiperidide)-Aluminate Bases: Lithium-Mediated Alumination or Lithiation/Alkylaluminium-Trapping Reagents?

Supporting Information

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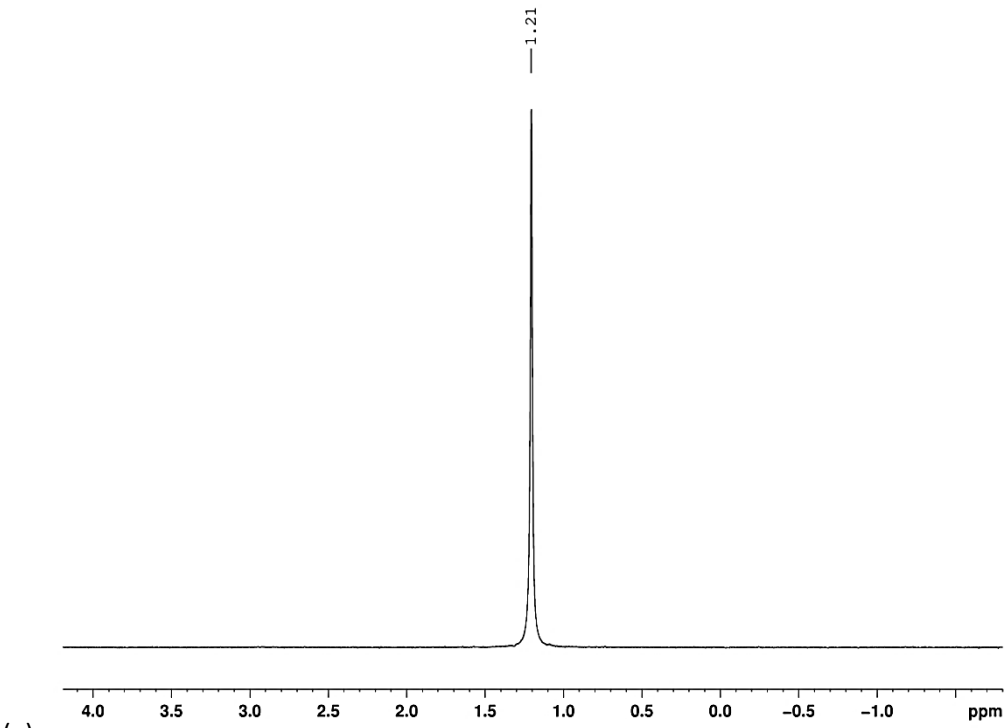
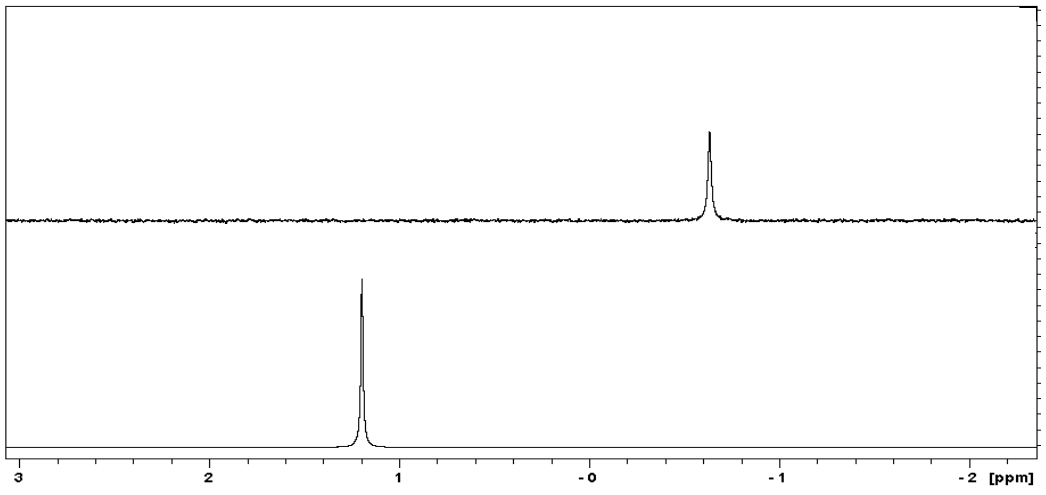


(a)



(b)

Figure S1. ^{7}Li NMR spectra ([D_8]THF, 300 K) of (a) crystalline [{Li(THF)$_4$}$^+${Al(TMP)(^{i}Bu)$_3$}$^-$] **1·(THF)$_4$** and (b) [{Li(THF)$_4$}$^+${Al(TMP)(^{i}Bu)$_3$}$^-$] **1·(THF)$_4$** at different concentrations (top = ~1 mg/mL, bottom = ~30 mg/mL) showing the changes in chemical shift of the [Li(THF)$_4$]$^+$ cation with concentration.

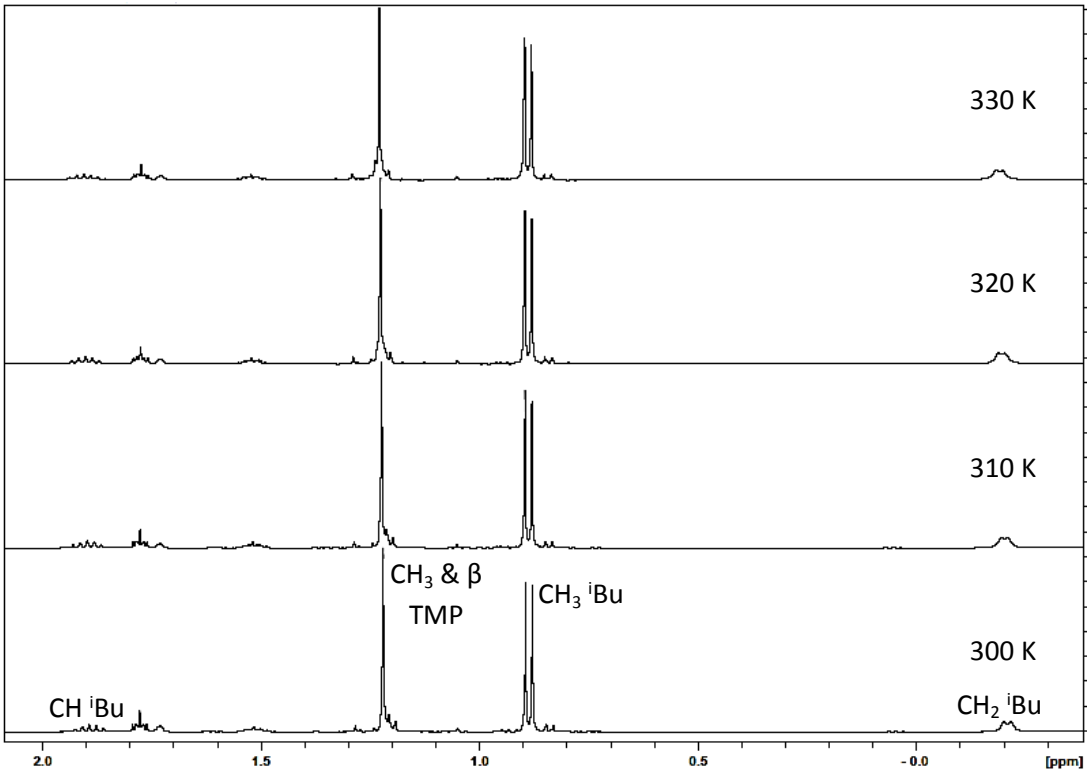


Figure S2. ^{1}H NMR spectra ([D_8]THF) of the variable temperature study performed on crystalline [{Li(THF)$_4$}$^+${Al(TMP)(^{i}Bu)$_3$}$^-$] **1·(THF)$_4$**.

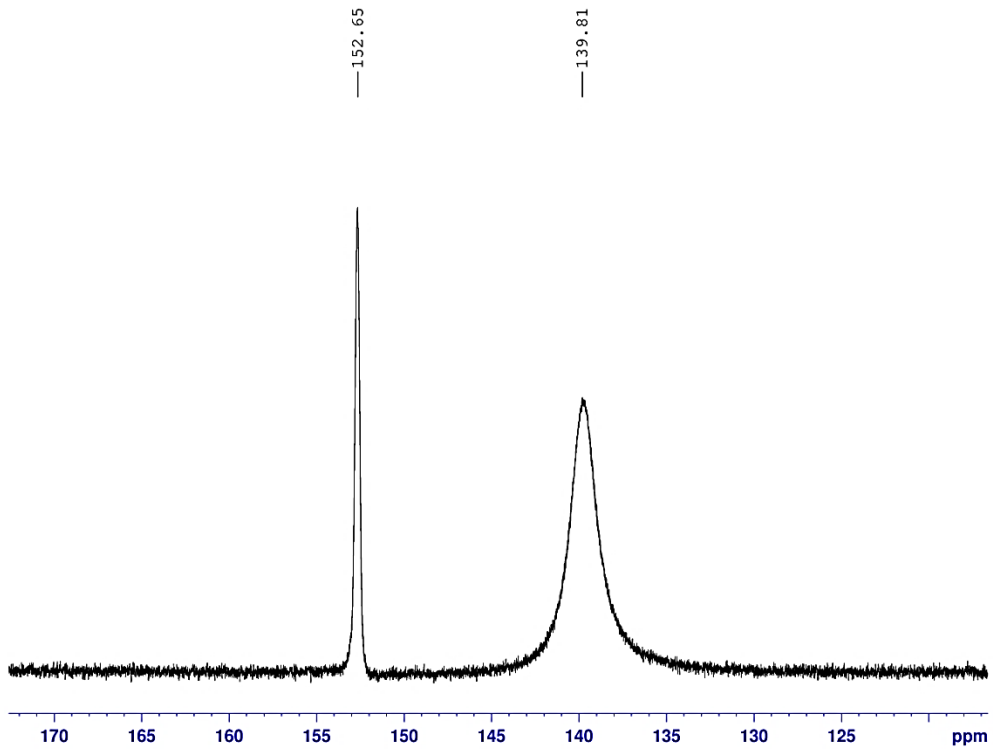


Figure S3. ^{27}Al NMR spectrum ([D_8]THF, 300 K) of crystalline [{Li(THF)$_4$}$^+${Al(TMP)(^{i}Bu)$_3$}$^-$] **1·(THF)$_4$** showing the ^{27}Al resonance at 139.81 ppm. Note that a small amount of [{Li(THF)$_4$}$^+${Al(^{i}Bu)$_4$}$^-$] (**3**) (at 152.65 ppm) was also present in the reaction mixture.

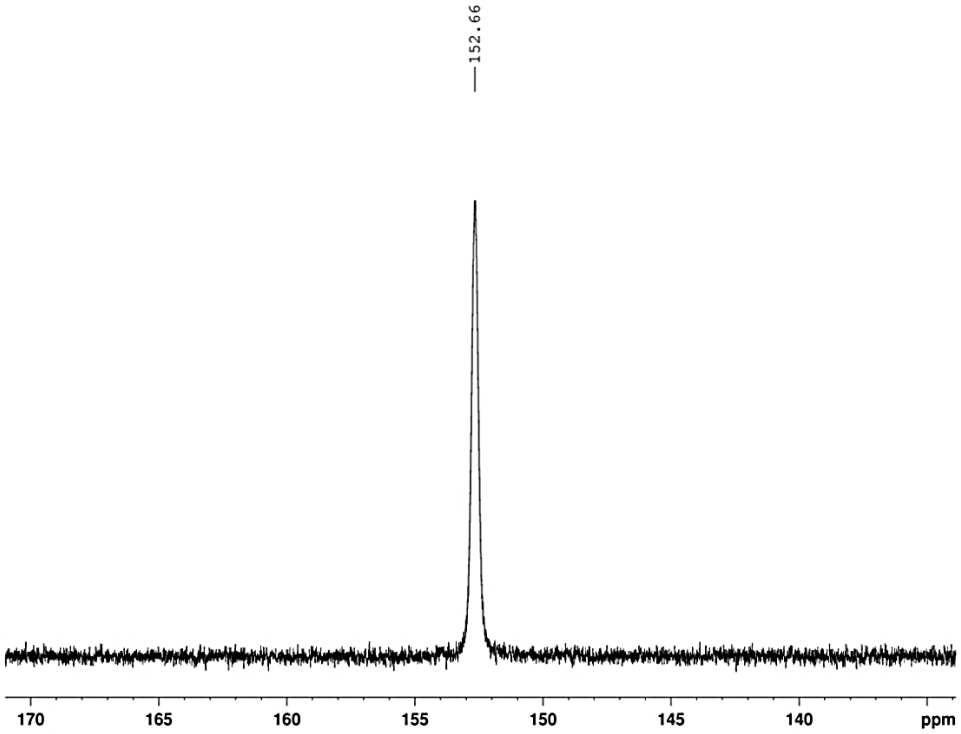


Figure S4. ^{27}Al NMR spectrum ([D_8]THF, 300 K) of [{Li(THF)$_4$}$^+${Al(^{i}Bu)$_4$}$^-$] (**3**).

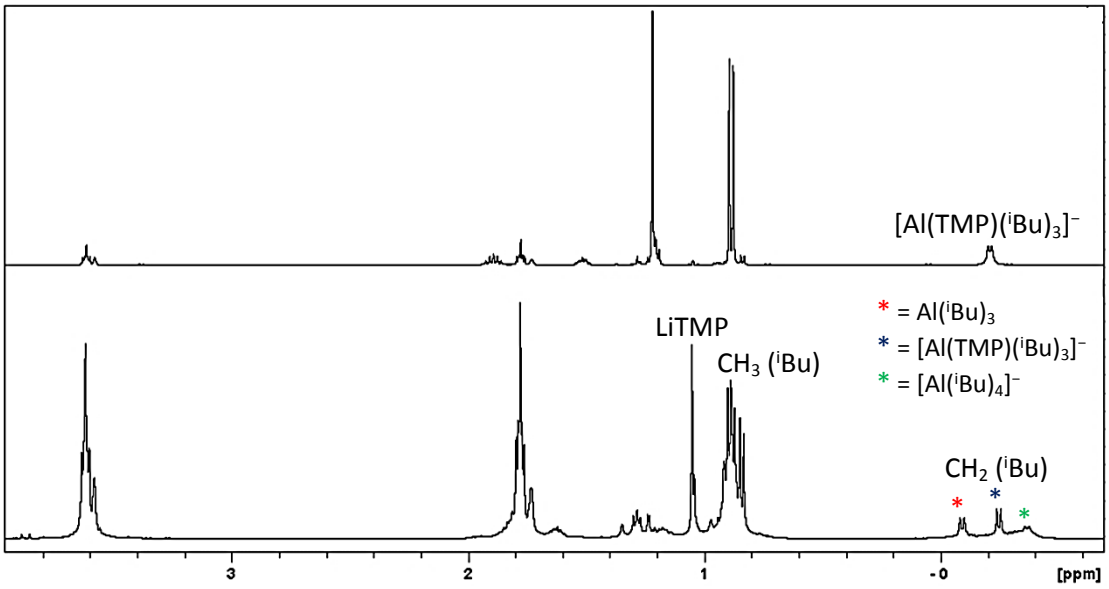


Figure S5. Overlay of ^{1}H NMR spectra ([D_8]THF) of [{Li(THF)$_4$}$^+${Al(TMP)(^{i}Bu)$_3$}$^-$] **1·(THF)$_4$** (top) and *in situ* [LiTMP + Al(^{i}Bu)$_3$] (**1**) (bottom) (273 K) showing the remarkable disimilarity between the two mixtures.

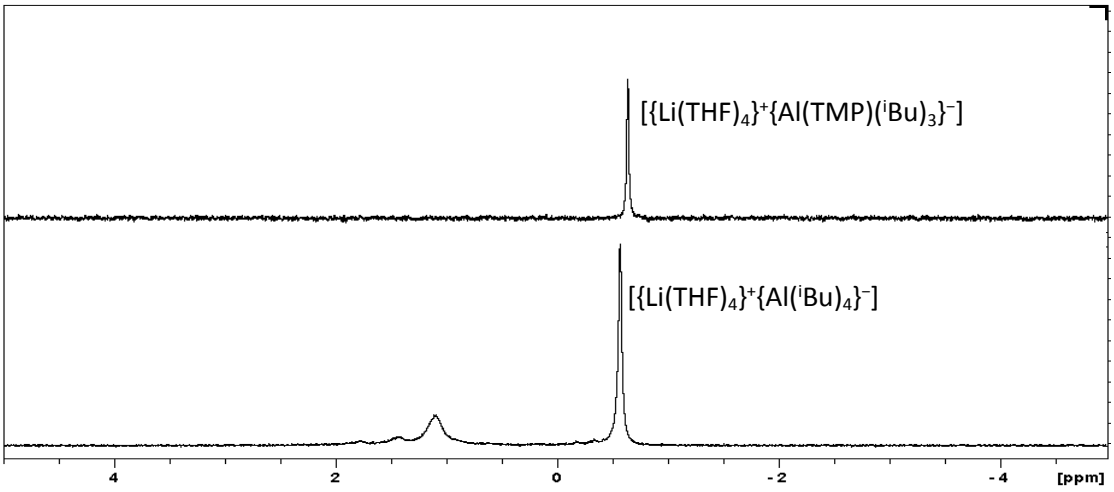


Figure S6. Overlay of ^{7}Li NMR spectra ([D_8]THF) of [{Li(THF)$_4$}$^+${Al(TMP)(^{i}Bu)$_3$}$^-$] **1·(THF)$_4$** (top) and *in situ* [LiTMP + Al(^{i}Bu)$_3$] (**1**) (bottom) (273 K) showing the common [Li(THF)$_4$]$^+$ resonance and the additional Li species that are present in the *in situ* mixture.

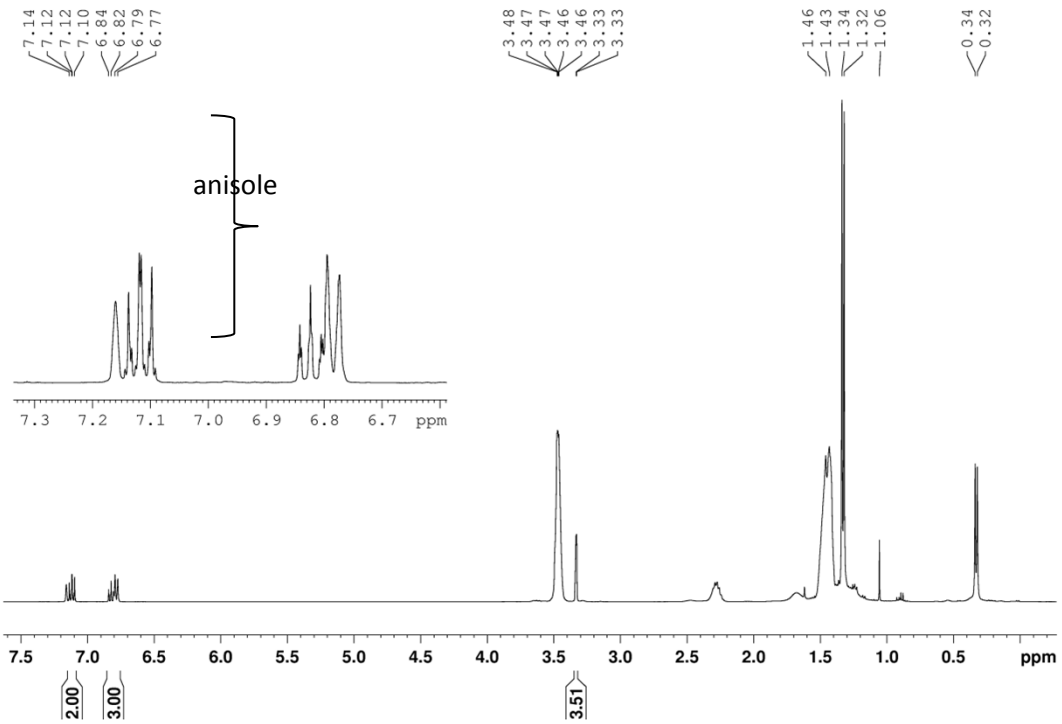


Figure S7. ^{1}H NMR spectrum (C_6D_6, 300 K) of crystalline [(THF)·Li(μ-TMP)(μ-^{i}Bu)Al(^{i}Bu)$_2$] **1·THF** + anisole after 24 hours stirring in THF, showing unreacted anisole.

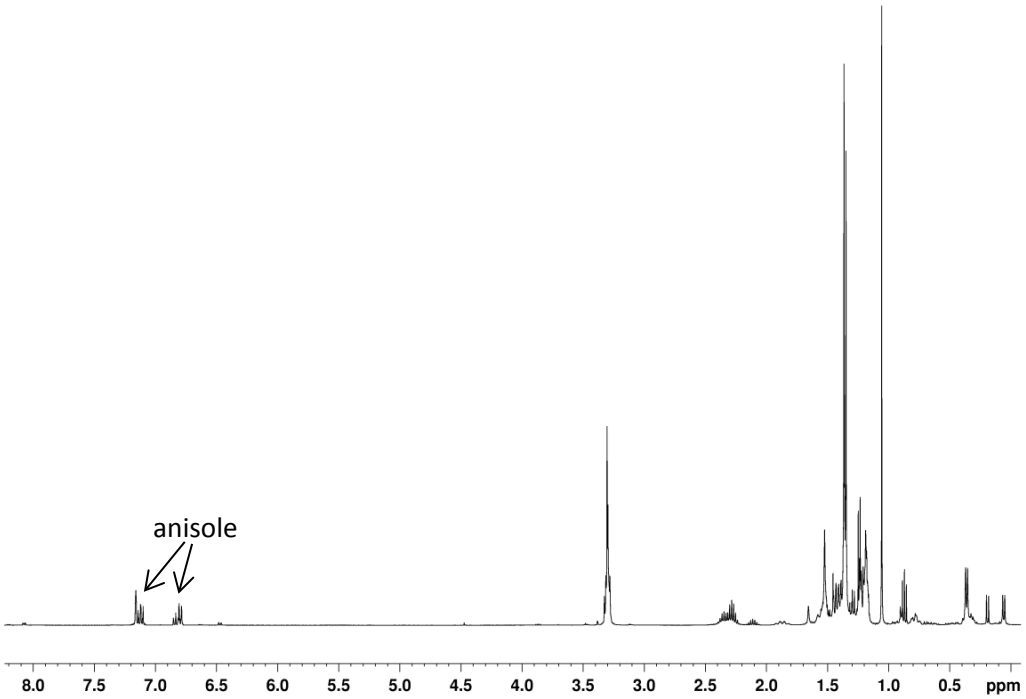


Figure S8. ^{1}H NMR spectrum (C_6D_6, 300 K) of *in situ* [LiTMP + Al(^{i}Bu)$_3$ + THF] (**1·THF**) + anisole in hexane, showing unreacted anisole. Note that there is a minute amount of metallation observed due to a trace excess of LiTMP present in the mixture.

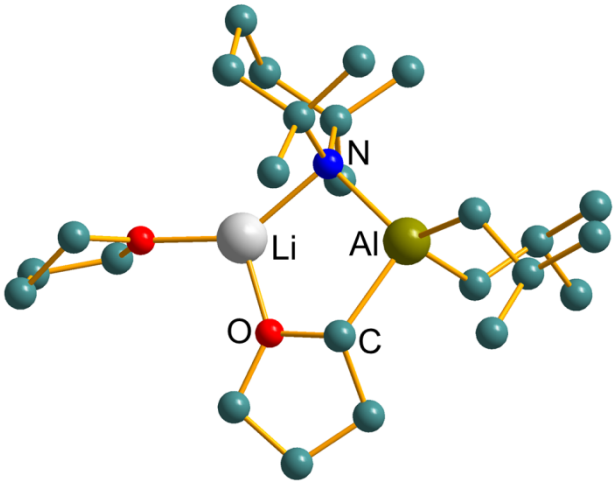


Figure S9. Known molecular structure of [(THF)·Li(μ-TMP)(μ-OC_4H_7)Al(^{i}Bu)$_2$] **4**. All hydrogen atoms are omitted for clarity.

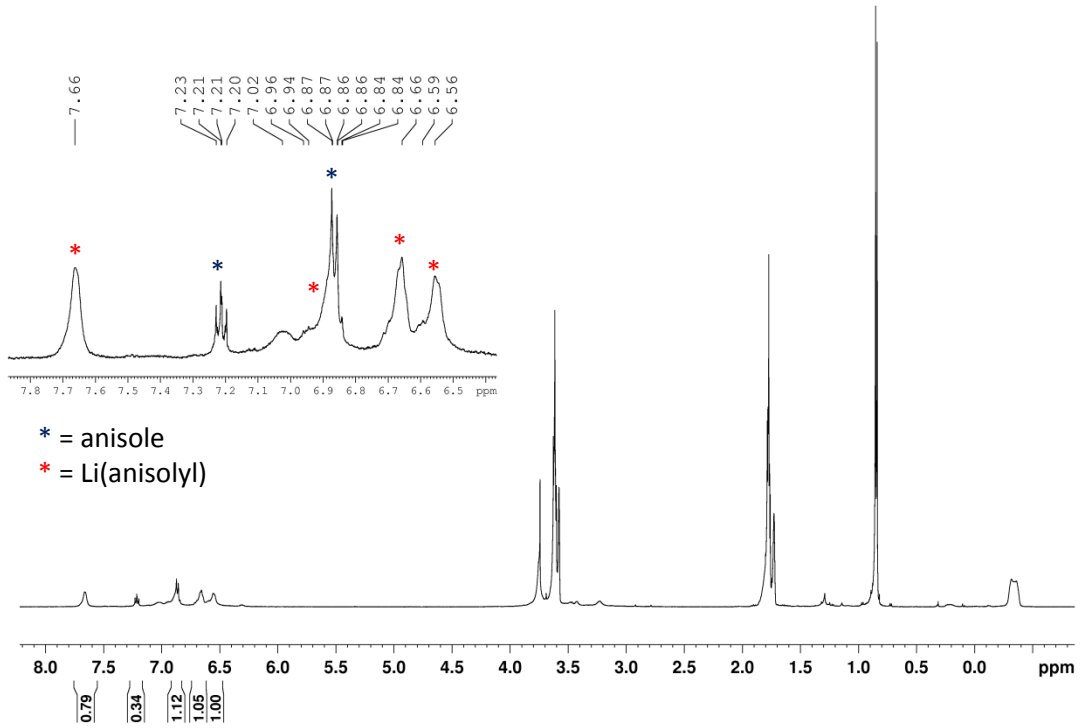


Figure S10. ^{1}H NMR spectrum ([D_8]THF, 300 K) of pre-prepared Li(anisolyl) + [{Li(THF)$_4$}$^+${Al(^{i}Bu)$_4$}$^-$] (**3**) showing the inefficient trapping by the salt.

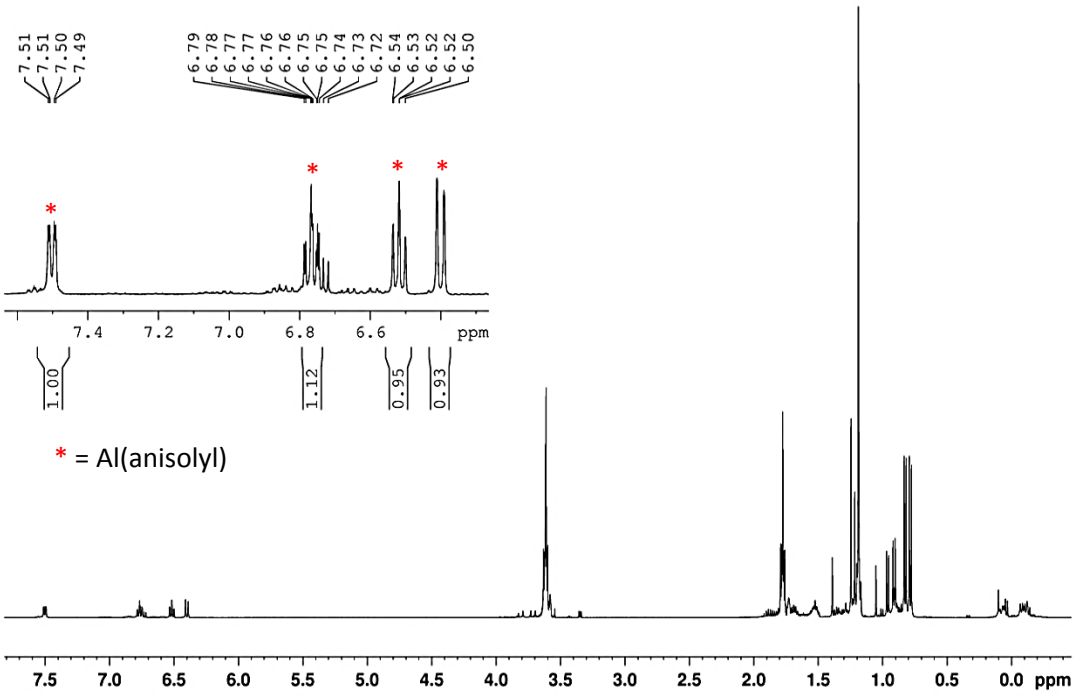


Figure S11. ^{1}H NMR spectrum ([D_8]THF, 300 K) of the reaction between pre-prepared Li(anisolyl) + Al(TMP)(^{i}Bu)$_2$ showing the near-quantitative Al(anisolyl) product.

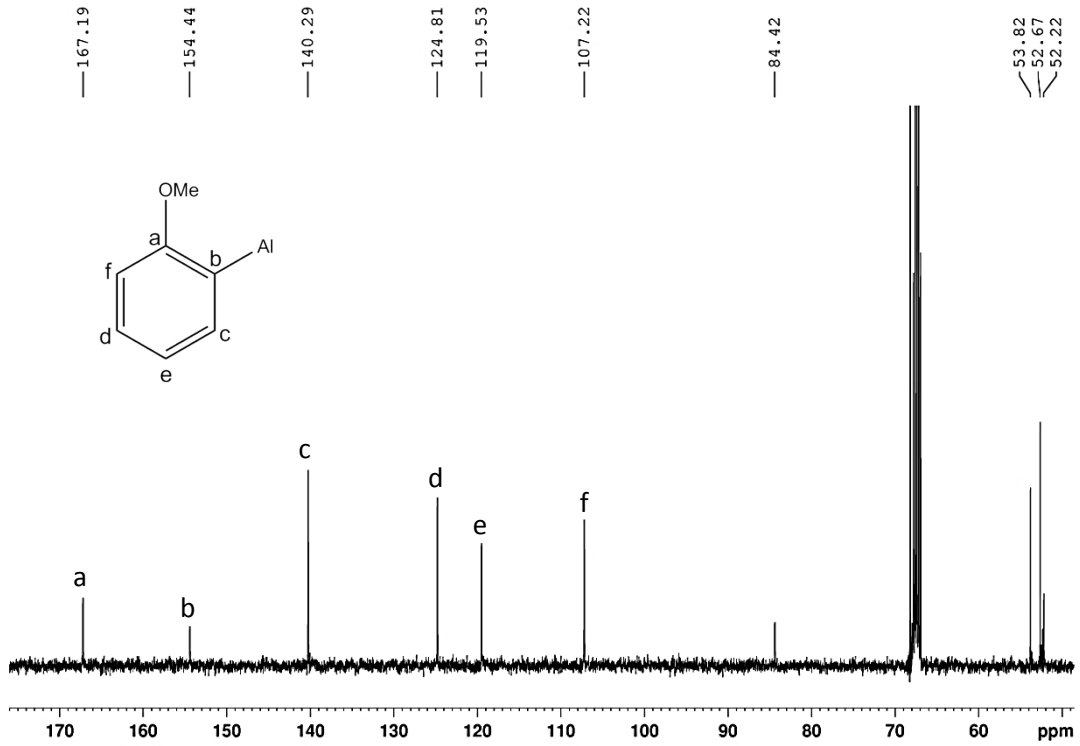


Figure S12. The aryl region of the ^{13}C NMR spectrum ([D_8]THF, 300 K) of the reaction between pre-prepared Li(anisolyl) + Al(TMP)(^{i}Bu)$_2$ showing the Al(anisolyl) product.

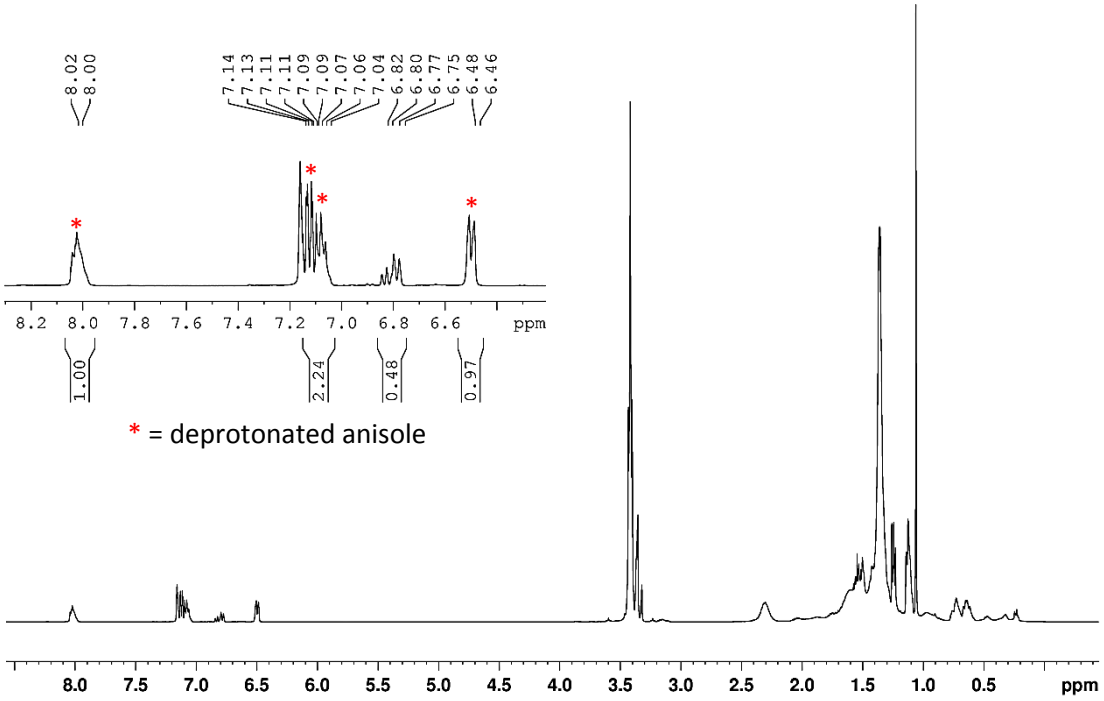


Figure S13. ^{1}H NMR spectrum (C_6D_6, 300 K) of the reaction between [LiTMP + Al(TMP)(^{i}Bu)$_2$] (**2**) + anisole in THF, showing the deprotonation of anisole producing the Al(anisolyl) complex.

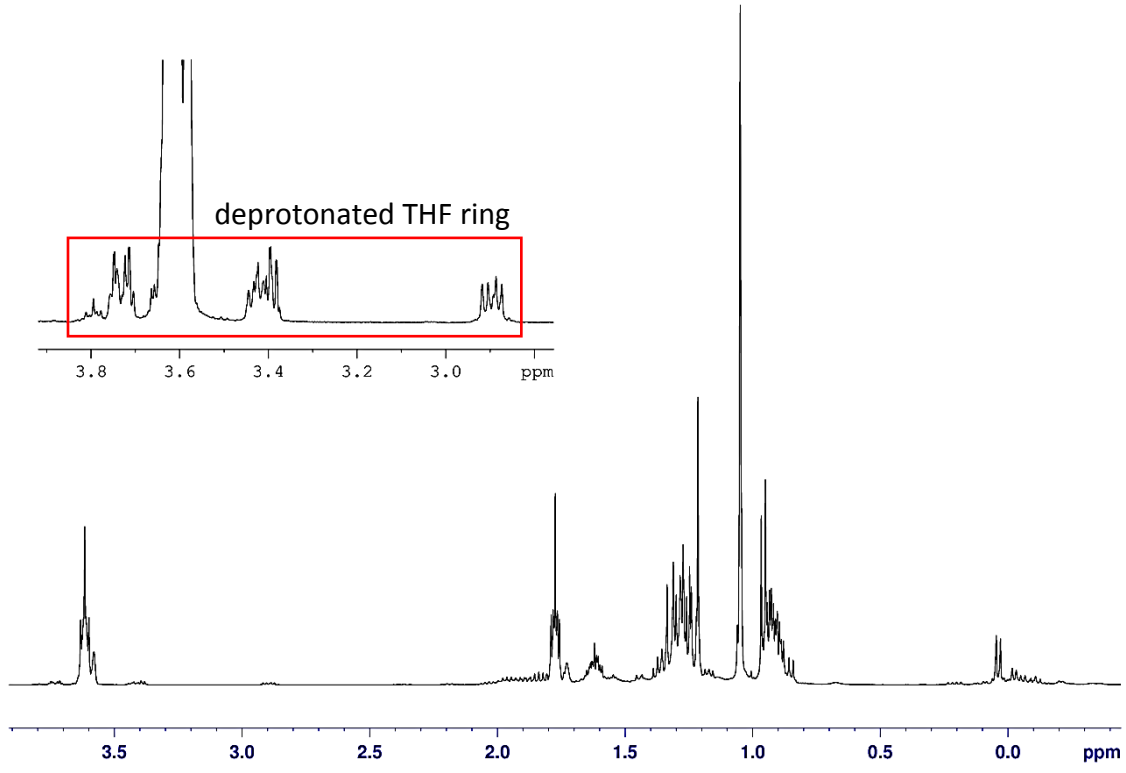


Figure S14. ^{1}H NMR spectrum ([D_8]THF, 300 K) of [LiTMP + Al(TMP)(^{i}Bu)$_2$] (**2**) after 24 hours stirring in THF, showing small resonances for deprotonated THF.

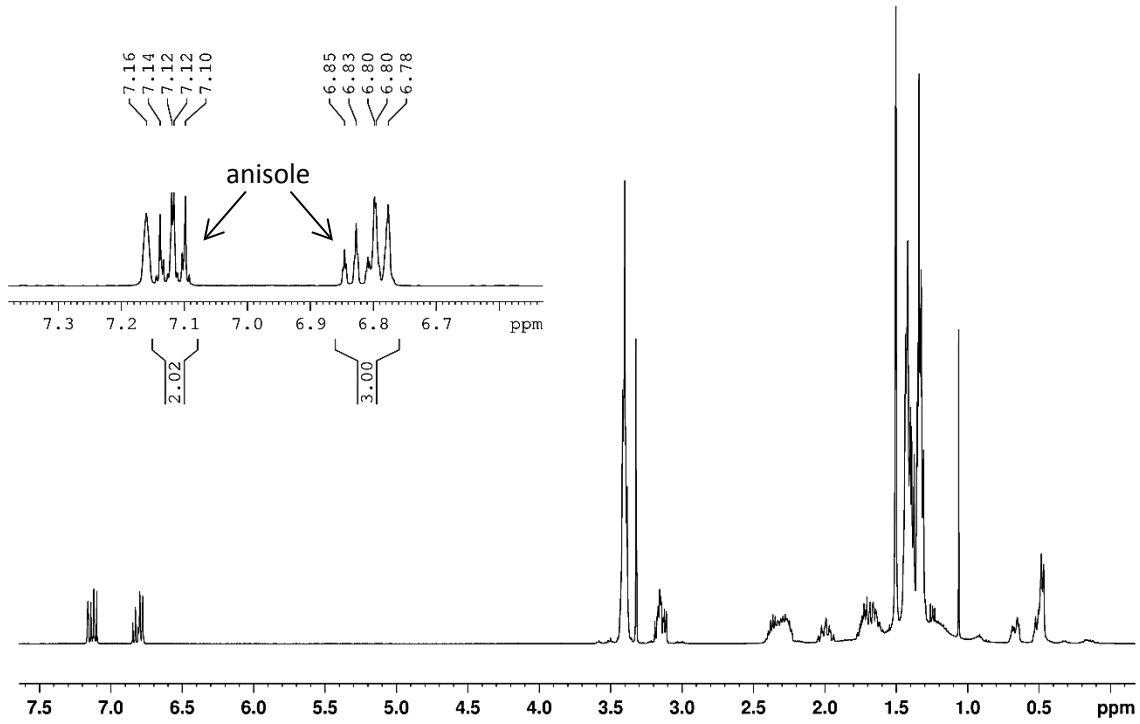


Figure S15. ^{1}H NMR spectrum ([D_8]THF, 300 K) of [(THF)·Li(μ-TMP)(μ-OC_4H_7)Al(^{i}Bu)$_2$] (**4**) + anisole in THF after stirring for 24 hours, showing unreacted anisole.

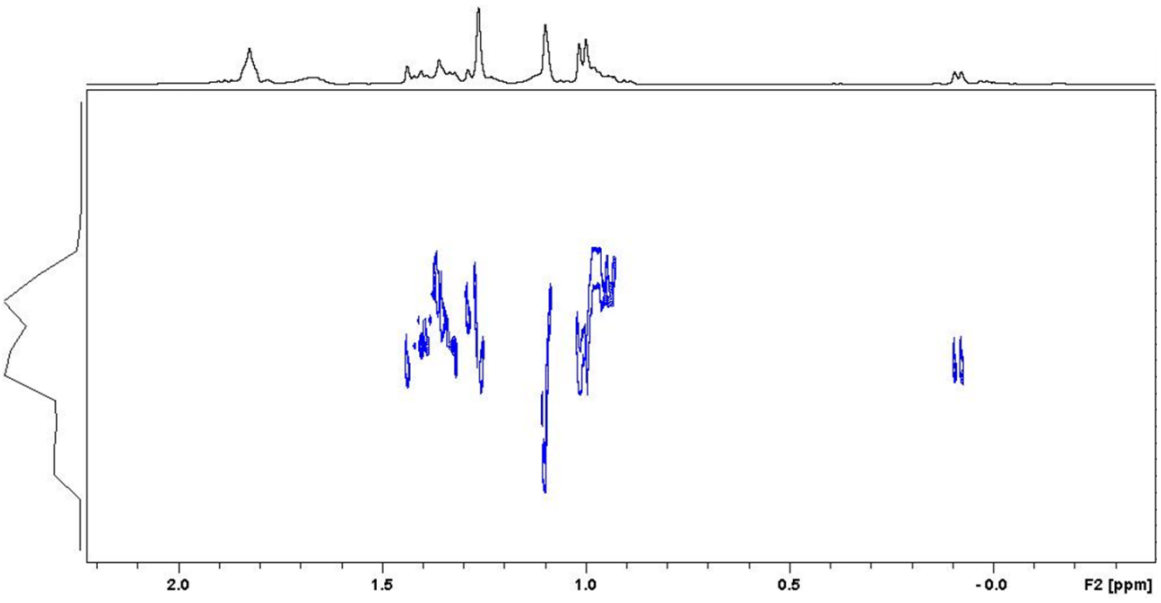


Figure S16. ^{1}H-DOSY NMR spectrum of [LiTMP + Al(TMP)(^{i}Bu)$_2$] (**2**) in bulk THF.

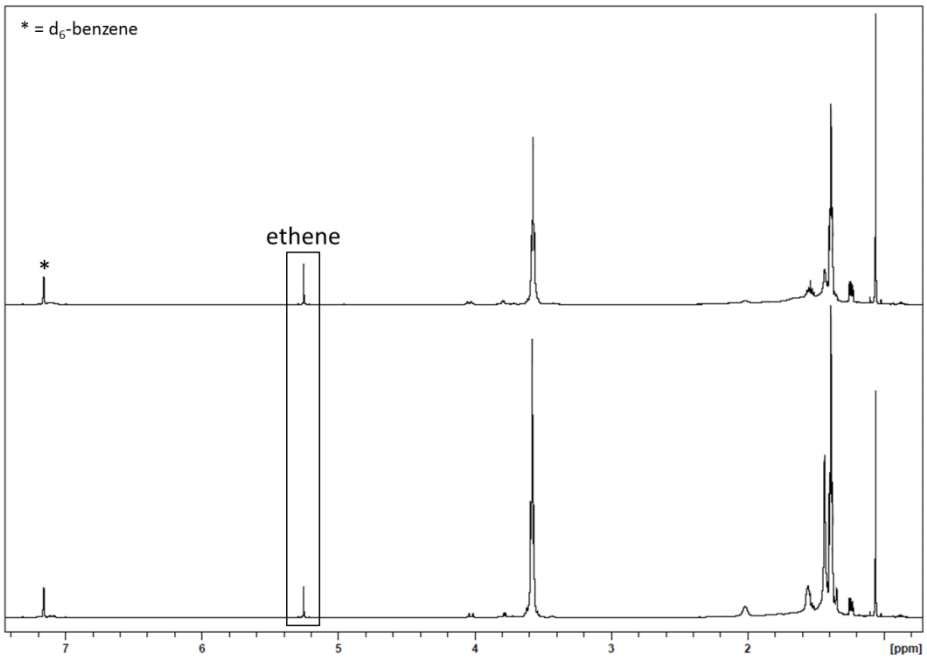


Figure S17. Overlay of ^{1}H NMR spectra (C_6D_6, 300 K) of LiTMP + THF after 30 mins (bottom) and 24 hours (top).

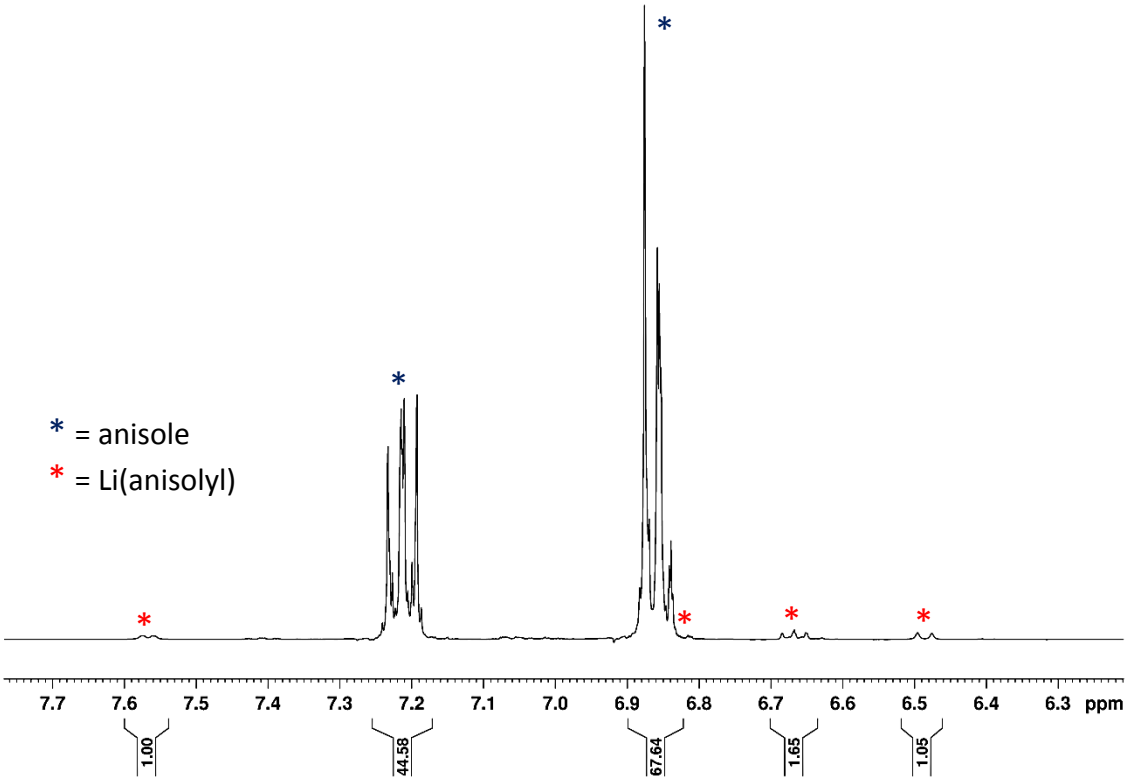


Figure S18. Part of the aryl region of the ^{1}H NMR spectrum ([D_8]THF, 300 K) of LiTMP + anisole in THF, showing that lithiation occurs but only to a small extent.

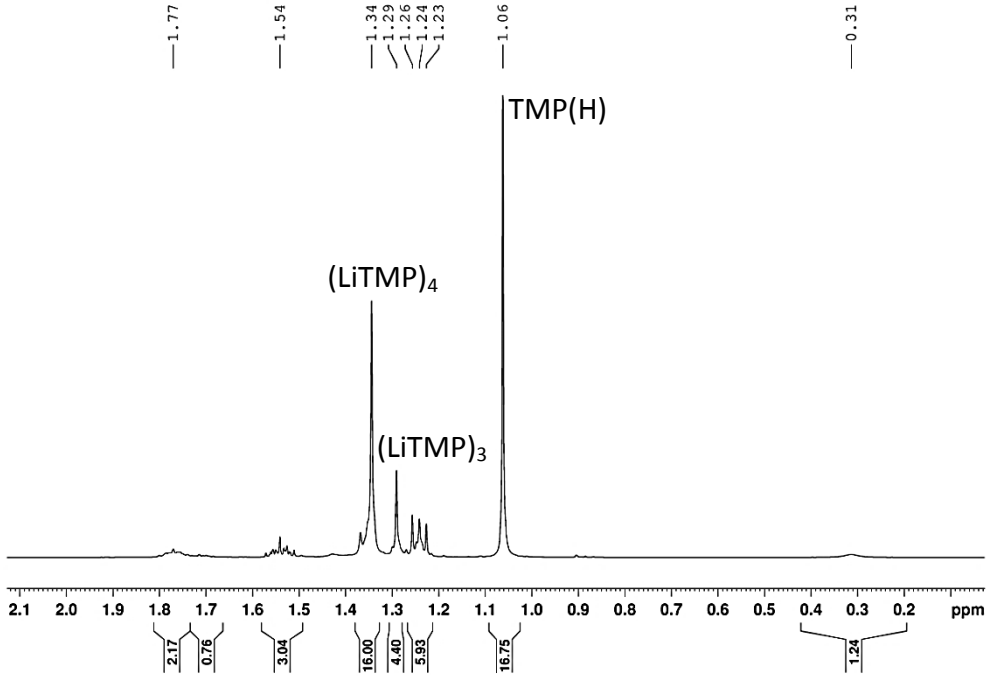


Figure S19. ^{1}H NMR spectrum (C_6D_6, 300 K) of pre-prepared Li(anisolyl) + TMP(H) showing formation of LiTMP.

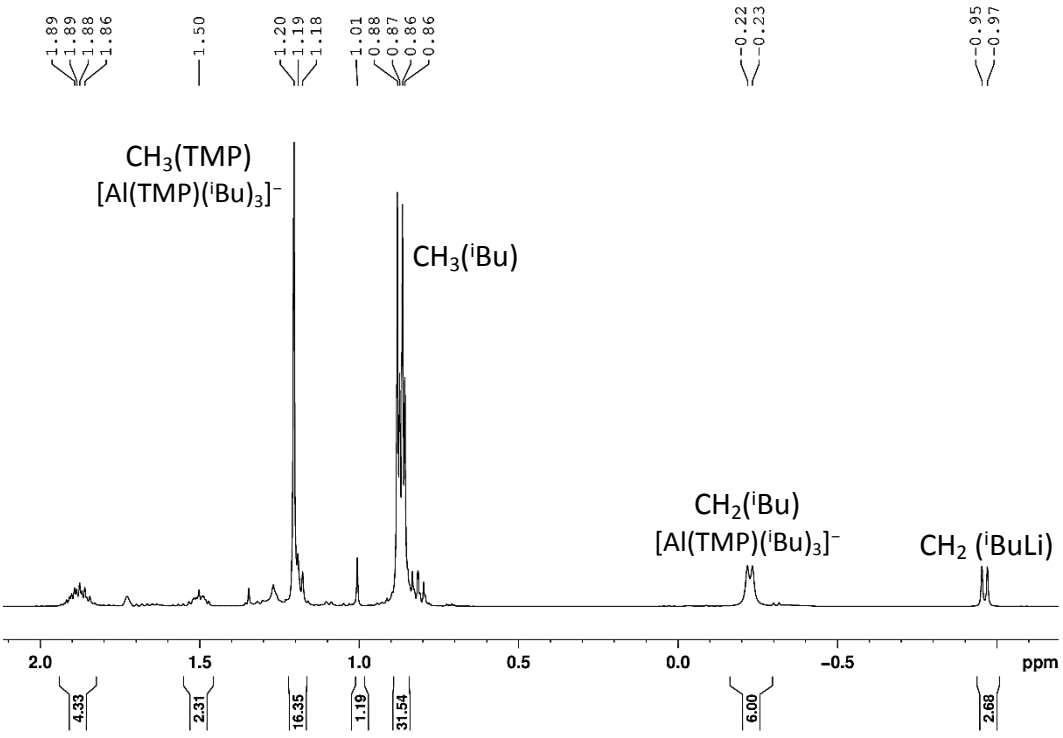


Figure S20. ^{1}H NMR spectrum ([D_8]THF, 300 K) of Al(TMP)(^{i}Bu)$_2$ + ^{i}BuLi.

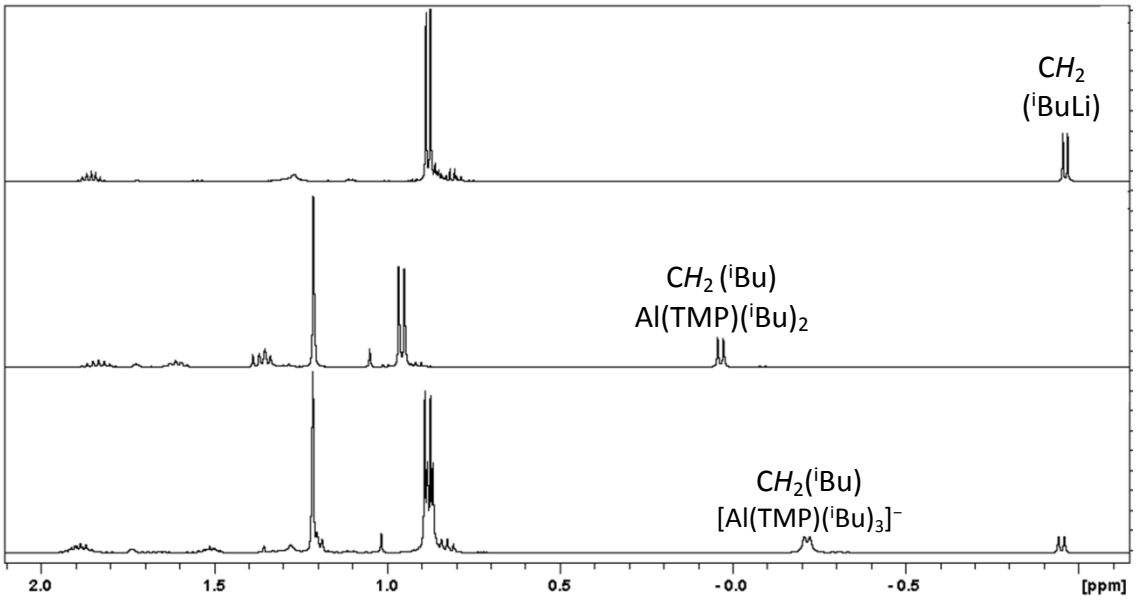


Figure S21. Overlay of ^{1}H NMR spectra ([D_8]THF, 300 K) of ^{i}BuLi (top), Al(TMP)(^{i}Bu)$_2$ (middle), and the mixture of both (bottom).

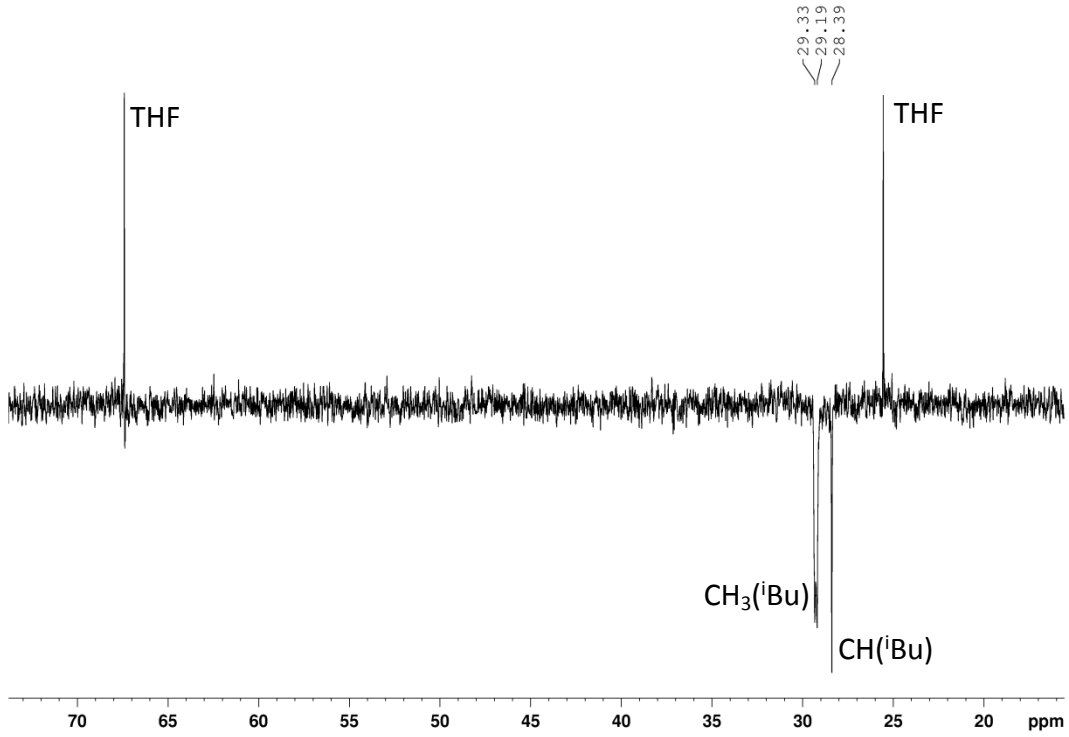


Figure S22. ^{13}Cdept135 NMR spectrum ([D_8]THF, 300 K) of [{Li(THF)$_4$}$^{+}${Al(^{i}Bu)$_4$}$^{-}$] (**3**). Note that the CH_2 resonance of ^{i}Bu is not visible.

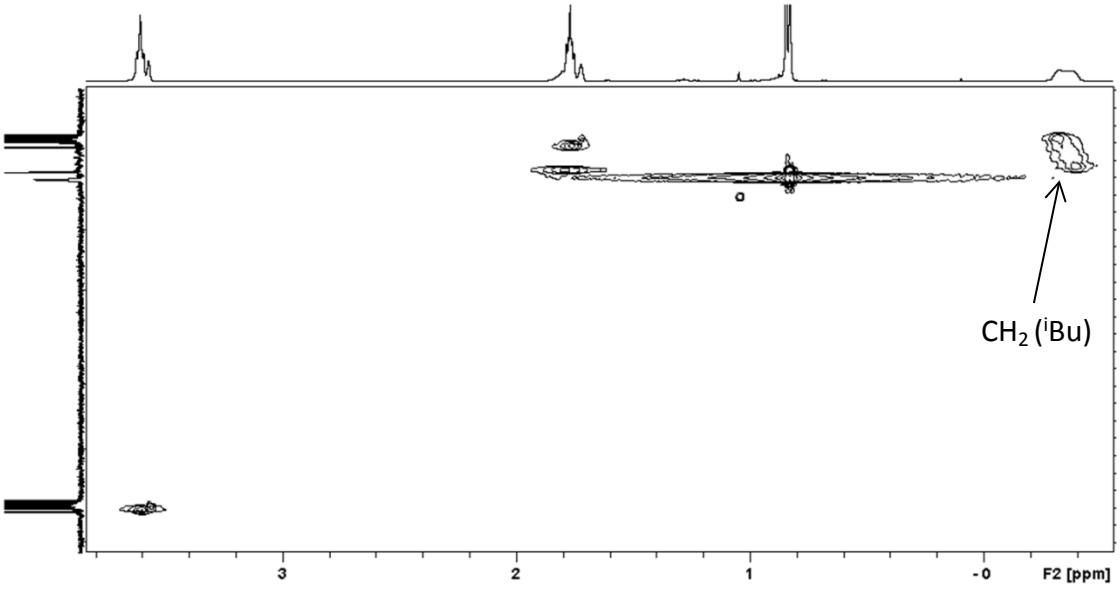


Figure S23. ^{1}H-^{13}C HSQC NMR spectrum ([D_8]THF, 300 K) of [{Li(THF)$_4$}$^+${Al(^{i}Bu)$_4$}$^-$] (**3**) showing the broadness of the CH_2-Al resonance.

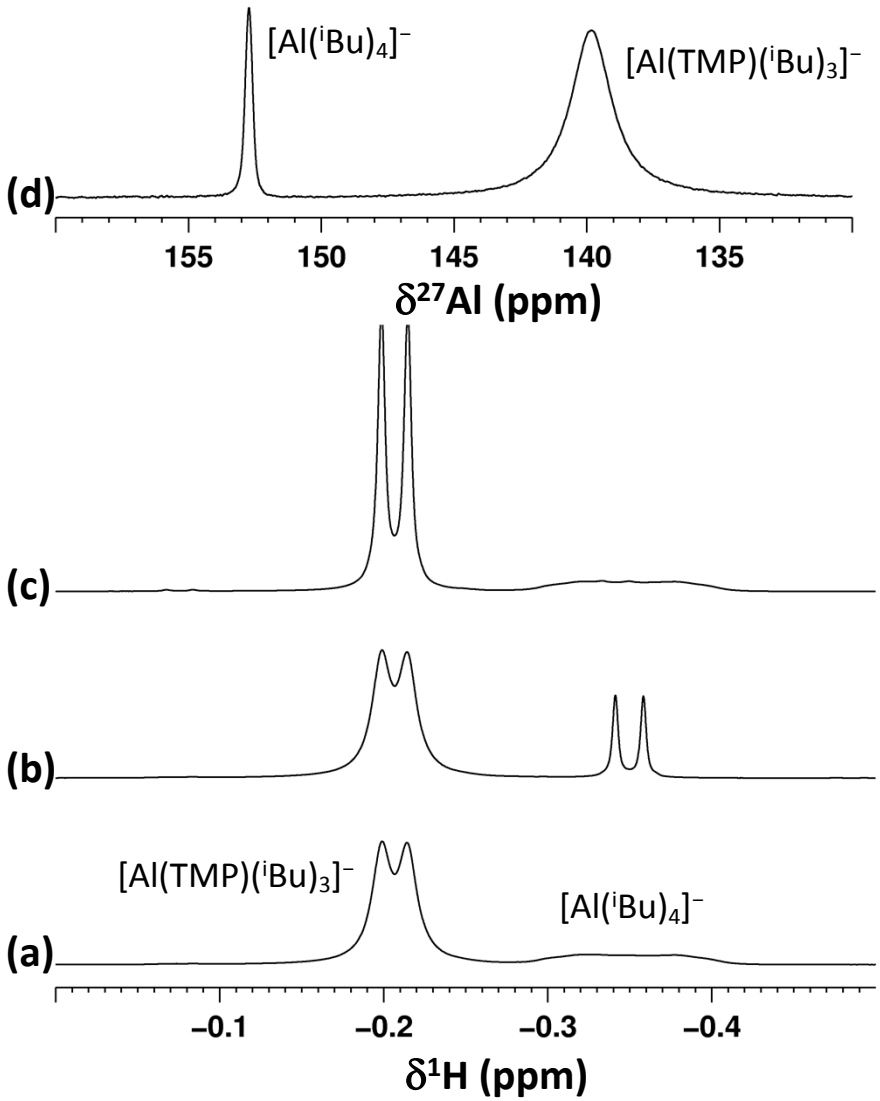


Figure S24. "Al-^{i}Bu" methylene proton resonance region of the 1D ^{1}H, ^{1}H-{^{27}Al} and associated ^{27}Al NMR spectra of a mixture of crystalline [{Li(THF)$_4$}$^+${Al(TMP)(^{i}Bu)$_3$}$^-$] **1·(THF)$_4$** and [{Li(THF)$_4$}$^+${Al(^{i}Bu)$_4$}$^-$] (**3**). **(a)** ^{1}H NMR spectrum showing broadened resonances for both species; **(b)** as for **(a)** but with continuous wave narrow-band ^{27}Al decoupling by irradiation at δ^{27}Al = 152.72 ppm; **(c)** as for **(a)** but with continuous wave narrow-band ^{27}Al decoupling by irradiation at δ^{27}Al = 139.84 ppm. **(d)** labelled ^{27}Al spectrum from S3.

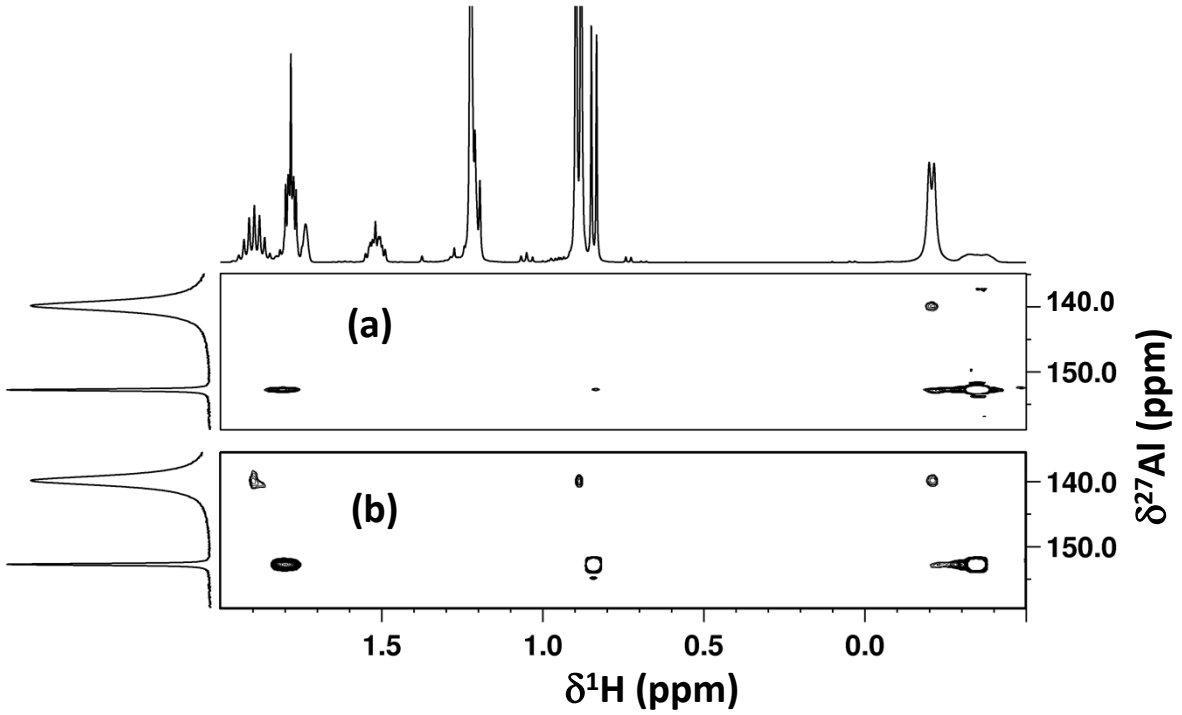


Figure S25. Correlation data confirming resonance relationships between ^{27}Al and ^{1}H nuclei. **(a)** Phase-sensitive gradient selected 2D [^{1}H, ^{27}Al] HSQC optimized for maximum signal intensity. **(b)** Phase-sensitive gradient selected 2D [^{1}H, ^{27}Al] HSQC-TOCSY revealing ^{27}Al-associated ^{i}Bu proton spin-systems for two independent species. It is particularly notable that the presence of a signal for the ^{i}Bu methine proton of the more symmetrical species is detected *via* HSQC-TOCSY below the THF signal at 1.78 ppm.

DFT Calculations on Lithium-Aluminium Compounds

Density Functional Theory Calculations were performed using the Gaussian computational package G03.

In this series of calculations the B3LYP density functionals and the 6-311G(d,p) basis set were used.

After each geometry optimisation, a frequency analysis was performed.

The energy values quoted include the zero point energy contribution.

Aims of the Calculations

To investigate the possible optimised geometries of the compound THF.LiAl(TMP)$_2$(^{i}Bu)$_2$.

In particular, to focus on the preferred bridging components between Li and Al which could be

(a) Two TMP anions

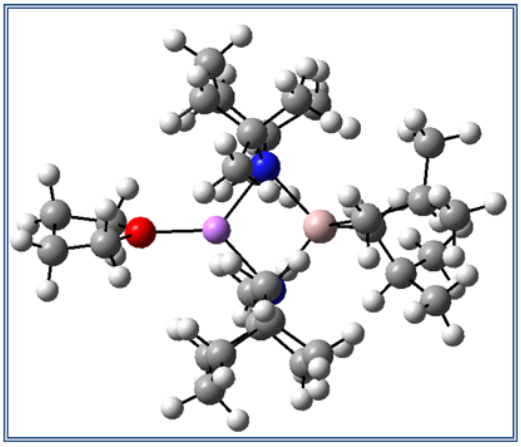
(b) Two ^{i}Bu anions

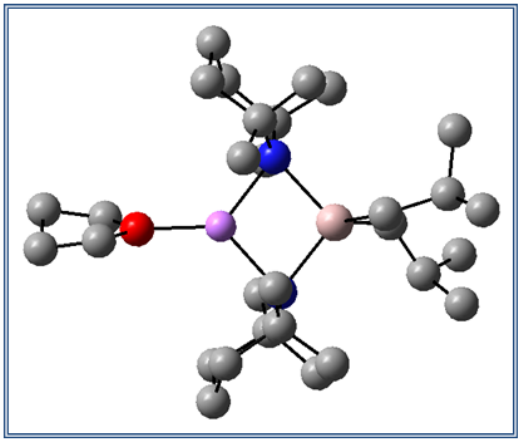
(c) One TMP anion and one ^{i}Bu anion.

Finally to ascertain the energy of formation from LiTMP and THF.Al(^{i}Bu)$_2$TMP of THF.LiAl(TMP)$_2$(^{i}Bu)$_2$

Case (a) THF.Li(μ-TMP)$_2$Al(iBu)$_2$

Model (i)





$THF.Li(\mu\text{-}TMP)_2Al(iBu)_2$

Model (i)

Li-O 1.983 Å

Li-N 2.082 Å 2.117 Å

Al-N 2.137 Å 2.108 Å

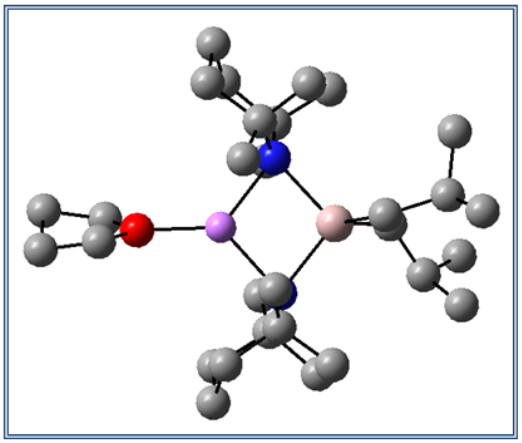
Al-C 2.056 Å 2.054 Å

Li-N-Al 79.5 ° 79.4 °

N-Li-N 101.3 °

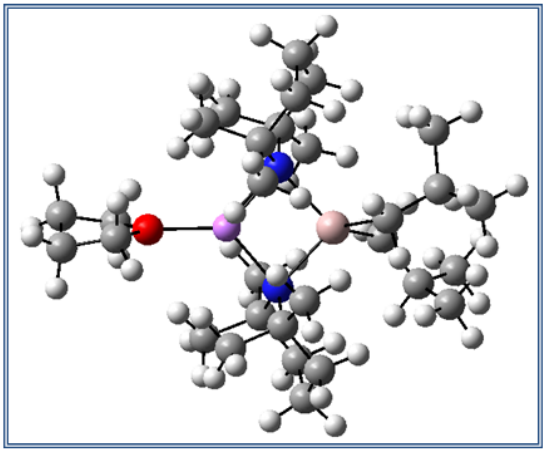
N-Al-N 99.8 °

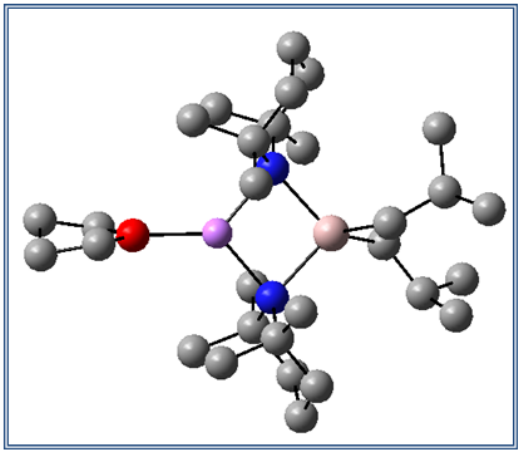
C-Al-C 104.4 °



$THF.Li(\mu\text{-}TMP)_2Al(iBu)_2$

Model (ii)



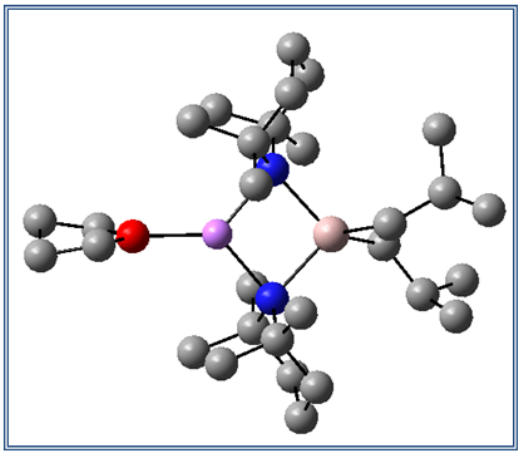


$THF.Li(\mu\text{-}TMP)_2Al(iBu)_2$

Model (ii)

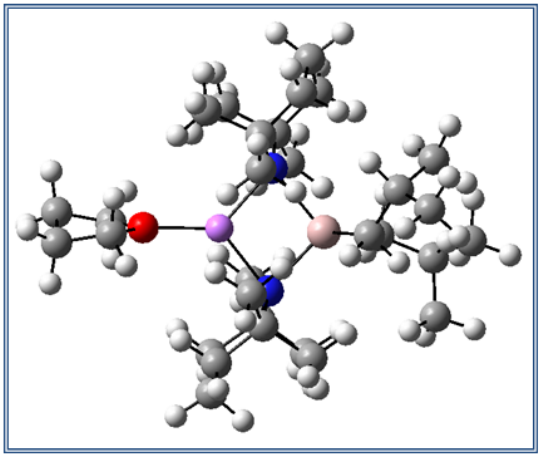
Li-O	**2.049 Å**	
Li-N	**2.060 Å**	**2.069 Å**
Al-N	**2.125 Å**	**2.130 Å**
Al-C	**2.078 Å**	**2.070 Å**

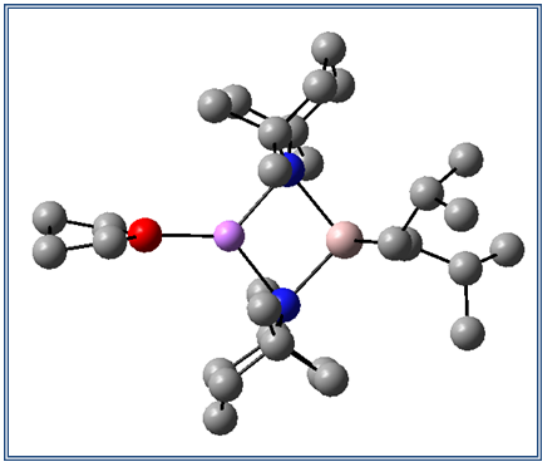
Li-N-Al	**82.6 °**	**82.7 °**
N-Li-N	**99.3 °**	
N-Al-N	**95.4 °**	
C-Al-C	**98.7 °**	



$THF.Li(\mu\text{-}TMP)_2Al(iBu)_2$

Model (iii)





THF.Li(μ-TMP)$_2$Al(iBu)$_2$

Model (iii)

Li-O **1.987 Å**

Li-N **2.078 Å 2.074 Å**

Al-N **2.110 Å 2.147 Å**

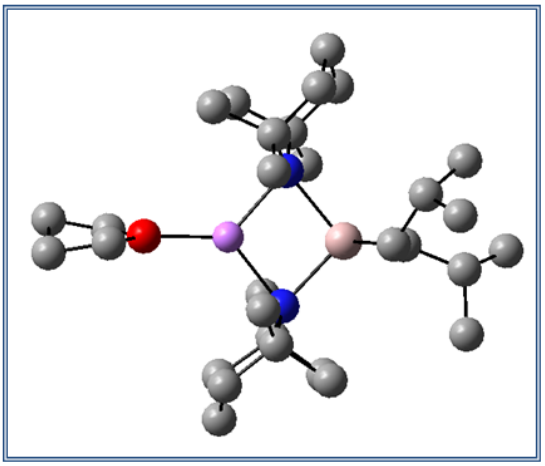
Al-C **2.065 Å 2.064 Å**

Li-N-Al 80.3 ° 81.3 °

N-Li-N 100.9 °

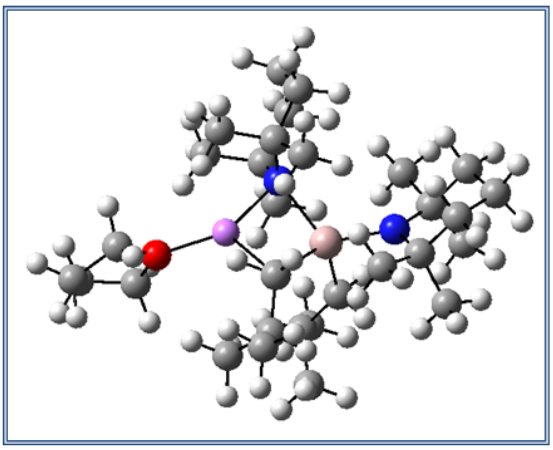
N-Al-N 97.5 °

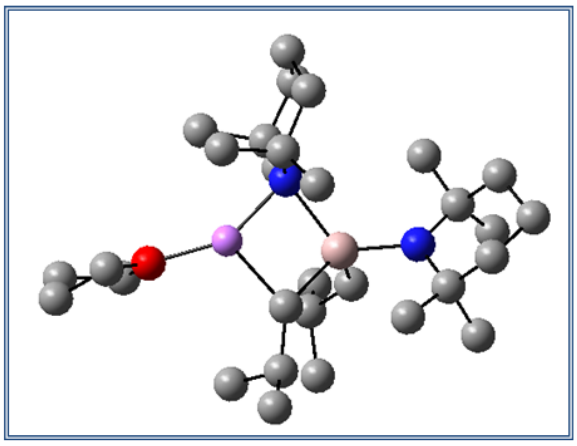
C-Al-C 101.0 °



Case (b) THF.Li(μ-TMP)(μ-^{i}Bu)Al(^{i}Bu)(TMP)

Model (i)

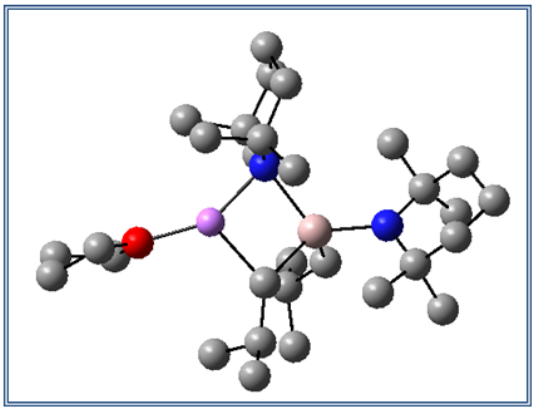




THF.Li(μ-TMP)(μ-iBu) Al(iBu)(TMP)

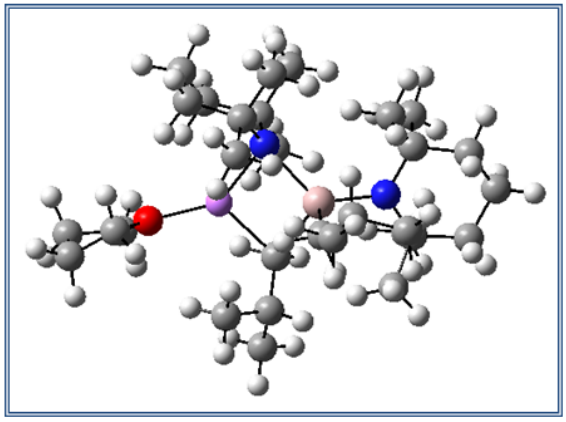
Model (i)

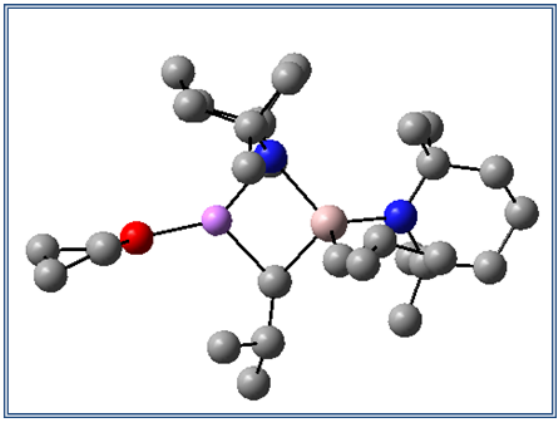
Li-O	**1.957 Å**
Li-N	**1.998 Å**
Li-C	**2.298 Å**
Al-N_{br}	**2.115 Å**
Al-N_{ter}	**1.961 Å**
Al-C_{br}	**2.147 Å**
Al-C_{ter}	**2.049 Å**
Li-N-Al	**81.3 °**
Li-C-Al	**74.1 °**
N-Li-C	**92.9 °**
N_{br}-AL-C_{br}	**94.1 °**
N_{br}-AL-C_{br}	**101.8 °**



THF.Li(μ-TMP)(μ-iBu) Al(iBu)(TMP)

Model (ii)

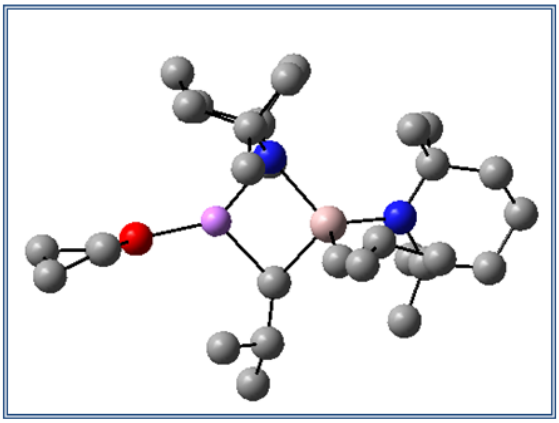




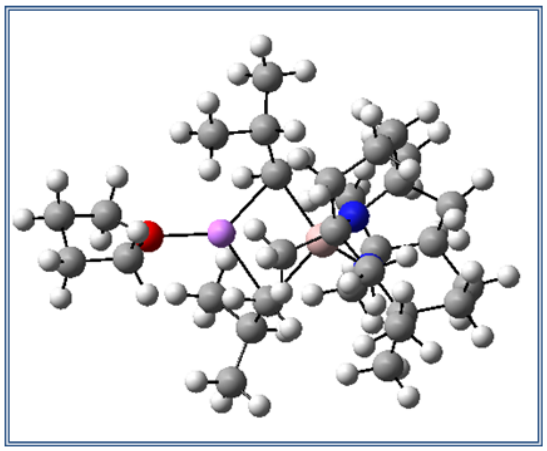
THF.Li(μ-TMP)(μ-iBu) Al(iBu)(TMP)

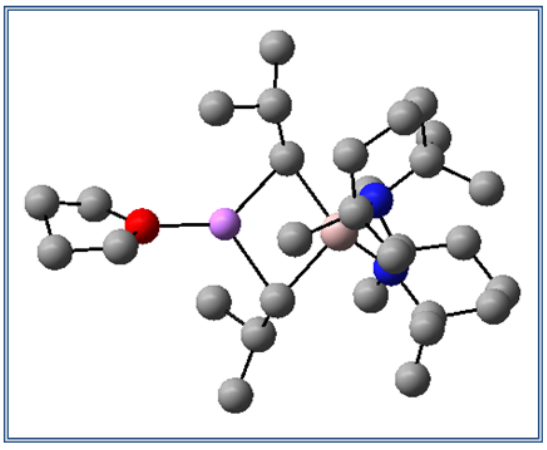
Model (ii)

Li-O	**1.971 Å**
Li-N	**2.003 Å**
Li-C	**2.257 Å**
Al-N_{br}	**2.137 Å**
Al-N_{ter}	**1.951 Å**
Al-C_{br}	**2.159 Å**
Al-C_{ter}	**2.036 Å**
Li-N-Al	**81.5 °**
Li-C-Al	**75.5 °**
N-Li-C	**96.6 °**
N_{br}-AL-C_{br}	**95.7 °**
N_{br}-AL-C_{br}	**109.9 °**



Case (c) THF.Li(μ-^{i}Bu)$_2$Al(TMP)$_2$

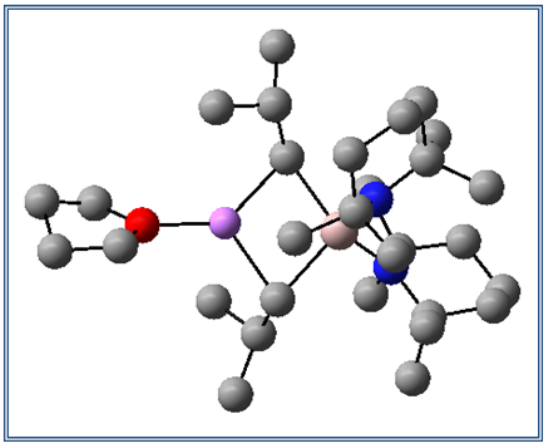




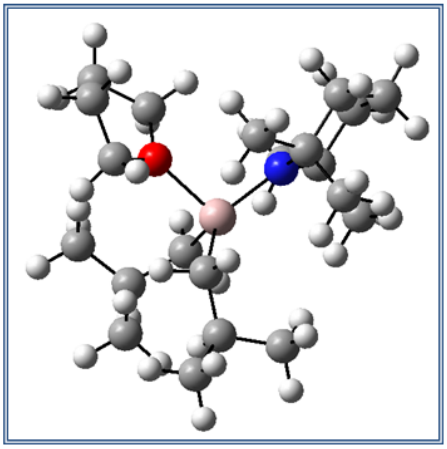
$THF.Li(\mu\text{-}^{i}Bu)_2Al(TMP)_2$

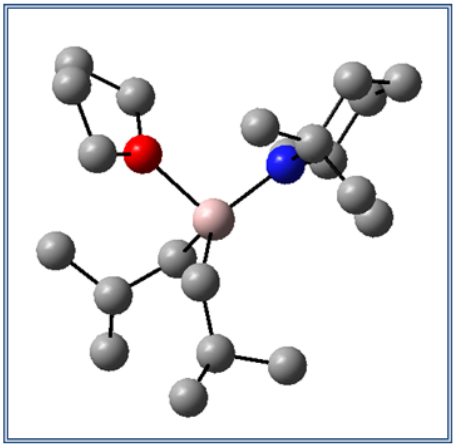
Li-O	**1.966 Å**	
Li-C	**2.167 Å**	**2.150 Å**
Al-C	**2.140 Å**	**2.176 Å**
Al-N	**1.963 Å**	**1.955 Å**

Li-C-Al	**75.2 °**	**76.3 °**
C-Li-C	**103.4 °**	
C-Al-C	**103.4 °**	
N-Al-N	**117.2 °**	



$THF.Al(TMP)(^{i}Bu)_2$

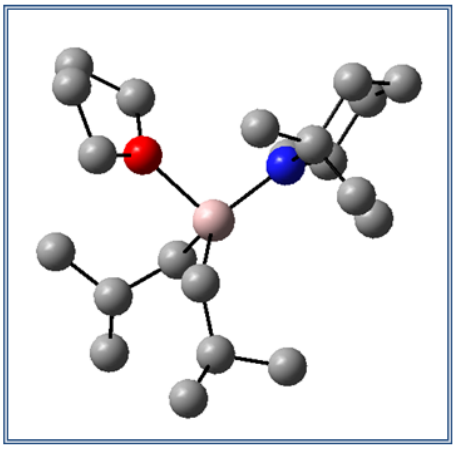




THF.Al(TMP)(^{i}Bu)$_2$

Al-O **2.059 Å**
Al-C **2.023 Å** **2.017 Å**
Al-N **1.896 Å**

C-Al-C **108.0 °**
C-Al-N **121.2 °** **121.7 °**
C-Al-O **99.4 °** **100.4 °**
N-Al-O **100.3 °**

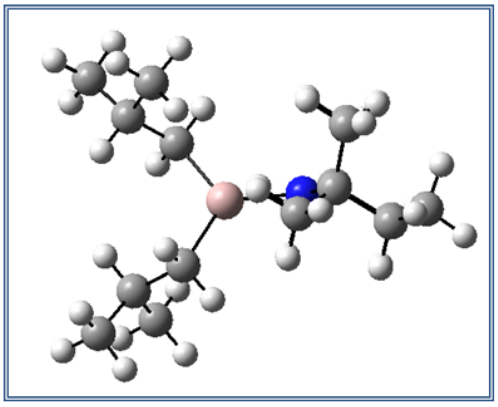


E = -1198.850198 a.u.

Al(TMP)(^{i}Bu)$_2$

Al-C **1.993 Å** **1.990 Å**
Al-N **1.840 Å**

C-Al-C **115.3 °**
C-Al-N **121.6 °** **123.1 °**



E = -966.442464 a.u.

Total Energies/a.u. and Relative Energies/kcal mol^{-1}

THF.Li(μ-TMP)$_2$Al(iBu)$_2$ (i)	-1614.805526	0.00
THF.Li(μ-TMP)$_2$Al(iBu)$_2$ (ii)	-1614.786463	11.96
THF.Li(μ-TMP)$_2$Al(iBu)$_2$ (iii)	-1614.798446	4.44
THF.Li(μ-TMP)(μ-iBu)Al(iBu)(TMP) (i)	-1614.789488	10.06
THF.Li(μ-TMP)(μ-iBu)Al(iBu)(TMP) (ii)	-1614.797795	4.85
THF.Li(μ-iBu)$_2$Al(TMP)$_2$	-1614.782013	14.75

Reactions

Energy of the Reactions:

¼(LiTMP)$_4$ + THF.Al(^{i}Bu)$_2$(TMP) = THF.Li(μ-TMP)$_2$Al(^{i}Bu)$_2$

ΔE = +14.16 kcal mol^{-1}

½(THF.LiTMP)$_2$ + THF.Al(^{i}Bu)$_2$(TMP) = THF.Li(μ-TMP)$_2$Al(^{i}Bu)$_2$ + THF

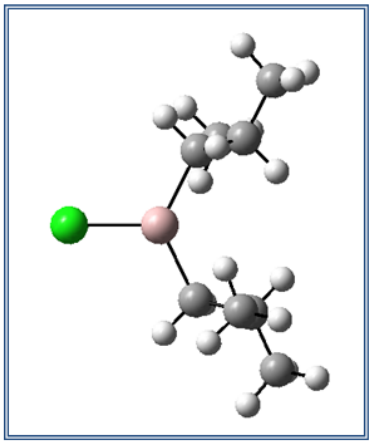
ΔE = +20.60 kcal mol^{-1}

½(THF.LiTMP)$_2$ + Al(^{i}Bu)$_2$(TMP) = THF.Li(μ-TMP)$_2$Al(^{i}Bu)$_2$

ΔE = +14.19 kcal mol^{-1}

$ClAl(iBu)_2$

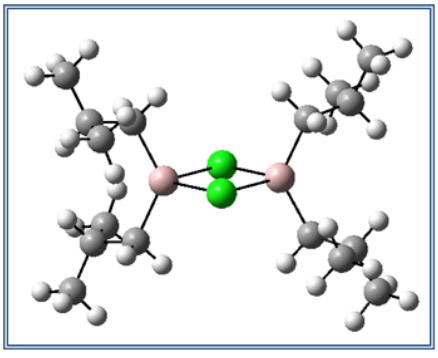
Cl-Al	2.140 Å	
Al-C	1.969 Å	1.969 Å
Cl-Al-C	116.3 °	116.3 °
C-Al-C	127.3 °	



E = -1018.315320 a.u.

$[ClAl(iBu)_2]_2$

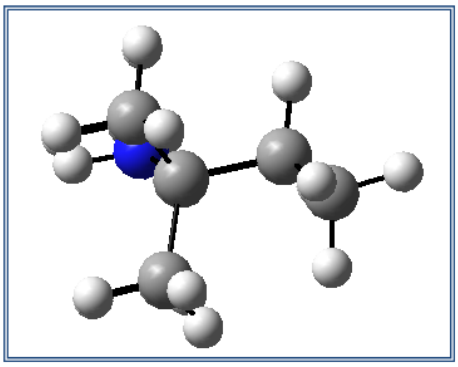
Cl-Al	2.356 Å
Al-C	1.968 Å
Cl-Al-Cl	88.3 °
Al-Cl-Al	91.7 °



E = -2036.660666 a.u.

TMPH

N-H	1.015 Å	
N-C	1.477 Å	1.477 Å
C-N-C	122.3 °	
C-N-H	110.0 °	110.0 °

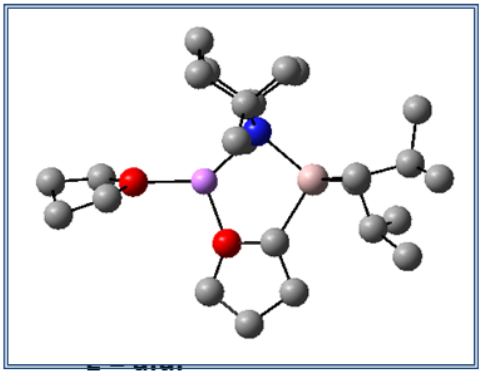


E = -409.003998 a.u.

E = -409.003998 a.u.

THF.Li(μ-TMP)(μ-OC_4H_7)Al(iBu_2)

$Li-O_{ter}$		1.980 Å
$Li-O_{br}$		1.845 Å
Li-N	2.036 Å	
N-Al	2.063 Å	
$O_{br}-C_{br}$		1.496 Å
C_{br}-Al		2.086 Å
Al-C_{ter}		2.051 Å 2.052 Å
$Li-O_{br}-C_{br}$	107.9 °	
$O_{br}-C_{br}$-Al	112.8 °	
C_{br}-Al-N		99.9 °
Al-N-Li		96.4 °
N-Li-O_{br}		112.8 °
N-Li-O_{ter}	137.1 °	
C_{ter}-Al-C_{ter}	107.8 °	



E = -409.003998 a.u.

Reactions

Energy of the Reactions:

$$\text{½(THF.LiTMP)}_2 + \text{THF.Al(}^i\text{Bu)}_2\text{(TMP)} = \text{THF.Li(μ-TMP)}_2\text{Al(}^i\text{Bu)}_2 + \text{THF}$$

ΔE = +20.60 kcal mol^{-1}

$$\text{½(THF.LiTMP)}_2 + \text{THF.Al(}^i\text{Bu)}_2\text{(TMP)} = \text{THF.Li(μ-TMP)(μ-OC}_4\text{H}_7\text{)Al(iBu}_2\text{)} + \text{TMPH}$$

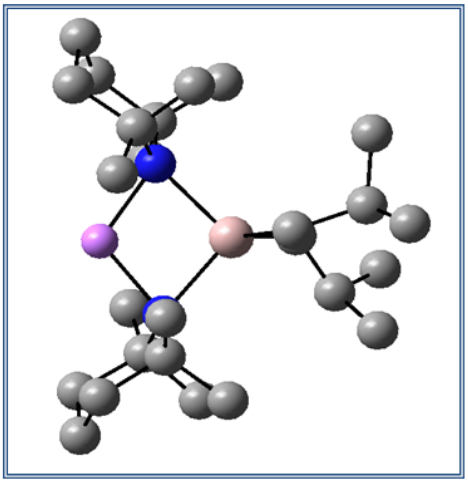
ΔE = -5.30 kcal mol^{-1}

$$\text{THF.Li(μ-TMP)}_2\text{Al(}^i\text{Bu)}_2 + \text{THF} = \text{THF.Li(μ-TMP)(μ-OC}_4\text{H}_7\text{)Al(iBu}_2\text{)} + \text{TMPH}$$

ΔE = -25.90 kcal mol^{-1}

Open Dimer of Li (μ-TMP)$_2$Al(iBu)$_2$

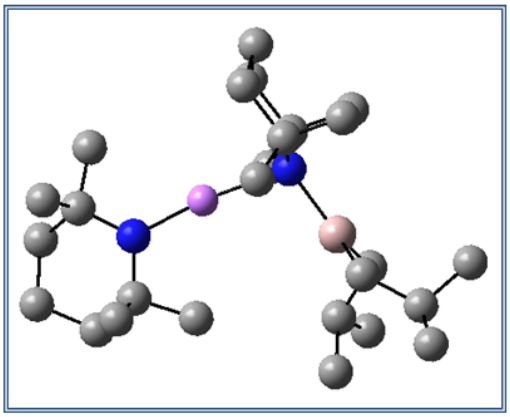
Model 1 The closed version



E = -1382.384657 a.u. (Rel E. = +5.53 kcal mol^{-1})

Open Dimer of Li $(\mu\text{-TMP})_2Al(iBu)_2$

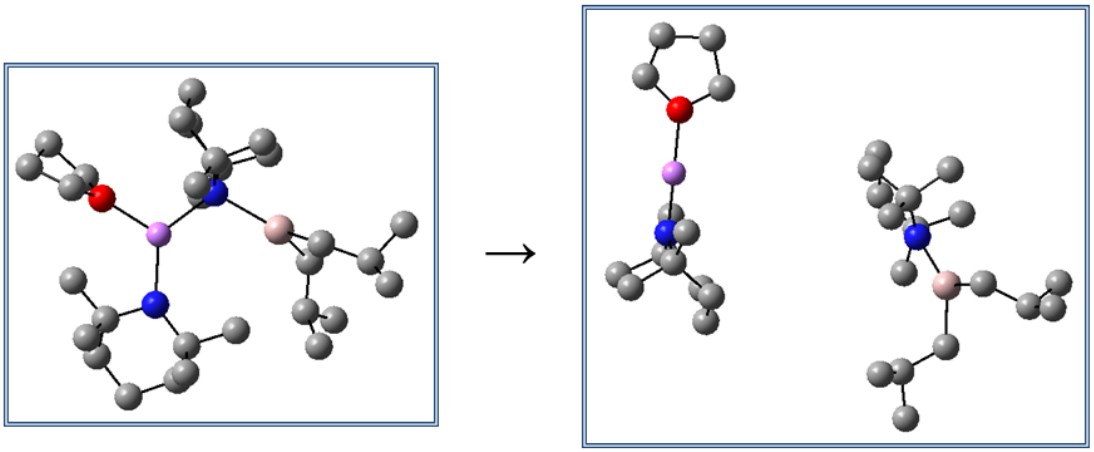
Model 2 The open version



E = -1382.393473 a.u. (Rel E. = 0.00 kcal mol^{-1})

Open Dimer of THF.Li $(\mu\text{-TMP})_2Al(iBu)_2$

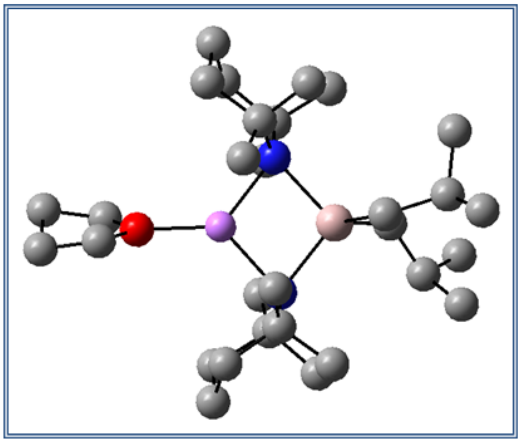
The open version



The Energy given by the sum of the two products is -1614.811704 a.u.

Open Dimer of THF.Li (μ-TMP)$_2$Al(iBu)$_2$

The closed version

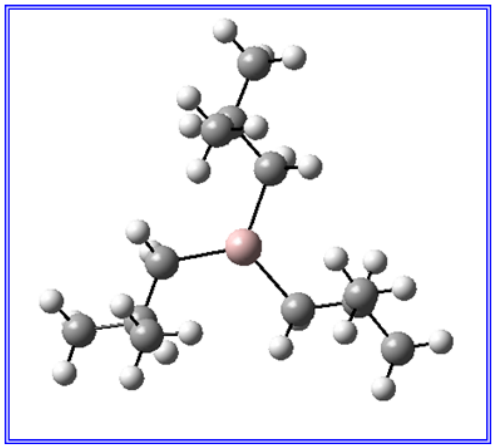


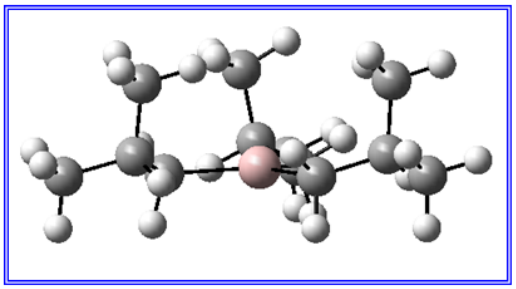
E = -1614.805526 a.u. (Rel. E. = 3.87 kcal mol^{-1})

Al^{i}Bu$_3$

Optimised Geometry

(Put in as C_1 optimises to ~C_3)





E = -715.793662 a.u.

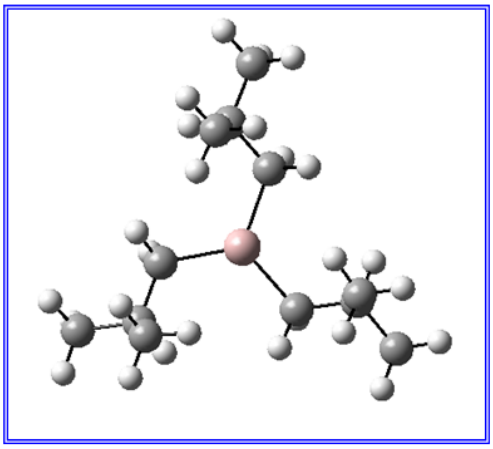
Al^iBu_3

Principal Bond Lengths/Å and Angles/°

Al-C 1.985, 1.985, 1.985

C-Al-C 120.0, 119.7, 119.6

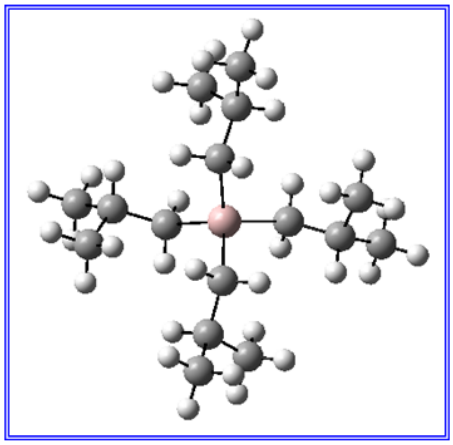
C-AL-C-C 170.3, 170.3, 170.3

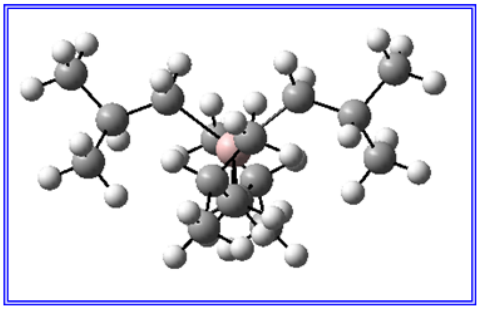


$[Al^iBu_4]^-$

Optimised Geometry

(Put in as C_1 optimises to S_4)





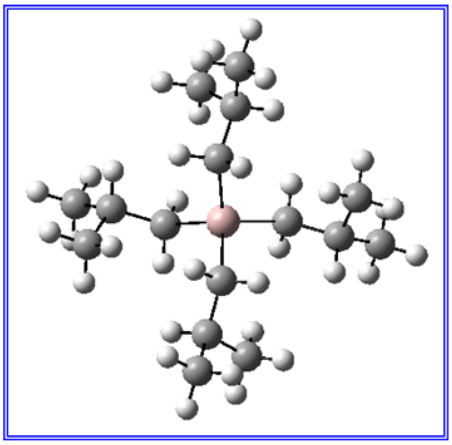
E = -873.623809 a.u.

$[Al^{i}Bu_4]^-$

Principal Bond Lengths/Å and Angles/°

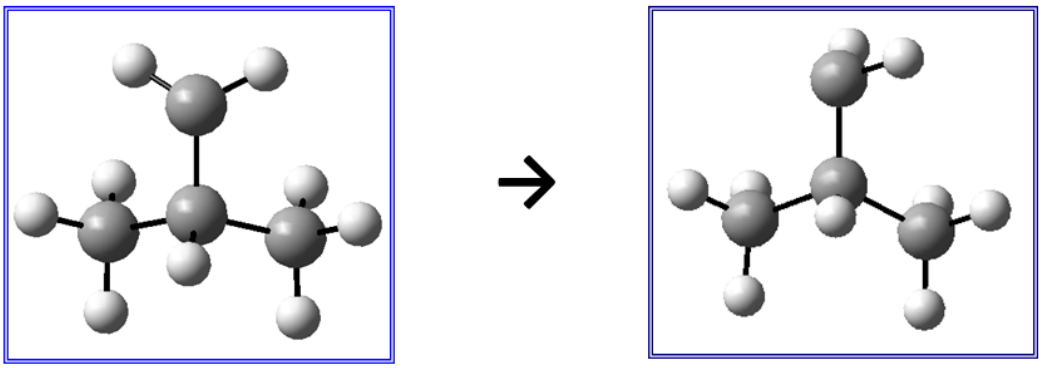
Al-C **2.058**

C-Al-C **112.3, 103.9**



$^{i}Bu^-$

Optimised Geometry



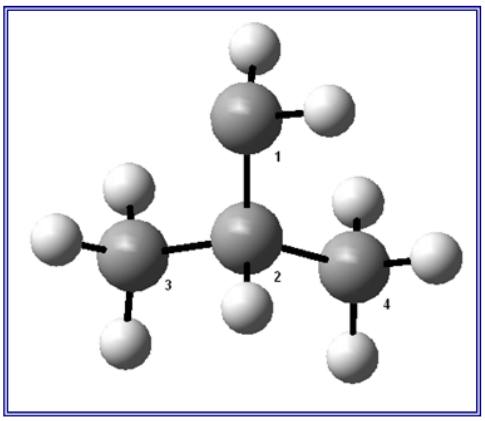
E = -157.701762 a.u.

$^{i}Bu^{-}$

Principal Bond Lengths/Å and Angles/°

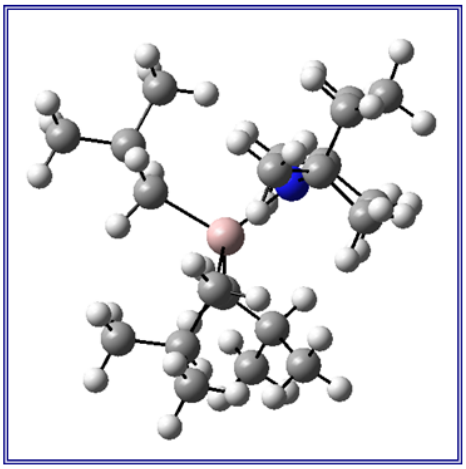
C_1-C_2	1.525
C_2-C_3	1.542
C_2-C_4	1.562

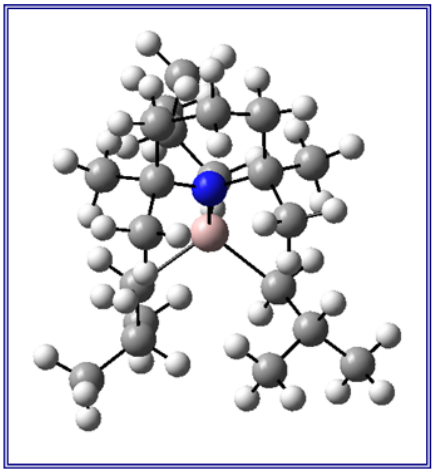
C_1-C_2-C_3	110.6
C_1-C_2-C_4	117.2
C_3-C_2-C_4	108.2



$[Al^{i}Bu_3TMP]^{-}$

Optimised Geometry



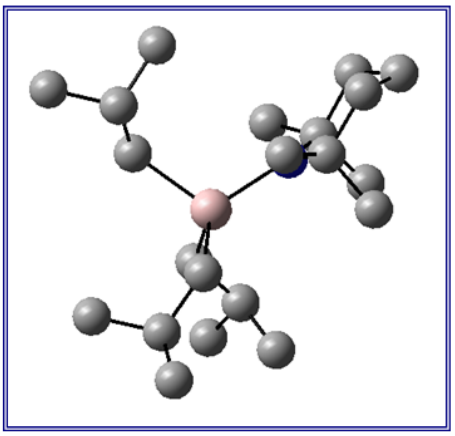


E = -1124.255779 a.u.

$[Al^{i}Bu_3TMP]^-$

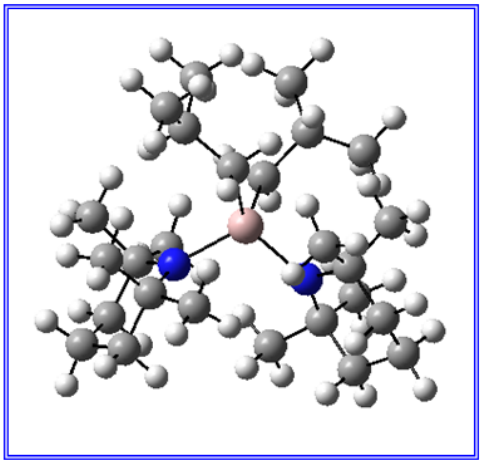
Principal Bond Lengths/Å and Angles/°

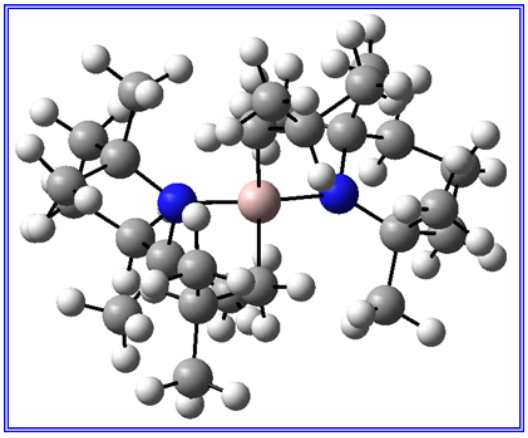
Al-C	2.055, 2.075, 2.076
Al-N	1.980
C-Al-C	109.1, 99.5, 104.4
C-Al-N	111.5, 112.3, 119.0



$[Al^{i}Bu_2TMP_2]^-$

Optimised Geometry

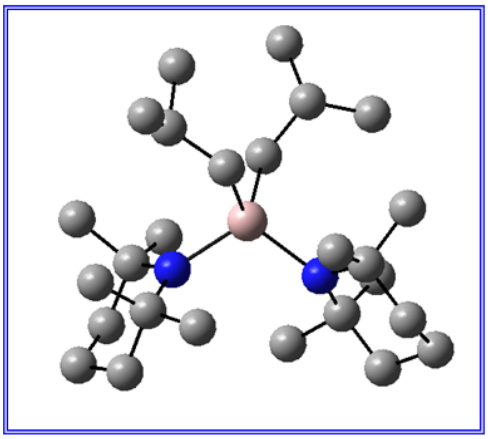




E = -1374.868784 a.u.

$[Al^{i}Bu_2TMP_2]^-$

Principal Bond Lengths/Å and Angles/°



Al-C 2.085, 2.078

Al-N 2.000, 2.024

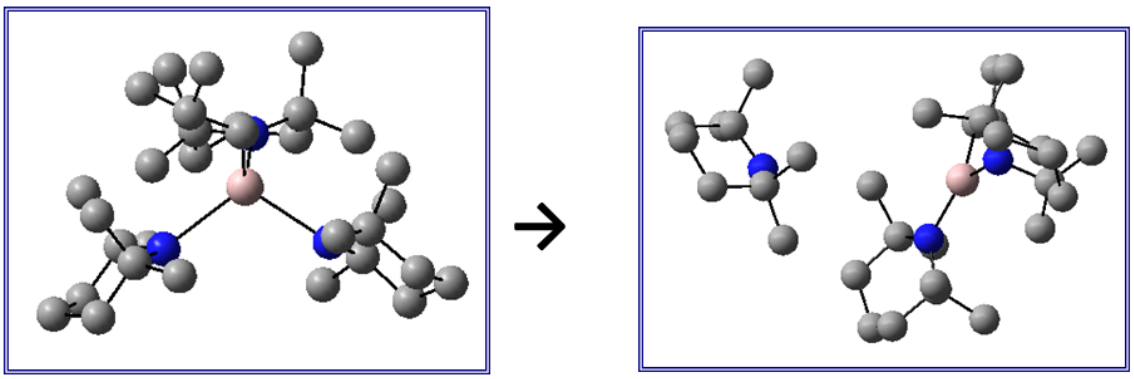
C-Al-C 102.3

N-Al-N 111.3

C-Al-N 113.2, 112.0,105.8, 111.7

$[Al^{i}BuTMP_3]^-$

On Optimisation

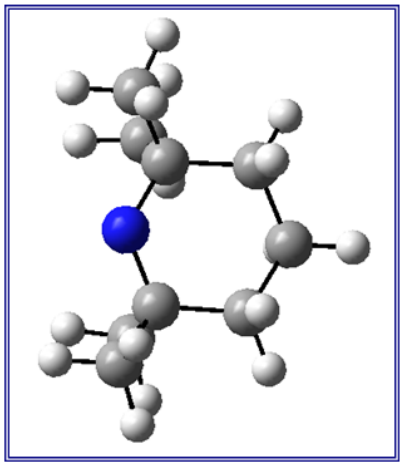


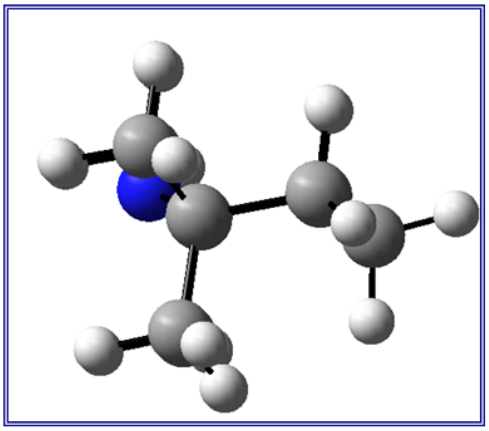
(Abandoned when N…Al distance was greater than 5 Å)

[TMP]$^-$

Optimised Geometry

(Put in as C_1 optimises to C_s)



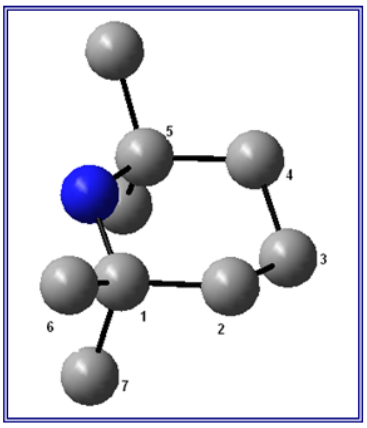


E = -408.380814 a.u.

[TMP]$^-$

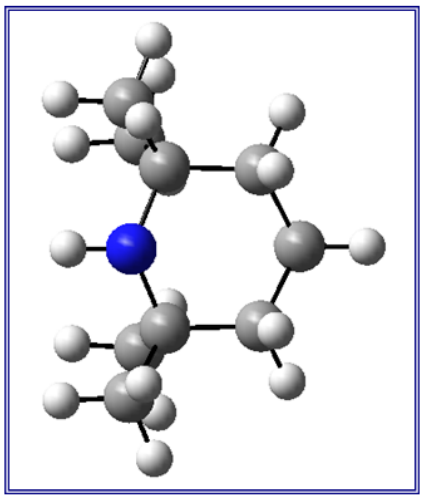
Principal Bond Lengths/Å and Angles/°

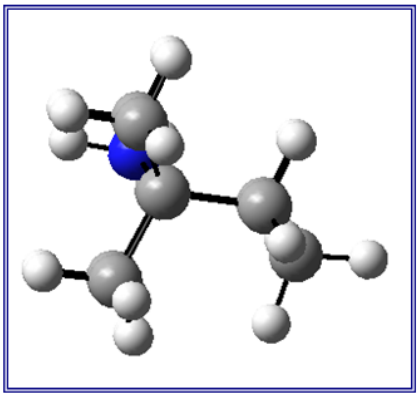
N-C_1	1.500
C_1-C_2	1.563
C_2-C_3	1.533
C_1-C_6	1.547
C_1-C_7	1.577
C_5-N-C_1	118.7
N-C_1-C_2	113.8
C_1-C_2-C_3	111.7
C_2-C_3-C_4	110.0
C_6-C_1-C_7	105.7



[TMPH]

Optimised Geometry (Put in as C_s)



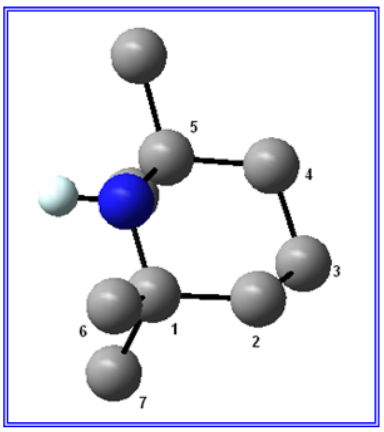


E = -409.003998 a.u.

[TMPH]

Principal Bond Lengths/Å and Angles/°

N-H	1.015	
$N-C_1$		1.477
C_1-C_2		1.543
C_2-C_3		1.532
C_1-C_6		1.539
C_1-C_7		1.550
C_5-N-C_1		122.3
$N-C_1-C_2$		108.0
$C_1-C_2-C_3$		112.9
$C_2-C_3-C_4$		110.3
$C_6-C_1-C_7$		107.8



Energies

$Al^iBu_3 + {}^iBu^- = [Al^iBu_4]^-$

$\Delta E = -80.63$ kcal mol^{-1}

$Al^iBu_3 + TMP^- = [Al^iBu_3TMP]^-$

$\Delta E = -51.02$ kcal mol^{-1}

$Al^iBu_2TMP + {}^iBu^- = [Al^iBu_3TMP]^-$

$\Delta E = -70.00$ kcal mol^{-1}

$Al^iBu_2TMP + TMP^- = [Al^iBu_2TMP_2]^-$

$\Delta E = -28.56$ kcal mol^{-1}

Energies

$Al^iBu_3 + TMPH = [Al^iBu_2TMP] + "{}^iBuH"$

$\Delta E = -12.37$ kcal mol^{-1}

$[Al^iBu_4]^- + TMPH = [Al^iBu_3TMP]^- + "{}^iBuH"$

$\Delta E = -1.81$ kcal mol^{-1}

$[Al^iBu_3TMP]^- + TMPH = [Al^iBu_2TMP_2]^- + "{}^iBuH"$

$\Delta E = +10.09$ kcal mol^{-1}

Energies

$[Al^{i}Bu_4]^- + TMP^- = [Al^{i}Bu_3TMP]^- + {}^{i}Bu^-$

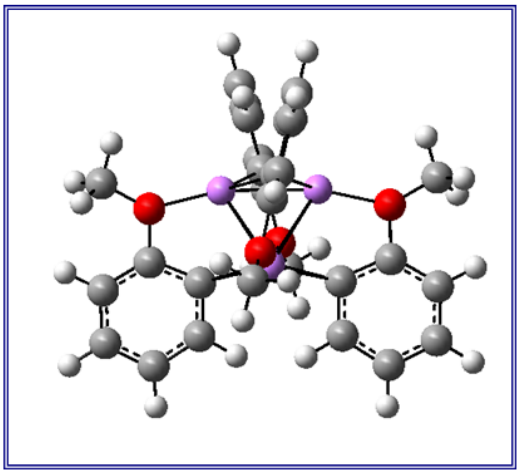
$\Delta E = +29.54$ kcal mol^{-1}

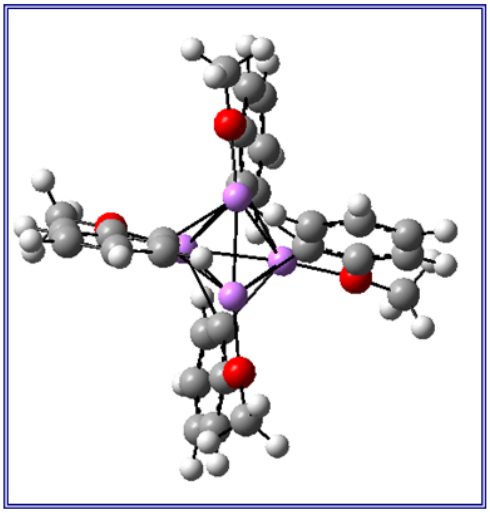
$[Al^{i}Bu_3TMP]^- + TMP^- = [Al^{i}Bu_2TMP_2]^- + {}^{i}Bu^-$

$\Delta E = +41.45$ kcal mol^{-1}

Li.Anisole-tetramer

Optimised Geometry



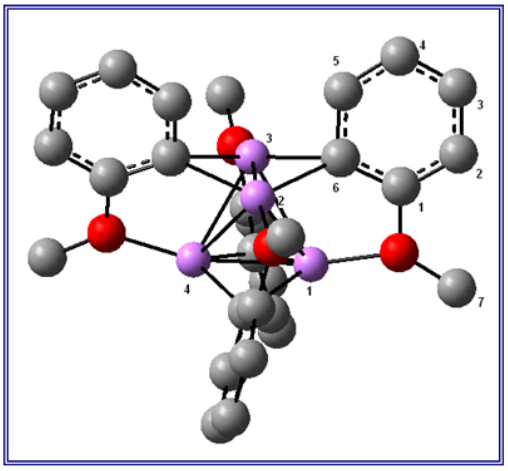


E = -1414.802162 a.u.

Li.Anisole-tetramer

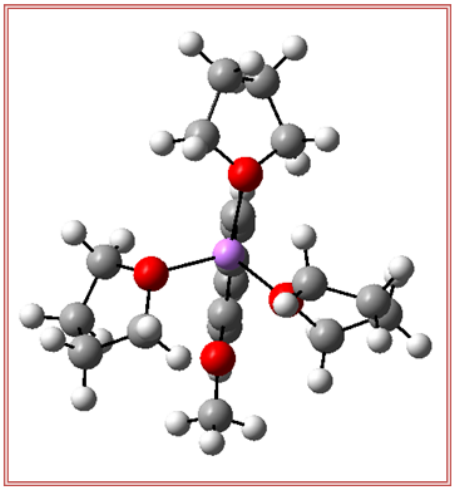
Principal Bond Lengths/Å and Angles/°

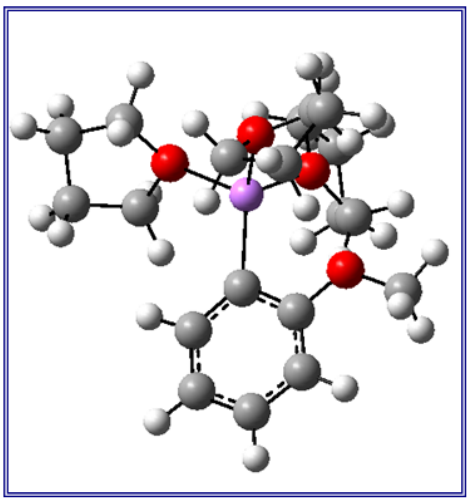
Li_1-O	1.919	Li_1-O-C_1	100.4
Li_2-C_6	2.247	Li_1-Li_2-Li_3	63.3
Li_3-C_6	2.205	Li_2-Li_3-Li_1	59.5
O-C_1	1.407	Li_3-Li_1-Li_2	57.3
O-C_7	1.421	Li_2-C_6-Li_3	67.6
C_1-C_2	1.392	C_5-C_6-Li_2	110.4
C_2-C_3	1.398	C_5-C_6-Li_3	94.5
C_3-C_4	1.386	C_1-C_6-Li_2	124.5
C_4-C_5	1.403	C_1-C_6-Li_3	138.0
C_5-C_6	1.408	O-C_1-C_2	121.0
C_6-C_1	1.408	C_1-C_2-C_3	118.6
		C_2-C_3-C_4	119.8
		C_3-C_4-C_5	119.2
		C_4-C_5-C_6	124.2
		C_5-C_6-C_1	113.1



$(THF)_3$Li.Anisole

Optimised Geometry



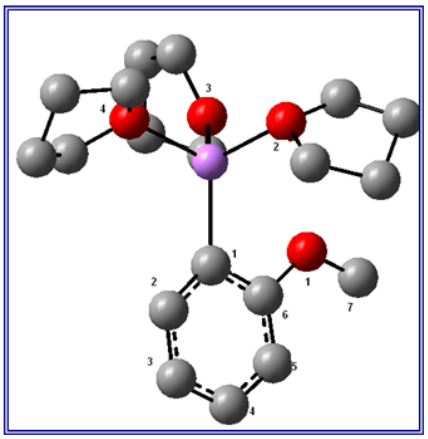


E = -1050.907932 a.u.

$(THF)_3Li.Anisole$

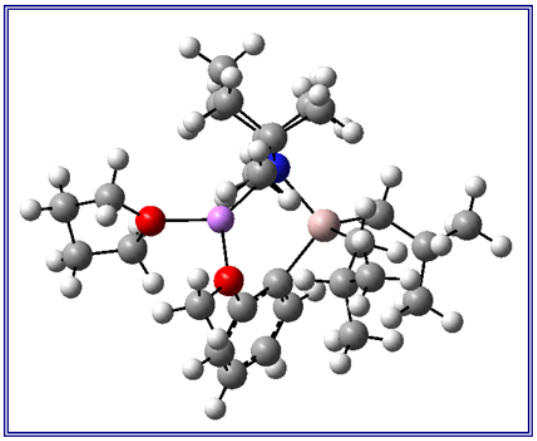
Principal Bond Lengths/Å and Angles/°

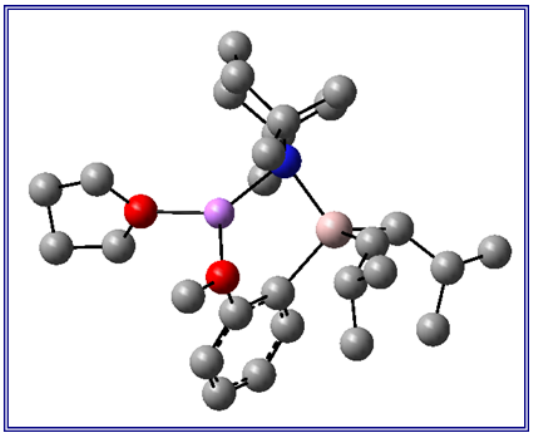
$Li\text{-}O_1$	2.981	$C_1\text{-}Li\text{-}O_2$	113.2
$Li\text{-}O_2$	2.023	$C_1\text{-}Li\text{-}O_3$	118.1
$Li\text{-}O_3$	2.019	$C_1\text{-}Li\text{-}O_4$	115.1
$Li\text{-}O_3$	2.052	$O_2\text{-}Li\text{-}O_3$	106.2
$Li\text{-}C_1$	2.116	$O_2\text{-}Li\text{-}O_4$	103.6
$C_1\text{-}C_2$	1.406	$O_3\text{-}Li\text{-}O_4$	98.8
$C_2\text{-}C_3$	1.403	$Li\text{-}C_1\text{-}C_2$	130.8
$C_3\text{-}C_4$	1.388	$Li\text{-}C_1\text{-}C_6$	116.0
$C_4\text{-}C_5$	1.399	$C_1\text{-}C_2\text{-}C_3$	124.5
$C_5\text{-}C_6$	1.398	$C_2\text{-}C_3\text{-}C_4$	119.1
$C_6\text{-}C_1$	1.406	$C_3\text{-}C_4\text{-}C_5$	119.6
$C_6\text{-}O_1$	1.411	$C_4\text{-}C_5\text{-}C_6$	118.8
$O_1\text{-}C_7$	1.412	$C_5\text{-}C_6\text{-}C_1$	124.8
		$C_6\text{-}C_1\text{-}C_2$	113.2
		$C_1\text{-}C_6\text{-}O_1$	114.4
		$C_6\text{-}O_1\text{-}C_7$	118.4



$THF.Li(\mu\text{-}TMP)(\mu\text{-}Anisole)Al(^{i}Bu)_2$

Optimised Geometry



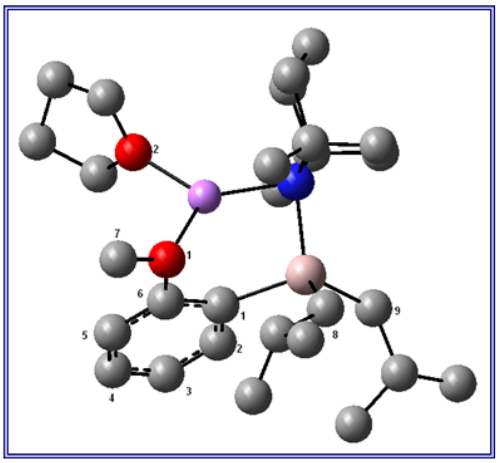


E = -1552.570337 a.u.

THF.Li(μ-TMP)(μ-Anisole)Al(^{i}Bu)$_2$

Principal Bond Lengths/Å and Angles/°

O_2-Li 1.976	O_2-Li-N	134.7	
Li-N	2.029	O_2-Li-O_1	103.5
N-Al	2.050	O_1-Li-N	120.7
Al-C_8 2.041	Li-N-Al	87.2	
Al-C_9 2.043	N-Al-C_1	101.3	
Al-C_1 2.101	N-Al-C_8	115.9	
C_1-C_6 1.404	N-Al-C_9	113.4	
C_6-O_1 1.403	C_8-Al-C_9	104.6	
O_1-Li 2.021	Al-C_1-C_6	125.9	
C_1-C_2 1.396	Al-C_1-C_2	119.0	
C_2-C_3 1.395	C_1-C_6-O_1	113.9	
C_3-C_4 1.391	C_6-O_1-C_7	119.4	
C_4-C_5 1.397	C_6-O_1-Li	89.5	
C_5-C_6 1.407	C_1-C_2-C_3	123.4	
O_1-C_7 1.423	C_2-C_3-C_4	119.6	
		C_3-C_4-C_5	119.8
		C_4-C_5-C_6	118.6
		C_5-C_6-C_1	124.5
		C_6-C_1-C_2	114.2



Energies of the Reactions

¼[Li.Anisole]$_4$ + ^{i}Bu$_2$AlTMP + THF = THF.Li(μ-Anisole)(μ-TMP)Al^{i}Bu$_2$

ΔE = -18.71 kcal mol^{-1}

THF.Li.Anisole + ^{i}Bu$_2$AlTMP = THF.Li(μ-Anisole)(μ-TMP)Al^{i}Bu$_2$

ΔE = -28.45 kcal mol^{-1}

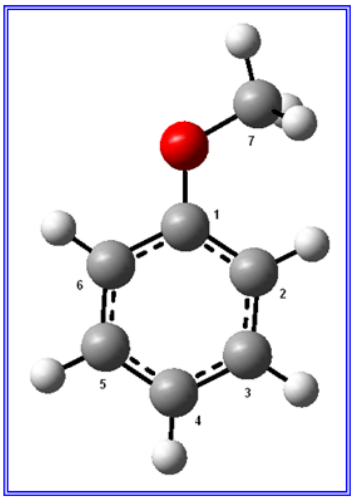
(THF)$_3$Li.Anisole + ^{i}Bu$_2$AlTMP = THF.Li(μ-Anisole)(μ-TMP)Al^{i}Bu$_2$ + 2 THF

ΔE = -9.39 kcal mol^{-1}

Anisole

Principal Bond Lengths/Å and Angles/°

C_1-C_2	1.397
C_2-C_3	1.397
C_3-C_4	1.390
C_4-C_5	1.397
C_5-C_6	1.387
C_6-C_1	1.401
C_1-O	1.365
O-C_7	1.420
C_1-C_2-C_3	119.5
C_2-C_3-C_4	121.0
C_3-C_4-C_5	119.2
C_4-C_5-C_6	120.6
C_5-C_6-C_1	120.1
C_6-C_1-C_2	119.7
C_6-C_1-O	115.7
C_1-O-C_7	118.5

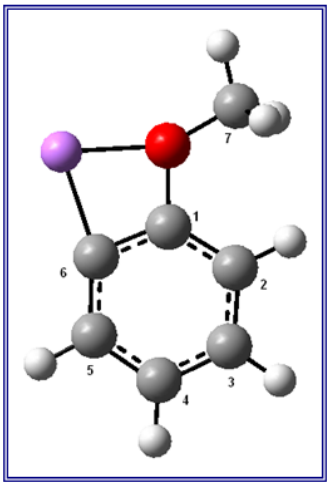


E = -346.729407 a.u.

Li.Anisole

Principal Bond Lengths/Å and Angles/°

C_1-C_2	1.390
C_2-C_3	1.399
C_3-C_4	1.391
C_4-C_5	1.401
C_5-C_6	1.400
C_6-C_1	1.396
C_1-O	1.444
O-C_7	1.419
Li-O	1.903
Li-C_6	1.964
C_1-C_2-C_3	117.0
C_2-C_3-C_4	120.0
C_3-C_4-C_5	120.0
C_4-C_5-C_6	122.7
C_5-C_6-C_1	114.0
C_6-C_1-C_2	126.3
C_6-C_1-O	111.8
C_1-O-C_7	119.4
C_1-O-Li	87.2
O-Li-C_6	74.9
C_5-C_6-Li	159.9

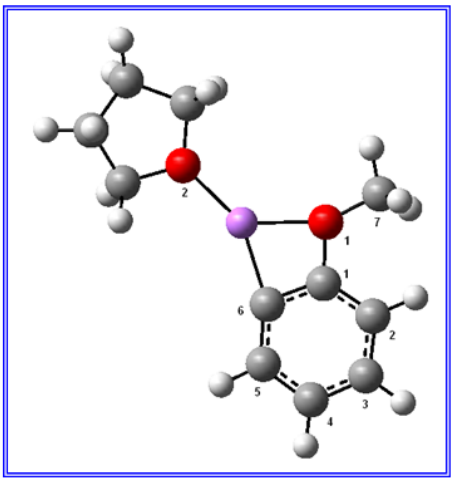


E = -353.654719 a.u.

THF.Li.Anisole

Principal Bond Lengths/Å and Angles/°

C_1-C_2	1.390
C_2-C_3	1.399
C_3-C_4	1.391
C_4-C_5	1.401
C_5-C_6	1.400
C_6-C_1	1.396
C_1-O_1	1.444
O_1-C_7	1.419
Li-O_1	1.903
Li-C_6	1.964
Li-O_2	1.903
C_1-C_2-C_3	117.2
C_2-C_3-C_4	119.9
C_3-C_4-C_5	119.9
C_4-C_5-C_6	123.0
C_5-C_6-C_1	113.7
C_6-C_1-C_2	126.3
C_6-C_1-O_1	111.9
C_1-O_1-C_7	119.2
C_1-O_1-Li	88.1
C_5-C_6-Li	158.7
O_1-Li-C_6	72.3
O_2-Li-C_6	151.5
O_2-Li-O_1	135.2



E = -586.083026 a.u.

Energies of the Reactions

Anisole + ¼[LiTMP]$_4$ = Li.Anisole + TMPH

ΔE = +30.48 kcal mol^{-1}

Anisole + ¼[LiTMP]$_4$ = ¼[Li.Anisole]$_4$ + TMPH

ΔE = +1.73 kcal mol^{-1}

Anisole + ½[THF.LiTMP]$_2$ = THF.Li.Anisole + TMPH

ΔE = +17.6 kcal mol^{-1}

Anisole + ½[THF.LiTMP]$_2$ + 2THF = (THF)$_3$Li.Anisole + TMPH

ΔE = -1.18 kcal mol^{-1}