Supporting Information

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Evaluating cis-2,6-Dimethylpiperidide (cis-DMP) as a Base Component in Lithium-Mediated Zincation Chemistry

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Table S1 Diffusion coefficients of standards in C$_6$D$_6$ solution compared to their FW and volumes.

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Table S3 Diffusion coefficients of standards in [D$_8$]THF solution compared to their FW and volumes.

Graph S1 log D – log FW representation from the $^1$H DOSY NMR data obtained for 1 and the standards TPhN, PhN, TMS at 300K in C$_6$D$_6$.

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Graph S3 log D – log FW representation from the $^1$H DOSY NMR data obtained for 1 and the standards TPhN, PhN, TMS at 300K in [D$_8$]THF.

Graph S4 log D – log V representation from the $^1$H DOSY NMR data obtained for 1 and the standards TPhN, PhN, TMS at 300K in [D$_8$]THF.
Figure S1. (a) $^1$H NMR spectrum (400.03 MHz, C$_6$D$_6$, 300K) of TMEDA.LiZn(cis-DMP)(Et)$_2$ (1) (b) Detail of same spectrum from 0-4 ppm.

Additional broad signals are observed at ~2.90 ppm adjacent to the major $\alpha$-CH DMP signal and at ~1.15 ppm adjacent to the CH$_3$ cis-DMP signal. A 2D COSY experiment in C$_6$D$_6$ solution revealed a similar coupling pattern for the minor species, suggesting that these signals may arise from a conformational isomer of 1. DOSY NMR showed these signals to have a very similar diffusion coefficient as the major peaks, consistent with them being a part of a species of similar formula weight/volume.

In [D$_8$]THF solution, the NMR spectra of 1 are simplified, showing a single set of signals consistent with the required 1:1:2 TMEDA:cis-DMP:ethyl ratio (see Figures S4-S6).

Figure S2. $^{13}$C NMR spectrum (100.60 MHz, C$_6$D$_6$, 300K) of TMEDA.LiZn(cis-DMP)(Et)$_2$ (1)
Figure S3. $^7$Li NMR spectrum (155.50 MHz, C$_6$D$_6$, 300K) of TMEDA.LiZn(cis-DMP)(Et)$_2$ (1).

**NMR data for compound 1 in [D$_8$]THF solution**

$^1$H NMR (400.03 MHz, [D$_8$]THF, 300 K) $\delta$ = 2.78-2.65 (m, 2H; $\alpha$-CH cis-DMP), 2.31 (s, 4H; CH$_2$ TMEDA), 2.16 (s, 12H; CH$_3$ TMEDA), 1.77-1.69 (m overlap with solvent signal, 1H; $\gamma$-CH$_2$ cis-DMP), 1.51-1.36 (m, 3H; 1 of $\gamma$-CH$_2$ and 2 of $\beta$-CH$_2$ cis-DMP), 1.22 (t, $^3$J(H,H) = 8.0 Hz, 6H; ZnCH$_2$CH$_3$), 0.98 (d, $^3$J(H,H) = 6.4 Hz, 6H; CH$_3$ cis-DMP), 0.79 (br s, 2H; $\beta$-CH$_2$ DMP), −0.13 ppm (q, $^3$J(H,H) = 8.0 Hz, 4H; ZnCH$_2$CH$_3$); $^{13}$C($^1$H) NMR (100.60 MHz, [D$_8$]THF, 300 K) $\delta$ = 58.6, 58.6 ($\alpha$-CH cis-DMP and CH$_2$ TMEDA), 46.0 (CH$_3$ TMEDA), 38.0 ($\beta$-CH$_2$ cis-DMP), 27.6 ($\gamma$-CH$_2$ cis-DMP), 25.0 (overlap with solvent peak CH$_3$ cis-DMP), 13.9 (ZnCH$_2$CH$_3$), 3.2 ppm (ZnCH$_2$CH$_3$); $^7$Li NMR (155.50 MHz, [D$_8$]THF, 300 K) $\delta$ = 2.35 ppm
Figure S4. $^1$H NMR spectrum (400.03 MHz, [D8]THF, 300K) of TMEDA.LiZn(cis-DMP)(Et)$_2$ (1).
Figure S5. $^{13}$C NMR spectrum (100.60 MHz, [D$_8$]THF, 300K) of TMEDA.LiZn(cis-DMP)(Et)$_2$ (1).

The signal in the $^{13}$C NMR spectrum corresponding to the cis-DMP methyl groups is at 25.0 ppm and masked by residual solvent signal- its position was determined by correlation in the HSQC spectrum. Even in concentrated samples, the signal corresponding to the ZnCH$_2$CH$_3$ remains as a baseline signal. However, the assignment is made as the 2D HSQC spectrum shows a correlation from 3.2 ppm in the $^{13}$C NMR spectrum to the triplet at -0.13 ppm in the $^1$H NMR spectrum.

Figure S6 $^7$Li NMR spectrum (155.50 MHz, [D$_8$]THF, 300K) of TMEDA.LiZn(cis-DMP)(Et)$_2$ (1).
Figure S7. $^1$H NMR spectrum (400.13 MHz, CDCl$_3$, 300K) for 2-iodo-$N,N$-diisopropylbenzamide (4).

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Figure S11. $^1$H NMR spectrum (400.13 MHz, CDCl$_3$, 300K) for 2-allyl-N,N-diisopropylbenzamide (7). The singlet at ~2.2ppm is due to a small amount of residual hexamethylbenzene (added as internal standard) remaining after purification.

Figure S12. $^{13}$C NMR spectrum (100.62 MHz, CDCl$_3$, 300K) for 2-allyl-N,N-diisopropylbenzamide (7).
Figure S13. $^1$H NMR spectrum (400.03 MHz, [D$_8$]THF, 300K) of [TMEDA.LiZn(cis-DMP)(2-[1-C(O)N(iPr)$_2$]C$_6$H$_4$)tBu] (8). Unknown protic impurity.
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(a) $^{13}$C NMR (100.60 MHz, D$_2$-THF, 300 K)

(b) 

(c)
Figure S14. (a) $^{13}$C NMR spectrum (100.60 MHz, $[D_8]$THF, 300K) of [TMEDA.LiZn(cis-DMP){2-[1-C(O)N(iPr)$_2$]C$_6$H$_4$}tBu] (8). (b) Detail of spectrum from 20-40 ppm. Signal at 36.4 ppm due to unknown impurity. (c) Detail of spectrum from 40-65 ppm. (d) Detail of spectrum from 130-185 ppm. Analysis of a sample at greater concentration confirmed position of the weak quaternary signals for Ar'; the additional signal at ~140ppm is due to presence of non-deprotonated N,N-diisopropylbenzamide in sample.
Figure S15 $^7$Li NMR spectrum (155.50 MHz, $[\text{D}_8]\text{THF}$, 300K) of [TMEDA.LiZn(cis-DMP){2-[1-C(O)N(iPr)$_2$]C$_6$H$_4}$tBu] (8).
Figure S16. $^1$H NMR spectrum (400.03 MHz, C$_6$D$_6$, 300K) of [{$(i$Pr)$_2$NC(Ph)(=O)}LiZn($cis$-DMP)$t$Bu$_2$] (5). Minor impurities at 0.8-0.9 ppm due to grease/small amounts of $cis$-DMP(H) hydrolysis product.

Figure S17. $^{13}$C NMR spectrum (100.60 MHz, C$_6$D$_6$, 300K) of [{$(i$Pr)$_2$NC(Ph)(=O)}LiZn($cis$-DMP)$t$Bu$_2$] (5). Quaternary signal of $t$Bu groups is not observed even in concentrated sample.
Figure S18. $^7$Li NMR spectrum (155.50 MHz, C$_6$D$_6$, 300K) of [(iPr)$_2$NC(Ph)(=O)]LiZn(cis-DMP)/Bu$_2$] (5).

**Determination of yield of 4 by NMR spectroscopy using internal standard.**

![Crude $^1$H NMR (CDCl$_3$)](image)

Figure S19: Representative example of spectrum (400.03 MHz, CDCl$_3$, 300K) of crude product mixture obtained after work-up, analysed in presence of 10 mol% hexamethylbenzene (green = aromatic signals corresponding to 4; red = aromatic signals corresponding to starting material 3).

The signal at 2.2 ppm corresponds to hexamethylbenzene. After work-up, 10 mol% of the integration standard was added to the crude product mixture. The standard signal integration was set to 1.8 H. The resulting integrals of the signals corresponding to 1H of ortho-iodinated product 4 were used to determine a yield of the product in the crude product mixture (in this example 65%). The signal at 7.32-7.28 ppm corresponds to 2H of recovered N,N-diisopropylbenzamide starting material 3 (in this example 20%).

**Deuterium Quench Experimental Procedure**

To a Schlenk flask under argon containing 2 (0.415 g, 1 mmol) suspended in hexane (5 mL) was added $N,N$-diisopropylbenzamide (0.170 g, 0.83 mmol). The mixture was stirred for three hours before the addition of deuterium oxide (1 mL). The mixture was stirred at room temperature for 1.5 hours. The organic phase was separated, dried (MgSO$_4$), filtered and concentrated. Analysis of the crude material was carried out by $^1$H and $^2$H NMR spectroscopy in CDCl$_3$ and CHCl$_3$, respectively. The extent of deuteriation was estimated by integration of
the $^1$H NMR spectrum aromatic signals (see Figure S20). The procedure was also carried out using 1 for metallation. (see Figure S22).

Figure S20. $^1$H NMR (400.03MHz, CDCl$_3$, 300K) spectrum of crude material obtained from D$_2$O quenching of reaction of N,N-diisopropylbenzamide with 1.

Figure S21. $^2$H NMR spectrum (76.77 MHz, CHCl$_3$, 300K) after D$_2$O quenching of reaction of N,N-diisopropylbenzamide with 1.
Figure S22. $^1$H NMR (400.03 MHz, CDCl$_3$, 300K) spectrum of crude material obtained from D$_2$O quenching of reaction of $N,N$-diisopropylbenzamide with 2.

Figure S23. $^2$H NMR spectrum (76.77 MHz, CHCl$_3$, 300K) after D$_2$O quenching of reaction of $N,N$-diisopropylbenzamide with 1.
Addition of TMEDA to pre-metallation complex 5

In a Young’s NMR tube, compound 5 was dissolved in C₆D₆ and ~1 equivalent of TMEDA was added. The resulting yellow solution was analysed at time intervals by ¹H NMR which indicated the formation of metallated N,N-diisopropylbenzamide, although reaction did not go to completion. After 3 days at room temperature, the ratio of metallated: coordinated aromatic substrate in the mixture was estimated at 2.5:1 by integration of the NMR signals (Figure S24).

![Figure S24. Effect of TMEDA addition to donor complex 5. Aromatic region of ¹H NMR (400.03 MHz, C₆D₆, 300K) spectra of (from top to bottom) 5 in absence of TMEDA; 1 molar equivalent of TMEDA after 0.5h; after ~3.5 h and after 3 days.](image)

Addition of benzamide substrate to 1 in absence of any donor solvent

Following an analogous procedure as for the formation of compound 5, in hexane solution, equimolar amounts of Li(cis-DMP), Et₂Zn (as 1M solution in hexane) and N,N-diisopropylbenzamide were mixed to give a yellow solution. Crystallisation did not occur but concentration of an aliquot of the reaction mixture under reduced pressure gave a yellow oil which was analysed by ¹H NMR spectroscopy (Figure S25). The signals in the aromatic region showed no metallation had occurred and showed a similar pattern to those observed in compound 5, consistent with the ethyl congener of this compound having formed. Consistent with this, iodosylation of the mixture gave no ortho-iodinated benzamide product (4).
Figure S25. $^1$H NMR (400.05 MHz, C$^6$D$^6$, 300 K) spectrum of oil obtained upon reaction of equimolar amounts of benzamide 3, Et$_2$Zn and Li(cis-DMP). The triplet at 0.9 ppm and additional signal under peak at 1.36 ppm due to remaining hexane in oil.

**NMR data for Li(cis-DMP)**

Li(cis-DMP) was formed by addition of an equimolar quantity of cis-DMP(H) to nBuLi in hexane solution. Removal of volatiles under reduced pressure gave Li(cis-DMP) as a yellow oil. $^1$H NMR (400.03 MHz, [D$_8$]THF, 300 K) $\delta$=2.70-2.63 (m, 2H; $\alpha$-CH cis-DMP), 1.82-1.69 (overlap with solvent signal, 3H; $\gamma$-CH$_2$ cis-DMP and 2H CH$_2$ THF), 1.43-1.38 (m, 3H; 1 of $\gamma$-CH$_2$ and 2 of $\beta$-CH$_2$ cis-DMP), 1.03 (d, $^3$J(H,H) = 6.4 Hz, 6H; CH$_3$ cis-DMP), 0.64-0.55 ppm (m, 2H; $\beta$-CH$_2$ DMP). $^7$Li NMR (155.50 MHz, [D$_8$]THF, 300 K) $\delta$=3.90 ppm.
Figure S26. $^1$H NMR spectrum (400.05 MHz, $\text{D}_8\text{-THF}$, 300 K) of Li(\textit{cis}-DMP). Some hexane (at 0.89 and 1.29 ppm) and \textit{cis}-DMP(H) (doublet at 0.96 ppm) remained in the yellow oil which was analysed.
1H DOSY NMR analysis of compound 1

**Instrumental Details:** The Diffusion-Ordered Spectroscopy (DOSY) NMR experiments were performed on a Bruker AVANCE 400 NMR spectrometer operating at 400.13 MHz for proton resonance under TopSpin (version 2.0, Bruker Biospin, Karlsruhe) and equipped with a BBFO-z-atm probe with actively shielded z-gradient coil capable of delivering a maximum gradient strength of 54 G/cm. Diffusion ordered NMR data was acquired using the Bruker pulse program dstegp3s employing a double stimulated echo with three spoiling gradients. Sine-shaped gradient pulses were used with a duration of 3 ms together with a diffusion period of 100 ms. Gradient recovery delays of 200 µs followed the application of each gradient pulse. Data was accumulated by linearly varying the diffusion encoding gradients over a range from 2% to 95% of maximum for 64 gradient increment values. DOSY plot was generated by use of the DOSY processing module of TopSpin. Parameters were optimized empirically to find the best quality of data for presentation purposes. Diffusion coefficients were calculated by fitting intensity data to the Stejskal-Tanner expression.

**Sample Preparation:** To an NMR tube containing compound 1 (20 mg) dissolved in deuterated solvent (C₆D₆ or [D₈]THF) was added tetraphenylnaphthalene (TPhN, 15 mg) phenylnaphthalene (PhN, 13.2 µL) and tetramethylsilane (TMS, 19.1 µL) as inert reference standards. The 1H DOSY NMR data was recorded at 300 K.

From the diffusion coefficients of the internal standards, linear calibration graphs were obtained by plotting logD versus logFW. Using the diffusion coefficients for the signals corresponding to 1, an estimate of the FW or volume of the species present in solution was obtained.

The data was also interpreted using volume (V) instead of FW. For this purpose, DFT calculations were used to determine the volumes of the standards used. A calibration graph of logD versus logV was obtained.

In addition the volume of 1, and its TMEDA-free and THF-solvated congeners were calculated by DFT calculations in order to compare these to the values estimated from the DOSY study.
**DOSY NMR study of 1 in C₆D₆ solution**

Table S1 shows the $D_{AV}$ for each standard. $D_{AV}$ is the mean of the D values obtained for each signal in the $^1$H dimension which corresponds to the standard (except for TMS, which gives a single resonance in the $^1$H spectrum). Graph S1 shows the linear calibration graph of logD versus log FW and Graph S2 shows the linear calibration graph of log D versus log V.

Table S1. Diffusion coefficients of standards in C₆D₆ solution compared to their FW and volumes.

| Compound | $10^{-10}D_{AV}$ (m²s⁻¹) | LogD | FW (g mol⁻¹) | logFW | V (cm³ mol⁻¹) | log(V) |
|----------|--------------------------|------|--------------|-------|--------------|--------|
| TPhN     | 7.24                     | -9.140126488 | 432.55 | 2.636036316 | 358.5 | 2.55448916 |
| PhN      | 11.9                     | -8.922995673 | 204.27 | 2.310204589 | 163.5 | 2.213517757 |
| TMS      | 19.0                     | -8.720561212 | 88.22 | 1.945567053 | 101.5 | 2.006466042 |

Graph S1. log D – log FW representation from the $^1$H DOSY NMR data obtained for 1 and the standards TPhN, PhN, TMS at 300K in C₆D₆.

Graph S2. log D – log V representation from the $^1$H DOSY NMR data obtained for 1 and the standards TPhN, PhN, TMS at 300K in C₆D₆.
From the DOSY study in C₆D₆, the different components of the mixture are separated in the diffusion dimension in the size sequence TPhN>'1'>PhN>cis-DMP(H)>TMS according to their increasing D values in the order TPhN<'1'<PhN<cis-DMP(H)<TMS (see Table S1).

The D value for the cis-DMP(H) present in the sample (due to hydrolysis) was D = 1.737 x 10⁻⁹ m² s⁻¹. Using the calibration graph, the FW_DOSY which is predicted is 104 g mol⁻¹, an error of -8.9% on the true value of 113.20 g mol⁻¹.

D values for the signals corresponding to the components of 1 are of similar magnitudes, and all intermediate between those of the standards TPhN and PhN, consistent with being a part of a multicomponent species in solution with a volume/FW intermediate between that of these two standards. For the signals of the cis-DMP anion D = 9.36 x 10⁻¹⁰ m² s⁻¹, for the ethyl signals D = 9.76 x 10⁻¹⁰ m² s⁻¹. The signals for TMEDA (overlap with cis-DMP peaks), with D = 9.80 x 10⁻¹⁰ m² s⁻¹.

For the signals in the ¹H spectrum corresponding to 1, D_ΔV = 9.58 E⁻¹⁰ m² s⁻¹

logD = -9.018679827.

Using the calibration graphs shown in Figure S1 and S2, FW_DOSY = 279.93 g mol⁻¹ and V_DOSY = 239.20 cm³ mol⁻¹.

The values obtained through DOSY studies were compared to the true FW of 1 and to the calculated volume of 1 (see Table S2).

Table S2: Calculated molar volumes of 1 and analogues.

| Compound                                      | Calculated Volume (cm³ mol⁻¹) |
|-----------------------------------------------|------------------------------|
| [(TMEDA)LiZn(cis-DMP)Et₂] (1)                 | 296.095                      |
| [LiZn(cis-DMP)Et₂]                            | 196.971                      |
| [(THF)LiZn(cis-DMP)Et₂]                       | 251.487                      |
| [(THF)₂LiZn(cis-DMP)Et₂]                     | 312.035                      |

The FW of 1 = 358.83 g mol⁻¹. Thus the FW_DOSY represents an error of -28.2% compared to this value.

Considering the volume of the species, the V_DOSY represents an error of -23.8% compared to the volume of 1 determined by DFT calculations.
DOSY study of 1 in [D₈]THF solution

Analysis of 1 by DOSY NMR was repeated as described previously, but using [D₈]THF as NMR solvent.

Figure S27: ¹H DOSY spectrum of 1 in [D₈]THF in at 300K in presence of inert standards 1,2,3,4-tetraphenynaphthalene (TPhN), 1-phenynaphthalene (PhN) and tetramethylsilane (TMS).

Table S3. Diffusion coefficients of standards in [D₈]THF solution compared to their FW and volumes.

| Compound | $10^{10} \text{D}_\text{Av}$ (m² s⁻¹) | LogD (g mol⁻¹) | FW (g mol⁻¹) | logFW | V (cm³ mol⁻¹) | log(V) |
|----------|----------------------------------|----------------|--------------|--------|--------------|--------|
| TPhN     | 7.78                             | -9.109206516   | 432.55       | 2.636036316 | 358.5       | 2.55448916 |
| PhN      | 13.0                             | -8.885722703   | 204.27       | 2.310204589 | 163.5       | 2.213517757 |
| TMS      | 20.1                             | -8.695940534   | 88.22        | 1.945567053 | 101.5       | 2.006466042 |
From the DOSY study in [D$_8$]THF, the components of the mixture are separated in the diffusion dimension in the size order TPhN > (ethyl; cis-DMP) > PhN > TMEDA > TMS according to their increasing D values. TPhN < (ethyl; cis-DMP) < PhN < TMEDA < TMS. D values for the signals corresponding to the ethyl (D = 9.46 x $10^{-10}$ m$^2$ s$^{-1}$) and cis-DMP (D = 9.00 x $10^{-10}$ m$^2$ s$^{-1}$) components of 1 are of similar magnitudes and lie intermediate between those of the standards TPhN and PhN, consistent with a species in solution with a volume/FW intermediate between that of these two standards. The D value of TMEDA is greater, lying between that of PhN and TMS standards, suggesting it is not part of the same species in solution.

Analysis of the D$_{AV}$ value for TMEDA gives FW$_{DOSY} = 114.45$ g mol$^{-1}$, close to TMEDA’s true FW of 116.20 g mol$^{-1}$. This is consistent with TMEDA being fully dissociated from 1 in THF solution.

For the signals in the $^1$H spectrum which correspond to the cis-DMP and ethyl components of 1:

D$_{AV}$ = 9.16 x $10^{-10}$ m$^2$ s$^{-1}$ therefore logD = -9.038.

Using the calibration graphs shown in Graph S3 and S4:
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\[ \text{FW}_{\text{DOSY}} = 341.97 \text{ g mol}^{-1} \text{ and } \text{V}_{\text{DOSY}} = 280.58 \text{ cm}^3 \text{ mol}^{-1} \]

Although \( \text{FW}_{\text{DOSY}} \) matches closely to the solid state FW of 1 (FW = 358.83), from the DOSY spectrum in THF, and from the D value, TMEDA is not part of the same species in solution.

The value obtained through DOSY NMR studies was compared to the FW and calculated volume of 1. It is possible that 1 exists as a \([\text{D}_8]\text{THF}\) solvated species so comparison to the volume and FW of a possible species \(\text{‘}([\text{D}_8]\text{THF})\text{LiZn}(\text{cis-DMP})\text{Et}_2\text{’}\).

Comparison of \( \text{FW}_{\text{DOSY}} \) and \( \text{V}_{\text{DOSY}} \) to a possible species \([([\text{D}_8]\text{THF})\text{LiZn}(\text{cis-DMP})\text{Et}_2]\) (for which FW = 322.79 g mol\(^{-1}\); V = 251.48 cm\(^3\) mol\(^{-1}\)) gives errors of +5.6% for FW and +10.4% for V.

Comparison of \( \text{FW}_{\text{DOSY}} \) and \( \text{V}_{\text{DOSY}} \) to a possible species \([([\text{D}_8]\text{THF})_2\text{LiZn}(\text{cis-DMP})\text{Et}_2]\) (FW = 402.95 g mol\(^{-1}\); V = 312.035 cm\(^3\) mol\(^{-1}\)) gives errors of -17.8% for FW and -11.2% for V.

DFT Calculations

Density Functional Theory Calculations were performed using the Gaussian computational package G03. In this series of calculations the B3LYP density functional 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.

Calculations considering reaction of zincate 2 with \(\text{N,N}-\text{diisopropylbenzamide}\).
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**Tm.Li(μ-DMP)(μ-′Bu)Zn′Bu**

**Principal Bond Lengths/Å and Angles/°**

| Bond            | Length/Å | Angle/° |
|-----------------|----------|---------|
| Li-Nmean        | 2.283    | 2.331   |
| Li-Napx         | 2.006    |         |
| Li-C2           | 2.808    |         |
| N-Zn            | 2.141    |         |
| Zn-C_{Bu(term)} | 2.050    |         |
| Zn-C_{1}        | 2.060    |         |
| N_{apx}-Li-N_{apx} | 82.5    |         |
| Li-N_{apx}-Zn   | 105.4    |         |
| N_{apx}-Zn-C_{1} | 114.5   |         |
| Zn-C_{1}-C_{2}  | 113.8    |         |
| C_{2}-C_{3}-Li  | 105.2    |         |
| C_{3}-Li-N_{apx} | 96.4    |         |

**Tm.Li(μ-DMP)(μ-ortho-PhCON(′Pr)_{2})Zn′Bu**

**Model 1**

E = -3258.239988 a.u.

**Tm.Li(μ-DMP)(μ-ortho-PhCON(′Pr)_{2})Zn′Bu**

**Principal Bond Lengths/Å and Angles/°**

| Bond            | Length/Å | Angle/° |
|-----------------|----------|---------|
| Li-N_{apx}      | 2.217    | 3.237   |
| Li-N_{apx}      | 2.936    |         |
| Li-C_{3}        | 5.934    |         |
| Li-C_{2}        | 4.138    | 5.623   |
| Li-C_{2}        | 3.089    | 4.336   |
| Li-C_{1}        | 3.252    |         |
| N-Zn            | 2.963    |         |
| Zn-C_{2}(term)  | 2.039    |         |
| Zn-C_{1}        | 2.061    |         |
| Li-O            | 1.983    |         |
| Li-N_{apx}-Zn   | 97.3     |         |
| N_{apx}-Zn-C_{1} | 112.8   |         |
| Zn-C_{2}-Li     | 68.6     |         |
| C_{3}-Li-N_{apx} | 79.8    |         |
| Zn-C_{1}-C_{2}  | 127.8    |         |
| C_{2}-C_{1}     | 118.9    |         |
| C_{1}-C_{2}     | 118.5    |         |
| C_{1}-C_{2}     | 120.4    |         |
Tm.Li(µ-DMP)(µ-ortho-PhCON(Pr)₂)ZnBu

Model 2 (twisting DMP of Model 1 by 180 °)

E = -3258.240274 a.u.
(0.18 kcal mol⁻¹ more stable than Model 1)

Tm.Li(µ-DMP)(µ-ortho-PhCON(Pr)₂)ZnBu

Principal Bond Lengths/Å and Angles/°

| Bond                  | Length/Å | Angle/° |
|-----------------------|----------|---------|
| Li-N₈a                | 2.2322732|         |
| Li-N₈b                | 2.974    |         |
| Li-C₁                 | 5.899    |         |
| Li-C₆                 | 4.1925164|         |
| Li-C₇                 | 3.1354367|         |
| Li-C₈                 | 3.285    |         |
| N-Zn                  | 2.930    |         |
| Zn-C₁₈(term)          | 2.044    |         |
| Zn-C₁₃                | 2.081    |         |
| Li-O                  | 1.975    |         |
| Li-N₈a-Zn             | 94.7     | 111.5   |
| N₈a-Zn-C₁₈            | 111.5    |         |
| Zn-C₁-Li              | 78.8     |         |
| C₁₈-Li-N₈a            | 128.3    |         |
| C₁₃-C₁₈               | 119.4    |         |
| C₁₃-C₁₀               | 118.7    |         |
| C₁₀-Li                | 130.2    |         |

Tm.Li(µ-DMP)(µ-ortho-PhCON(Pr)₂)ZnBu

Model 3 (rotating benzamide of Model 2 by 180 °)

E = -3258.241025 a.u.
(0.47 kcal mol⁻¹ more stable than Model 2)
Tm.Li(µ-DMP)(µ-ortho-PhCON(Pr)_2)ZnBu

Principal Bond Lengths/Å and Angles°

| Bond                  | Length/Å | Angle/°  |
|-----------------------|----------|----------|
| Li-N                  | 2.317    | 112.5    |
| Li-C                  | 2.113    |          |
| Li-C                  | 5.007    |          |
| Li-C                  | 4.153    | 117.1    |
| Li-C                  | 3.107    |          |
| Li-C                  | 3.207    |          |
| Zn-N                  | 2.043    |          |
| Zn-C, (term)          | 2.052    |          |
| Zn-C, (term)          | 2.073    |          |
| Li-O                  | 1.984    |          |
| N=C, Li               | 112.5    |          |
| Zn-C, Li              | 110.6    |          |
| Zn-C, N               | 110.6    |          |
| Zn-C, C               | 110.5    |          |
| Zn-C, C               | 119.7    |          |
| Zn-C, C               | 127.8    |          |
| C,C, C                | 118.7    |          |
| C,C, O                | 119.2    |          |
| C-O, Li               | 129.2    |          |

Energies

Energies of Tm.Li(µ-DMP)(µ-PhCON(Pr)_2)ZnBu

(i) ortho \( E = -3258.241025 \) a.u. \( \text{rel. en.} = 0.00 \text{ kcal mol}^{-1} \)

(ii) meta \( E = -3258.233213 \) a.u. \( \text{rel. en.} = 4.90 \text{ kcal mol}^{-1} \)

(iii) para \( E = -3258.228475 \) a.u. \( \text{rel. en.} = 7.88 \text{ kcal mol}^{-1} \)

Energetics

Energies of the Reactions:

\[
\text{PhCON(Pr)_2 + Tm.Li(µ-DMP)(µ-Bu)ZnBu = Tm.Li(µ-DMP)(µ-ortho-PhCON(Pr)_2)ZnBu + "BuH"} \\
\Delta E = -27.01 \text{ kcal mol}^{-1}
\]

\[
\text{PhCON(Pr)_2 + Tm.Li(µ-DMP)(µ-Bu)ZnBu = Tm.Li(µ-DMP)(µ-meta-PhCON(Pr)_2)ZnBu + "BuH"} \\
\Delta E = -22.11 \text{ kcal mol}^{-1}
\]

\[
\text{PhCON(Pr)_2 + Tm.Li(µ-DMP)(µ-Bu)ZnBu = Tm.Li(µ-DMP)(µ-para-PhCON(Pr)_2)ZnBu + "BuH"} \\
\Delta E = -19.13 \text{ kcal mol}^{-1}
\]
Product of the Reaction

In the previous section we examined the possible products where the bridging t-Bu group had been replaced by the benzamide species.

Here we examine the product where the bridging DMP group has been substituted by the benzamide species.

\[ \text{Tm.Li(µ-t-Bu)(µ-ortho-PhCON}'(iPr)\rangle_2\rangle Zn\rangle t-Bu} \]

\[ E = -3086.159480 \text{ a.u.} \]

### Principal Bond Lengths/Å and Angles/°

| Bond/Angle | Length/Å | Angle/° |
|------------|----------|---------|
| Li-H₄C₆  | 2.174 2.160 |        |
| Li-C₇     | 2.538    |        |
| Li-C₈     | 2.549    |        |
| Li-C₉     | 4.065 4.048 |        |
| Li-C₁₀    | 3.403 4.113 |        |
| Li-C₁₁    | 2.549    |        |
| Zn-C₆₂ (heli) | 2.063 |        |
| Zn-C₇     | 2.097    |        |
| Li-O      | 1.062    |        |
| Li-C₁₀-C₁₁ | 122.8    |        |
| C₆₂-C₁₀-D₈ | 113.5    |        |
| C₈-C₉-Zn   | 121.5    |        |
| C₁₀-C₁₁-C₁ | 130.1    |        |
| C₁₉-C₁₀    | 119.4    |        |
| C₁₀-C₁₁    | 119.5    |        |
| C₁₉-C₁₉    | 132.3    |        |
| C₁₉-C₁₉    | 132.3    |        |
| O-Li-C₁₀ | 102.6    |        |
Energetics

Energies of the Reactions:

\[
\text{PhCON('Pr)_2 + Tm.Li(\mu-\text{DMP})(\mu-\text{Bu})Zn'Bu} = \\
\text{Tm.Li(\mu-\text{Bu})(\mu-\text{ortho-PhCON('Pr)_2})Zn'Bu + HDMP} \\
\Delta E = -2.90 \text{ kcal mol}^{-1}
\]

\[
\text{PhCON('Pr)_2 + Tm.Li(\mu-\text{DMP})(\mu-\text{Bu})Zn'Bu} = \\
\text{Tm.Li(\mu-\text{DMP})(\mu-\text{ortho-PhCON('Pr)_2})Zn'Bu + }'\text{BuH}'' \\
\Delta E = -27.01 \text{ kcal mol}^{-1}
\]

A Related Reaction

Examined the product of the reaction of 
\[\text{Li(\mu-\text{DMP})(\mu-\text{Bu})Zn'Bu and PhCON('Pr)_2}\]

\[
\text{PhCON('Pr)_2.Li(\mu-\text{Bu})(\mu-\text{DMP})Zn'Bu}
\]

\[\text{PhCON('Pr)_2 is now co-ordinating to Li} \]

\[E = -3068.960932 \text{ a.u.}\]
PhCON(\textit{i}Pr) \textsubscript{2}Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)Zn\textsubscript{t}Bu

Principal Bond LengthsÅ and Angles°

| Bond                  | Length (Å) |
|-----------------------|------------|
| Li-N<sub>o</sub>      | 1.927      |
| H-Zn                  | 2.120      |
| Zn-C<sub>o</sub>-term | 2.042      |
| C<sub>o</sub>-H<sub>z</sub>-H<sub>y</sub> | 2.969      |
| C<sub>o</sub>-H<sub>y</sub>-H<sub>z</sub> | 1.531      |
| Li-C<sub>o</sub>-H<sub>y</sub> | 2.406      |
| Li-O                  | 1.875      |
| Li-C<sub>y</sub>      | 5.426      |
| Li-C<sub>o</sub>      | 4.9095.121 |
| Li-C<sub>z</sub>      | 3.9354.210 |
| Li-C<sub>t</sub>      | 3.515      |
| Li-N<sub>o</sub>-Zn    | 95.2       |
| N<sub>o</sub>-Zn-C<sub>o</sub>-H<sub>y</sub> | 113.0      |
| Zn-C<sub>o</sub>-H<sub>y</sub>-H<sub>z</sub> | 110.6      |
| C<sub>o</sub>-H<sub>y</sub>-C<sub>o</sub>-H<sub>z</sub> | 101.8      |
| C<sub>o</sub>-H<sub>z</sub>-Li-N<sub>n</sub> | 113.3      |
| C-O-Li                | 145.4      |

PhCON(\textit{i}Pr) \textsubscript{2}Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)Zn\textsubscript{t}Bu

Energies of the Reactions

\[
\text{PhCON(\textit{i}Pr)} \textsubscript{2} + \text{Tm.Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)Zn\textsubscript{t}Bu} = \\
\text{Tm + PhCON(\textit{i}Pr)} \textsubscript{2}.\text{Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)Zn\textsubscript{t}Bu} \\
\Delta E = -5.05 \text{ kcal mol}^{-1}
\]

Compare with:

\[
\text{PhCON(\textit{i}Pr)} \textsubscript{2} \text{ + Tm.Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)Zn\textsubscript{t}Bu} = \\
\text{Tm.Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)+"BuH"} \\
\Delta E = -27.01 \text{ kcal mol}^{-1}
\]

Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)Zn\textsubscript{t}Bu

In the next section:

Examined the species Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)Zn\textsubscript{t}Bu,

formed by the reaction of LiDMP and Zn(\textit{Bu})\textsubscript{2} in the

absence of a co-ordinating solvent such as Tm.

Then looked at the two possible reactions of PhCON(Pr\textsubscript{2}) with Li(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)(\textit{t}Bu)Zn\textsubscript{t}Bu

i.e. (a) co-ordination at Li

and (b) replacing the bridging \textit{Bu} group
Li(µ-DMP)(µ-ʻBu)ZnʻBu

Model 1 Optimised Geometry

E = -2432.238631 a.u.

Li(µ-DMP)(µ-ʻBu)ZnʻBu

Principal Bond Lengths/Å and Angles/°

| Bond          | Length/Å | Angle/° |
|---------------|----------|---------|
| Li-N	ext{deg} | 1.874    |         |
| Li-C₁         | 2.281    |         |
| Li-C₂         | 2.083    |         |
| N-Zn          | 2.113    |         |
| Zn-C\text{but}(term) | 2.017   |         |
| Zn-C₁         | 2.151    |         |
| Li-N	ext{deg}-Zn | 74.0     |         |
| N	ext{deg}-Zn-C₁ | 108.1    |         |
| C\text{r}-Li-N	ext{deg} | 112.1   |         |
| Zn-C\text{r}-Li | 65.7     |         |
| C\text{r}-C\text{r}-Li | 76.2     |         |
| Zn-C\text{r}-C₂ | 127.9    |         |

Li(µ-DMP)(µ-ʻBu)ZnʻBu

Model 1a twisted bridging ʻBu group by 180° Optimised Geometry

E = -2432.239663 a.u.
(more stable by 0.65 kcal mol⁻¹ than Model 1)
**Supporting Information**

**Li(μ-DMP)(μ-^t^Bu)Zn^t^Bu**

**Principal Bond Lengths/Å and Angles/°**

| Bond                  | Length/Å | Angle/° |
|-----------------------|----------|---------|
| Li-N_{mp}             | 1.891    |         |
| Li-C₁                 | 3.007    |         |
| Li-C₂                 | 2.350    |         |
| N-Zn                  | 2.110    |         |
| Zn-C_{Bu}(term)       | 2.013    |         |
| Zn-C₁                 | 2.162    |         |
| Li-N_{mp}-Zn          | 73.4     |         |
| N_{mp}-Zn-C₁         | 103.8    |         |
| Zn-C₁-C₂             | 116.1    |         |
| Zn-C₁-Li             | 68.3     |         |
| C₁-C₂-Li             | 61.3     |         |
| C₁-Li-N_{mp}          | 114.5    |         |

**Li(μ-DMP)(μ-^t^Bu)Zn^t^Bu**

Model 2 twisted bridging DMP group by 180°

Optimised Geometry

\[ E = -2432.233200 \text{ a.u.} \]

**Li(μ-DMP)(μ-^t^Bu)Zn^t^Bu**

**Principal Bond Lengths/Å and Angles/°**

| Bond                  | Length/Å | Angle/° |
|-----------------------|----------|---------|
| Li-N_{mp}             | 1.882    |         |
| Li-C₁                 | 2.204    |         |
| Li-C₂                 | 2.058    |         |
| N-Zn                  | 2.104    |         |
| Zn-C_{Bu}(term)       | 2.026    |         |
| Zn-C₁                 | 2.193    |         |
| Li-N_{mp}-Zn          | 73.8     |         |
| N_{mp}-Zn-C₁         | 106.0    |         |
| Zn-C₁-Li             | 66.2     |         |
| C₁-Li-N_{mp}          | 114.0    |         |
| C₁-C₂-Li             | 73.8     |         |
Li(μ-DMP)(μ-tBu)Zn-tBu

Model 2a twisted bridging tBu group by 180°

Optimised Geometry

E = -2432.233745 a.u.
(more stable by 0.34 kcal mol⁻¹ than Model 2)

Li(μ-DMP)(μ-tBu)Zn-tBu

Principal Bond Lengths/Å and Angles/°

| Bond                  | Length/Å  | Angle/°   |
|-----------------------|-----------|-----------|
| Li-N_{emp}            | 1.901     |           |
| Li-C₁                 | 2.060     |           |
| Li-C₂                 | 2.342     |           |
| N-Zn                  | 2.102     |           |
| Zn-CH₃_{term}         | 2.023     |           |
| Zn-C₁                 | 2.207     |           |
| Li-N_{emp}-Zn         | 73.5      |           |
| N_{emp}-Zn-C₁         | 102.3     |           |
| Zn-C₁-Li              | 68.4      |           |
| C₁-Li-N_{emp}         | 115.7     |           |
| C₁-C₂-Li              | 59.9      |           |

Li(μ-DMP)(μ-tBu)Zn-tBu

Summary

| Model  | Total Energy (a.u.) | Relative Energy (kcal mol⁻¹) |
|--------|---------------------|-----------------------------|
| Model 1| -2432.238631.a.u.   | +0.65                       |
| Model 1a| -2432.239663.a.u.  | 0.00                        |
| Model 2| -2432.233200.a.u.   | +4.06                       |
| Model 2a| -2432.233745.a.u.  | +3.71                       |
| Model 3| -2432.209470.a.u.   | +18.95                      |
| Model 3a| -2432.211055.a.u.  | +17.95                      |
Li(μ-^t^Bu)(μ-DMP)Zn^t^Bu

Energies of the Reactions

Tm + Li(μ-^t^Bu)(μ-DMP)Zn^t^Bu = Tm Li(μ-^t^Bu)(μ-DMP)Zn^t^Bu
\[ ΔE = -13.53 \text{ kcal mol}^{-1} \]

PhCON(Pr)₂ + Li(μ-^t^Bu)(μ-DMP)Zn^t^Bu = PhCON(Pr)₂ Li(μ-^t^Bu)(μ-DMP)Zn^t^Bu
\[ ΔE = -18.58 \text{ kcal mol}^{-1} \]

(These values confirm that the benzamide is a better donating solvent with respect to Li(μ-^t^Bu)(μ-DMP)Zn^t^Bu)

Li(μ-DMP)(μ-ortho-PhCON(Pr)₂)Zn^t^Bu

Model 1

\[ E = -2910.607609 \text{ a.u.} \]

Li(μ-DMP)(μ-ortho-PhCON(Pr)₂)Zn^t^Bu

Principal Bond Lengths/Å and Angles/°

| Bond               | Length/Å | Angle/° |
|--------------------|----------|---------|
| Li-Nax            | 1.929    |         |
| Li-C₁             | 4.517    |         |
| Li-C₄             | 3.522/4.662 |       |
| Li-C₂             | 2.449/2.555 |       |
| Li-C₃             | 2.787    |         |
| N-Zn              | 2.391    |         |
| Zn-C₄(steric)     | 2.918    |         |
| Zn-C₃             | 2.673    |         |
| Li-O              | 1.873    |         |
| Li-Nax-Zn         | 79.0     | 108.0   |
| Nax-Zn-C₄        | 67.5     |         |
| C₄-Li-Nax        | 99.7     |         |
| Zn-C₄-C₃         | 132.7    |         |
| C₄-C₃-C          | 119.6    |         |
| C₃-C-O           | 117.4    |         |
| C-O-Li           | 113.8    |         |
Li(μ-DMP)(μ-ortho-PhCON(Pr)₂)Zn⁺Bu

Energies of the Reactions

PhCON(Pr)₂ + Li(μ⁻Bu)(μ-DMP)Zn⁺Bu = Li(μ-ortho-PhCON(Pr)₂)(μ-DMP)Zn⁺Bu + “BuH”
\[ ΔE = -32.13 \text{ kcal mol}^{-1} \]

PhCON(Pr)₂ + Li(μ⁻Bu)(μ-DMP)Zn⁺Bu = PhCON(Pr)₂Li(μ⁻Bu)(μ-DMP)Zn⁺Bu
\[ ΔE = -18.58 \text{ kcal mol}^{-1} \]

PhCON(Pr)₂ + Tm.Li(μ-DMP)(μ⁻Bu)Zn⁺Bu = Tm.Li(μ-ortho-PhCON(Pr)₂)(μ-DMP)Zn⁺Bu + “BuH”
\[ ΔE = -27.01 \text{ kcal mol}^{-1} \]

Li(μ-DMP)(μ-ortho-PhCON(Pr)₂)Zn⁺Bu

Energies of the Reactions

The previous values indicate that

(a) the substitution reaction of PhCON(Pr)₂ with Li(μ⁻Bu)(μ-DMP)Zn⁺Bu is energetically preferred to the coordination reaction

(b) the presence of Tm co-ordinated to Li makes the substitution of the ‘Bu less energetically favoured

DFT calculations of volumes for DOSY study

Tm.Li(μ-DMP)(μ-Et)ZnEt

Optimised Geometry

\[ E = -2622.711880 \text{ a.u.} \]
\[ \text{Volume} = 296.095 \text{ cm}^3/\text{mol} \]
**Tm.Li(μ-DMP)(μ-Et)ZnEt**

**Principal Bond Lengths/Å and Angles/°**

| Bond        | Length/Å | Angle/° |
|-------------|----------|---------|
| Li-N        | 2.331    | N-Li-N  | 82.9    |
| Li-N2       | 2.244    | Li-N2-Zn| 81.4    |
| Li-N3       | 2.004    | N2-Zn-C1| 112.2   |
| Li-C1       | 2.964    | Zn-C1-Li| 69.4    |
| Zn-N3       | 2.081    | C1-Li-N  | 96.7    |
| Zn-C1       | 2.087    | N2-Zn-C3| 120.8   |
| Zn-C2       | 2.033    | Zn-C1-C2| 109.4   |
| C2-C3       | 1.543    | Zn-C2-C3| 118.2   |
| C2-C4       | 1.538    |         |         |

**Li(μ-DMP)(μ-Et)ZnEt**

**Optimised Geometry**

**E = -2275.062824 a.u.**

**Volume = 196.971 cm³/mol**

**Li(μ-DMP)(μ-Et)ZnEt**

**Principal Bond Lengths/Å and Angles/°**

| Bond        | Length/Å | Angle/° |
|-------------|----------|---------|
| Li-N        | 1.889    | Li-N-Zn | 73.4    |
| Li-C1       | 2.065    | N-Zn-C1 | 103.3   |
| Zn-N        | 2.103    | Zn-C1-Li| 69.8    |
| Zn-C1       | 2.117    | C1-Li-N | 113.5   |
| Zn-C2       | 1.982    | N-Zn-C3 | 126.2   |
| C1-C2       | 1.549    | Zn-C2-C3| 122.4   |
| C2-C4       | 1.537    | Zn-C2-C4| 117.2   |
Energy of Reactions

\[ Tm + \frac{3}{4}(\text{LiDMP})_4 + \text{ZnEt}_2 = Tm.\text{Li}(\mu-\text{DMP})(\mu-\text{Et})\text{ZnEt} \]
\[ \Delta E = -11.60 \text{ kcal mol}^{-1} \]

\[ \frac{3}{4}(\text{LiDMP})_4 + \text{ZnEt}_2 = \text{Li}(\mu-\text{DMP})(\mu-\text{Et})\text{ZnEt} \]
\[ \Delta E = +6.63 \text{ kcal mol}^{-1} \]

\[ Tm + \text{Li}(\mu-\text{DMP})(\mu-\text{Et})\text{ZnEt} = Tm.\text{Li}(\mu-\text{DMP})(\mu-\text{Et})\text{ZnEt} \]
\[ \Delta E = -18.23 \text{ kcal mol}^{-1} \]

**THF.\text{Li}(\mu-\text{DMP})(\mu-\text{Et})\text{ZnEt}**

Optimised Geometry

\[ E = -2507.488525 \text{ a.u.} \]
\[ \text{Volume} = 251.487 \text{ cm}^3/\text{mol} \]

**THF.\text{Li}(\mu-\text{DMP})(\mu-\text{Et})\text{ZnEt}**

Principal Bond Lengths/A and Angles/°

| Bond     | Length/A | Angle/° |
|----------|----------|---------|
| Li-O     | 1.922    |         |
| Li-N     | 1.935    |         |
| Li-C1    | 2.235    |         |
| Zn-N     | 2.088    | 107.2   |
| Zn-C1    | 2.089    | 75.8    |
| Zn-C2    | 1.991    | 107.2   |
| C1-C2    | 1.544    | 116.2   |
| C1-C3    | 1.537    | 119.1   |
| C2-C3    |         |         |
| C2-C4    |         |         |
Supporting Information

**THF.Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt**

On Optimisation

\[
E = -2507.488525 \text{ a.u.}
\]

**Energy of Reactions**

\[
\text{THF} + \frac{1}{4}(\text{LiDMP})_4 + \text{ZnEt}_2 = \text{THF.Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt} \\
\Delta E = -11.06 \text{ kcal mol}^{-1}
\]

\[
\frac{1}{4}(\text{LiDMP})_4 + \text{ZnEt}_2 = \text{Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt} \\
\Delta E = +6.63 \text{ kcal mol}^{-1}
\]

\[
\text{THF} + \text{Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt} = \text{THF.Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt} \\
\Delta E = -17.69 \text{ kcal mol}^{-1}
\]

\[
\text{THF} + \text{Tm.Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt} = \text{THF.Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt+Tm} \\
\Delta E = +0.54 \text{ kcal mol}^{-1}
\]

**\((\text{THF})_2.\text{Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt}**

**Model 1  Optimised Geometry**

\[
E = -2739.896669 \text{ a.u.} \\
\text{Volume} = 312.035 \text{ cm}^3/\text{mol}
\]
\( (\text{THF})_2\text{Li(\(\mu\)-DMP)(\(\mu\)-Et)ZnEt} \)

**Principal Bond Lengths/Å and Angles/°**

| Bond   | Length/Å | Angle/° |
|--------|----------|---------|
| Li-O₁  | 2.053    |         |
| Li-O₂  | 2.031    |         |
| Li-N   | 1.986    | 103.8   |
| Li-C₁  | 2.519    | 100.2   |
| Zn-N   | 2.084    | 68.1    |
| Zn-C₁  | 2.061    | 98.5    |
| Li-N-Zn| 2.003    | 80.1    |
| C₁⁻C₂  | 1.543    | 112.0   |
| C₁⁻C₄  | 1.538    | 109.4   |
| O₁⁻Li-O₂| 96.7     |         |

**Model 2  Optimised Geometry**

\[ E = -2739.897080 \text{ a.u.} \]

**Volume = 314.125 \text{ cm}^3/\text{mol}**
Supporting Information

(THF)$_2$.Li($\mu$-DMP)($\mu$-Et)ZnEt

Principal Bond Lengths/Å and Angles/°

| Bond          | Distance/Å | Angle/° |
|---------------|------------|---------|
| Li-O$_1$      | 2.023      |         |
| Li-O$_2$      | 2.035      |         |
| Li-N          | 1.980      |         |
| Li-C$_1$      | 2.543      |         |
| Zn-N          | 2.090      |         |
| Zn-C$_1$      | 2.059      |         |
| Zn-C$_3$      | 2.003      |         |
| C$_1$-C$_2$   | 1.543      |         |
| C$_2$-C$_3$   | 1.541      |         |
| Li-N-Zn       | 80.1       |         |
| Zn-C$_1$-C$_2$| 112.3      |         |
| Zn-C$_1$-C$_3$| 108.5      |         |
| O$_1$-Li-O$_2$| 96.3       |         |

Energy of Reactions

2THF + $\frac{1}{4}$(LiDMP)$_4$ + ZnEt$_2$ = (THF)$_2$.Li($\mu$-DMP)($\mu$-Et)ZnEt
$\Delta$E = -17.99 kcal mol$^{-1}$

THF + THF.Li($\mu$-DMP)($\mu$-Et)ZnEt = (THF)$_2$.Li($\mu$-DMP)($\mu$-Et)ZnEt
$\Delta$E = -6.92 kcal mol$^{-1}$

2THF + Li($\mu$-DMP)($\mu$-Et)ZnEt = (THF)$_2$.Li($\mu$-DMP)($\mu$-Et)ZnEt
$\Delta$E = -24.62 kcal mol$^{-1}$

2THF + Tm.Li($\mu$-DMP)($\mu$-Et)ZnEt = (THF)$_2$.Li($\mu$-DMP)($\mu$-Et)ZnEt + Tm
$\Delta$E = -6.39 kcal mol$^{-1}$