

SUPPORTING INFORMATION

Title: Suppressing the Anionic Fries Rearrangement of Aryl Dialkylcarbamates; the Isolation of a Crystalline *ortho*-Deprotonated Carbamate

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Ref. No.: O200701096

Experimental Procedures

General Synthetic and Analytical Details. Except for the preparation of *O,N,N*-dimethylphenylcarbamate **2** and *O,N,N*-diethylphenylcarbamate **7**, all reactions and manipulations were carried out under an inert atmosphere of dry nitrogen, using standard double manifold and glove-box techniques. Solvents were distilled off sodium (toluene) or sodium-potassium amalgam (THF, hexane) immediately prior to use. The base 2,2,6,6-tetramethylpiperidine (HTMP) was purchased from Aldrich and stored over molecular sieve (4 Å) and organometallic reagents were purchased from Aldrich (*n*-BuLi, Et₂Zn). Purchased chemicals were used without further purification. The preparation of lithium diethyl(2,2,6,6-tetramethylpiperidido)zincate **1**^{Et} is described elsewhere.^[1] NMR data were collected on a Bruker DRX 400 FT NMR spectrometer (400.133 MHz for ¹H) or a Bruker DRX 500 FT NMR spectrometer (500.052 MHz for ¹H, 125.752 MHz for ¹³C, 194.397 MHz for ⁷Li). Spectra were obtained at 27 °C and chemical shifts are internally referenced to [D]₈-THF or CDCl₃ and calculated relative to TMS (¹H, ¹³C) or to externally referenced to LiOH/D₂O (⁷Li). Chemical shifts are expressed in δ (ppm) values. The following abbreviations are used: s = singlet, d = doublet, t = triplet, quart = quartet, m = multiplet, and br = broad.

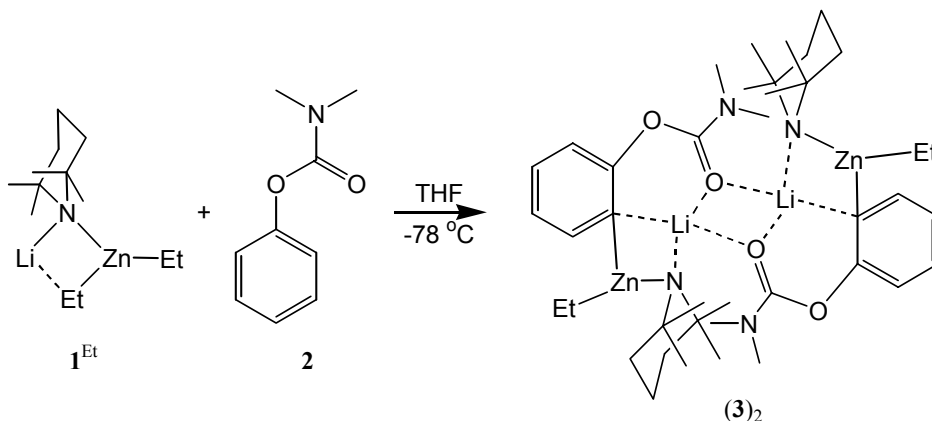
General Crystallographic Details. Data were collected using the ‘oil drop technique’^[2] to mount a crystal on a Nonius Kappa-CCD equipped with an Oxford Cryostream low-temperature device. The structure was solved using direct methods,^[3] with refinement, based on *F*², by full-matrix least squares technique.^[4] Non-hydrogen atoms were refined anisotropically and a riding model with idealised geometry was employed. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-650402. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of O-phenyl-N,N-dimethylcarbamate 2.

A 250 mL three-necked round-bottomed flask equipped with a rubber septum, stopper and high shear Teflon overhead stirrer was charged with phenol (9.67g, 0.103 mol), anhydrous potassium carbonate (28.77 g, 0.208 mol) and diethyl ether (200 mL) and the suspension rapidly stirred for ca. 10 min. under ambient conditions. Dimethylcarbamoyl chloride (10 mL, 0.11 mol) was added *via* syringe and after allowing the mixture to stir for ca. 24 h., was quenched by the addition of a solution of sodium hydroxide (20.09g, 0.50 mol) in water (100 mL). After the hot solution had cooled to ambient temperature, the ethereal layer was separated from the aqueous. The aqueous layer was then shaken with diethyl ether (2 × 100 mL). The combined diethyl ether extracts were washed with water (100 mL), dried (MgSO₄) and concentrated *in vacuo* to afford a pale yellow oil. Distillation under reduced pressure from 4 Å molecular

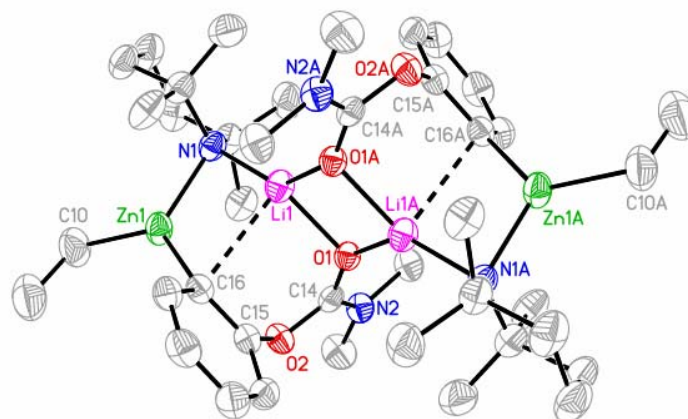
sieves afforded **2** as a colourless mobile oil. Yield 2.51 g, (14.8 %). ^1H NMR spectroscopy (400 MHz, CDCl_3 , 27 °C, TMS): 7.34 (dd, 2H, 3,5-Ph), 7.17 (tt, 1H, 4-Ph), 7.10 (dd, 2H, 2,6-Ph), 3.09 (s, 3H, NMe), 3.00 (s, 3H, NMe).

*Synthesis of lithium O-[2-{ethyl(2,2,6,6-tetramethylpiperidido)zinc}phenyl]-N,N-dimethylcarbamate **3**.*



A solution of *n*-BuLi (1.2 mL, 1.6 M in hexanes, 1.92 mmol) in THF (2 mL) held at -78 °C under N_2 was treated with HTMP (0.32 mL, 2 mmol) and the pale yellow solution warmed to room temperature. The solution was re-cooled to -78 °C and a solution of diethylzinc (2 mL, 1.0 M in hexane, 2 mmol) was added followed by 5 minutes stirring, whereupon *O,N,N*-dimethylphenyl carbamate (0.2 mL, 0.2 g, 1.21 mmol) was introduced in a single portion. The solution was warmed to ambient temperature and stirred for ca. 2h. The resultant brick red emulsion was concentrated *in vacuo* to give a dark red oil which was dissolved in toluene (0.5 mL). Storage at -30 °C for ca. 2 d. afforded title compound **3** as a colourless crystalline deposit. Yield 165 mg (30 %), m. p. 108-110 °C. Found, C 60.07, H 8.00, N 5.93 %. Calcd. for $\text{C}_{40}\text{H}_{66}\text{Li}_2\text{N}_2\text{O}_4\text{Zn}_2 \cdot \text{C}_7\text{H}_8$, C 62.46, H 8.25, N 6.20 %. ^1H NMR spectroscopy (500 MHz, $[\text{D}]_8$ -THF, 27 °C, TMS): 7.70 (br, m, 0.65H, 3-Ar#2), 7.54 (br, m, 0.35H, 3-Ar#3), 7.31 (dd, 0.7H, 3,5-Ph#1), 7.21 (dd, 1H, tol), 7.15 (m, 1.5H, tol), 7.14 (m, 0.3H, 4-Ph#1), 7.10 (dd, 0.7H, 2,6-Ph#1), 7.06 (br, m, 0.7H, 4-Ar#3 + 6-Ar#3), 6.98 (br, m, 0.65H, 6-Ar#2), 6.96 (br, m, 0.65H, 4-Ar#2), 6.76 (br, m, 0.35H, 5-Ar#3), 6.69 (br, m, 0.65H, 5-Ar#2), 3.13 (s, 2H, NMe#2), 3.12 (s, 1H, NMe#3), 3.08 (s, 1.3H, NMe#1), 3.07 (s, 1H, NMe#3), 3.01 (s, 2H, NMe#2), 2.95 (s, 1.3H, NMe#1), 2.33 (s, 1.5H, tol), 1.71 (br, m, 2H, TMP- CH_2 #2/3), 1.40 (br, t, 2H, TMP- CH_2 #2/3), 1.31 (m, 2H, TMP- CH_2 #2/3), 1.22 (t, 3H, ZnCH_2Me #2/3), 1.19 (br, s, 6H, CMe#2/3), 1.08 (s, 4H, CMe#2/3), 1.07 (s, 2H, CMe#2/3), 0.13 (m, 0.7H, ZnCH_2 #3), 0.04 (m, 1.3H, ZnCH_2 #2). ^7Li NMR spectroscopy (194 MHz, $[\text{D}]_8$ -THF, 27 °C, LiOH/ D_2O): -1.93. ^1H NMR spectroscopy (500 MHz, $[\text{D}]_8$ -THF, 27 °C after heating to 50 °C, TMS): 7.32 (dd, 0.7H, 3,5-Ph#1), 7.21 (dd, 1H, tol), 7.16 (m, 1.5H, tol), 7.15 (m, 0.3H, 4-Ph#1), 7.11 (dd, 0.7H, 2,6-Ph#1), 7.02-6.98 (m, 2H, Ar#4), 6.73 (br, m, 1H, Ar#4), 6.33 (br, m, 1H, Ar#4), 3.08 (s, 1.3H, NMe#1), 3.02 (br, m, 6H, NMe#4), 2.96 (s, 1.3H, NMe#1), 2.34 (s, 1.5H, tol), 1.70 (br, m, 2H, TMP-

CH₂#4), 1.34 (br, t, 2H, TMP-CH₂#4), 1.31 (m, 2H, TMP-CH₂#4), 1.24 (t, 3H, ZnCH₂Me#4), 1.19 (br, s, 6H, CMe#4), 1.09 (s, 4H, CMe#4), 1.08 (s, 2H, CMe#4), 0.15 (m, 2H, ZnCH₂#4). ⁷Li NMR spectroscopy (194 MHz, [D₈]-THF, 27 °C after heating to 50 °C, LiOH/D₂O): -1.52. X-ray crystal data: C₄₇H₇₄Li₂N₄O₄Zn₂, *M* = 903.72, triclinic, space group *P*-1, *a* = 9.853(2), *b* = 11.140(2), *c* = 12.319(3) Å, *a* = 100.68(3), *β* = 102.61(3), *γ* = 105.75(3)°, *V* = 1226.2(4) Å³, *Z* = 1, ρ_{calcd} = 1.224 g cm⁻³, Mo-K_α radiation, λ = 0.71073 Å, μ = 1.021 mm⁻¹, *T* = 180(2)K. 11227 data (4977 unique, *R*_{int} = 0.0548, θ < 26.37°) were collected. *wR*2 = 0.1543, conventional *R* = 0.0658 on *F* values of 3362 reflections with *F*² > 2σ(*F*²), *S* = 1.028, 262 parameters. Residual electron density extrema ±0.660 eÅ⁻³. Data were collected on a Nonius Kappa-CCD equipped with an Oxford Cryostream low-temperature device. The structure was solved using direct methods (G. M. Sheldrick, *Acta Crystallogr., Sect. A*, **1990**, *46*, 467–473) with refinement, based on *F*², by full-matrix least squares technique (G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.). Non-hydrogen atoms were refined anisotropically and a riding model with idealised geometry was employed. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-650402. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).



Molecular structure of (3)₂ plotted at 40% probability. Lattice toluene molecule omitted for clarity.

C16–Zn1	2.054(4)	C16–Zn1–N1	110.31(15)
C10–Zn1	2.008(5)	Zn1–N1–Li1	85.6(2)
N1–Zn1	2.033(4)	N1–Li1–O1	128.5(4)
N1–Li1	2.057(8)	N1–Li1–O1A	139.6(4)
O1–Li1	2.003(8)	O1–Li1–O1A	88.4(3)
O1A–Li1	1.939(7)	Li1–O1–Li1A	91.6(3)
C15–C16–Zn1	126.6(3)	C16–C15–O2–C14	83.1(5)

Selected bond lengths (Å) and angles (°) in (3)₂.

Synthesis of 2-hydroxy-N,N-dimethylbenzamide 5.

A well-stirred suspension of 2-hydroxybenzoic acid (2.00 g, 14.49 mmol) in thionyl chloride (5 mL) was heated at reflux for ca. 4 h. under nitrogen after which the pale yellow solution was cooled to room temperature. Concentration *in vacuo* gave an opaque yellow oil which was diluted with dry diethyl ether (5 mL) and the resulting white suspension treated with a solution of dimethylamine in THF (2M, 18 mL, 36.0 mmol) and the orange suspension allowed to stand for ca. 20 h. before quenching with water (10 mL). Concentration *in vacuo* gave an aqueous slurry to which a solution of 37% aqueous hydrochloric acid (0.5 mL) in water (10 mL) was added. Filtration under suction gave a cream powder that was dried under suction in air. Recrystallisation from the minimum quantity of boiling acetonitrile afforded the title compound as large colourless blocks. Yield 1.29g (54.0 %) ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 9.92 (br, s, 1H, OH), 7.31 (t, 1H, Ar), 7.29 (d, 1H, Ar), 6.98 (dd, 1H, Ar), 6.82 (dt, 1H, Ar), 3.14 (s, 6H, NMe).

Analysis of the solution behaviour of 3 at room temperature.

A portion of zincated carbamate **3** was dissolved in THF (1 mL) and stirred at ambient temperature for 1h. Water (1 mL) was added and the solution allowed to stand overnight. 32 % HCl (aq) (0.1 mL) was added and the emulsion extracted with diethyl ether. Drying over MgSO₄ and concentrating to dryness gave a red oil. The ¹H NMR spectrum was recorded in CDCl₃. The sample was then doped with authentic 2-hydroxy-N,N-dimethylbenzamide **5** and the spectrum re-recorded. ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 9.90 (br, s, 0.2H, OH, **5**), 7.35 (dd, 2H, 3,5-Ph, **2**), 7.33 (t, 0.3H, Ar, **5**), 7.31 (d, 0.3H, Ar, **5**), 7.18 (tt, 1H, 4-Ph, **2**), 7.10 (dd, 2H, 2,6-Ph, **2**), 6.99 (dd, 0.3H, Ar, **5**), 6.79 (dt, 0.3H, Ar, **5**), 3.16 (s, 2H, NMe, **5**), 3.10 (s, 3H, NMe, **2**), 3.00 (s, 3H, NMe, **2**). ¹H NMR spectroscopy after doping with **5** (400 MHz, CDCl₃, 27 °C, TMS): 9.932 (br, s, 2H, OH, **5**), 7.33 (dd, 2H, 3,5-Ph, **2**), 7.32 (t, 2H, Ar, **5**), 7.30 (d, 2H, Ar, **5**), 7.18 (tt, 1H, 4-Ph, **2**), 7.10 (dd, 2H, 2,6-Ph, **2**), 6.99 (dd, 2H, Ar, **5**), 6.82 (dt, 2H, Ar, **5**), 3.15 (s, 12H, NMe, **5**), 3.09 (s, 3H, NMe, **2**), 3.00 (s, 3H, NMe, **2**).

Analysis of the solution behaviour of 3 at elevated temperature.

A portion of **3** was dissolved in THF (1 mL) and stirred at ambient temperature for 1h. before being refluxed for ca. 30 s. After cooling to room temperature, water (1 mL) was added and the solution allowed to stand overnight. 32 % HCl (aq) (0.1 mL) was added and the emulsion extracted with diethyl ether. Drying over MgSO₄ and concentrating to dryness gave a red oil. The ¹H NMR spectrum was recorded in CDCl₃. The sample was then doped with authentic **5** and the spectrum re-recorded. ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 9.89 (br, s, 0.2H, OH, **5**), 7.34 (dd, 2H, 3,5-Ph, **2**), 7.31 (t, 0.3H, Ar, **5**), 7.29 (d, 0.3H, Ar, **5**), 7.17 (tt, 1H, 4-Ph, **2**), 7.09 (dd, 2H, 2,6-Ph, **2**), 6.98 (dd, 0.3H, Ar, **5**), 6.79 (dt, 0.3H, Ar, **5**), 3.14 (s, 2H, NMe, **5**), 3.09 (s, 3H, NMe, **2**), 3.00 (s, 3H, NMe, **2**). ¹H NMR

spectroscopy after doping with **5** (400 MHz, CDCl₃, 27 °C, TMS): 9.89 (br, s, 0.7H, OH, **5**), 7.34 (dd, 2H, 3,5-Ph, **2**), 7.32 (t, 0.7H, Ar, **5**), 7.30 (d, 0.7H, Ar, **5**), 7.17 (tt, 1H, 4-Ph, **2**), 7.10 (dd, 2H, 2,6-Ph, **2**), 6.99 (dd, 0.7H, Ar, **5**), 6.81 (dt, 0.7H, Ar, **5**), 3.13 (s, 4H, NMe, **5**), 3.09 (s, 3H, NMe, **2**), 2.99 (s, 3H, NMe, **2**).

Attempted synthesis of O-(2-iodophenyl)-N,N-dimethylcarbamate 6.

Pre-isolated **1^{Et}** (0.136 g, 0.5 mmol) was combined with carbamate **2** (0.08 mL, 0.5 mmol) in a Schlenk tube and THF (1 mL) added at -78 °C under N₂ and the reaction mixture was stirred for 1 h. at that temperature. I₂ (254 mg, 1 mmol) was added and stirring continued for 1 h. at -78 °C. The mixture was left to reach room temperature, quenched using excess Na₂S₂O₃ and washed with HCl. Extraction (Et₂O) was followed by drying (MgSO₄) and concentration *in vacuo* to yield a yellow oil that spectroscopic analysis revealed to be unreacted **2**. ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 7.34 (dd, 2H, 3,5-Ph), 7.17 (tt, 1H, 4-Ph), 7.10 (dd, 2H, 2,6-Ph), 3.09 (s, 3H, NMe), 3.00 (s, 3H, NMe).

Synthesis of O-(2-iodophenyl)-N,N-dimethylcarbamate 6 using 1 eq. 1^{Et}.

Pre-isolated **1^{Et}** (0.136 g, 0.5 mmol) was combined with carbamate **2** (0.08 mL, 0.5 mmol) in a Schlenk tube and THF (1 mL) added at -78 °C under N₂. After stirring for 15 mins. the reaction mixture was allowed to reach room temperature, whereupon it was stirred for a further hour. The mixture was returned to -78 °C and I₂ (254 mg, 1 mmol) was added. The mixture was left to attain room temperature, whereupon reaction was quenched using excess Na₂S₂O₃ and washed with HCl. Extraction (Et₂O) was followed by drying (MgSO₄) and concentration *in vacuo* to yield a yellow oil for spectroscopic analysis. Yield 53.5 % **6**, 18 % **5**, 28.5 % **2** (by ¹H NMR spectroscopy). ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 9.93 (br, s, 0.2H, OH, **5**), 7.79 (dd, 1H, Ar, **6**), 7.34 (m, 2.6H, Ar, **2** + **5** + **6**), 7.18 (dd, 1H, Ar, **6**), 7.17 (tt, 0.7H, 4-Ph, **2**), 7.10 (dd, 1.3H, 2,6-Ph, **2**), 6.99 (dd, 0.3H, Ar, **5**), 6.93 (dt, 1H, Ar, **6**), 6.82 (dt, 0.3H, Ar, **5**), 6.72 (dt, 0.3H, Ar, **5**), 3.18 (s, 3H, NMe, **6**), 3.16 (s, 1.5H, NMe, **5**), 3.10 (s, 1.6H, NMe, **2**), 3.03 (s, 3H, NMe, **6**), 3.01 (s, 1.6H, NMe, **2**).

Synthesis of O-(2-iodophenyl)-N,N-dimethylcarbamate 6 using 1 eq. 1^{Et} with an extended reaction time.

Pre-isolated **1^{Et}** (0.136 g, 0.5 mmol) was combined with carbamate **2** (0.05 mL, 0.3 mmol) in a Schlenk tube and THF (2 mL) added at -78 °C under N₂. After stirring for 15 mins. the reaction mixture was allowed to reach room temperature, whereupon it was stirred for 3 h. The mixture was returned to -78 °C and I₂ (350 mg, 1.4 mmol) was added. The mixture was left to reach room temperature before being quenched with excess Na₂S₂O₃ and washed with HCl. Extraction (Et₂O) was followed by drying (MgSO₄) and concentration *in vacuo* to yield a yellow oil for spectroscopic analysis. Yield 35 % **6**, 18 % **5**, 47 % **2** (by ¹H NMR spectroscopy). ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 9.91 (s,

0.3H, OH, **5**), 7.78 (dd, 1H, Ar, **6**), 7.34 (m, 4H, Ar, **2 + 5 + 6**), 7.18 (dd, 1H, Ar, **6**), 7.17 (tt, 1.3H, 4-Ph, **2**), 7.10 (dd, 2.6H, 2,6-Ph, **2**), 6.98 (dd, 0.5H, Ar, **5**), 6.92 (dt, 1H, Ar, **6**), 6.83 (dt, 0.5H, Ar, **5**), 6.76 (dt, 0.5H, Ar, **5**), 3.17 (s, 3H, NMe, **6**), 3.14 (s, 2.5H, NMe, **5**), 3.09 (s, 4.3H, NMe, **2**), 3.02 (s, 3H, NMe, **6**), 3.00 (s, 4.3H, NMe, **2**).

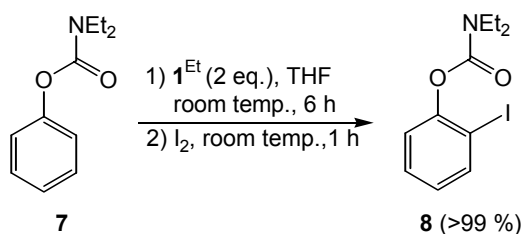
Synthesis of O-phenyl-N,N-diethylcarbamate 7.

A 250 mL round-bottomed flask equipped with a high shear Teflon overhead stirrer was charged with phenol (9.42g, 0.100 mol), sodium hydroxide pellets (10.11 g, 0.253 mol) and dry THF (100 mL) and the suspension rapidly stirred for ca. 10 min. under ambient conditions. Diethylcarbamoyl chloride (10 mL, 0.079 mol) was added *via* syringe in two portions and after allowing the mixture to stir for ca. 16 h., was quenched by the addition of water (100 mL). The resultant mixture was concentrated *in vacuo* to remove all THF. The oily aqueous solution was then extracted with diethyl ether (3 × 100 mL). The combined diethyl ether extracts were dried (MgSO₄) and concentrated *in vacuo* to afford an opaque pale yellow oil. Distillation under reduced pressure with heating from 4 Å molecular sieves afforded the title compound as a colourless mobile oil. Yield 11.4 g, (74.8 %). ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 7.34 (dd, 2H, 3,5-Ph), 7.17 (tt, 1H, 4-Ph), 7.12 (dd, 2H, 2,6-Ph), 3.39 (m, 4H, NCH₂), 1.21 (m, 6H, Me).

Synthesis of O-(2-iodophenyl)-N,N-diethylcarbamate 8 using 1 eq. 1^{Et}.

Pre-isolated **1^{Et}** (0.136 g, 0.5 mmol) was dissolved in THF (2 mL) and carbamate **7** (0.1 mL, 0.54 mmol) was added at room temperature. After stirring for ca. 4 h. the mixture was cooled to 0 °C and I₂ (350 mg, 1.38 mmol) was added. The mixture was allowed to reach room temperature and stirred overnight., after which the reaction was quenched with Na₂S₂O₃ (aq). Extraction (Et₂O), drying (MgSO₄) and concentration *in vacuo* gave a mobile amber oil for spectroscopic analysis. Yield 53 % **8**, 47 % **7** (by ¹H NMR spectroscopy). ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 7.79 (dd, 1H, Ar, **8**), 7.33 (m, 2.6H, Ar, **7 + 8**), 7.18 (dd, 1H, Ar, **8**), 7.17 (tt, 1.8H, 4-Ph, **7**), 7.11 (dd, 0.8H, 2,6-Ph, **7**), 6.92 (dt, 1H, Ar, **8**), 3.53 (quart, 2H, NCH₂, **8**), 3.39 (m, 5.5H, NCH₂, **7 + 8**), 1.32 (t, 3H, Me, **8**), 1.22 (m, 8.5H, Me, **7 + 8**).

Synthesis of O-(2-iodophenyl)-N,N-diethylcarbamate 8 using 2 eq. 1^{Et} with an extended reaction time.



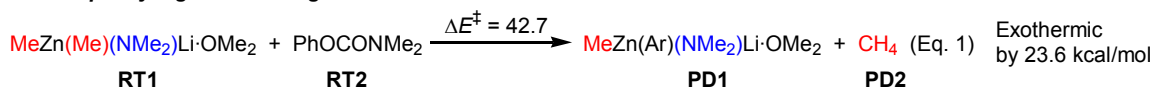
Pre-isolated **1**^{Et} (0.272 g, 1.0 mmol) was dissolved in THF (4 mL) and carbamate **7** (0.1 mL, 0.54 mmol) was added at room temperature. After stirring for ca. 6 h. the mixture was cooled to 0 °C and I₂ (619 mg, 2.45 mmol) was added. The mixture was allowed to reach room temperature and stirred for 1h., after which the reaction was quenched with water (10 mL). Extraction (Et₂O), drying (MgSO₄) and concentration *in vacuo* gave a viscous amber oil for spectroscopic analysis. Yield >99 % **8** (by ¹H NMR spectroscopy). ¹H NMR spectroscopy (400 MHz, CDCl₃, 27 °C, TMS): 7.79 (dd, 1H, Ar), 7.34 (m, 1H, Ar), 7.17 (dd, 1H, Ar), 6.92 (dt, 1H, Ar), 3.52 (quart, 2H, NCH₂), 3.39 (quart, 2H, NCH₂), 1.32 (t, 3H, Me), 1.22 (s, 3H, Me).

DFT Calculations

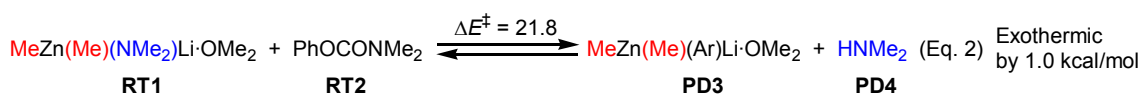
Procedural Details. All calculations were carried out using the Gaussian 03 program package.^[5] Geometries of the reactants, intermediates, transition states, and products were optimized without any symmetry restriction using the B3LYP hybrid density functional method.^[6] We used Ahlrichs' SVP^[7] all-electron basis set for the Zn atom and 6-31G* for the other atoms. Geometry optimization and vibrational analysis were performed at the level. All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the same level of theory (the number of imaginary frequencies, NIMAG, was 0 for minima and 1 for TSs). All the transition states structures and the reaction coordinates (Hessian eigenvectors with negative eigenvalues) were examined visually. The intrinsic reaction coordinate (IRC) method^[8] was used to track minimum energy paths from transition structures to the corresponding local minima. For the final B3LYP/6-31G* optimized geometries, we performed single point energy calculations using B3LYP/6-31++G**(SVP for Zn).

Scheme S1. Summary of plausible reaction pathways modelled using DFT calculations (ΔE^\ddagger kcal/mol, Ar = 2-Me₂N(O=)COC₆H₄). Optimization carried out at B3LYP level using 6-31G* basis set for H, C, N, O atoms, and SVP for Zn atoms. Subsequent, single point energy calculations were performed at B3LYP 6-31++G**/SVP level.

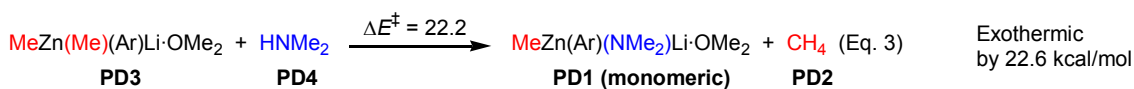
One-step alkyl ligand exchange



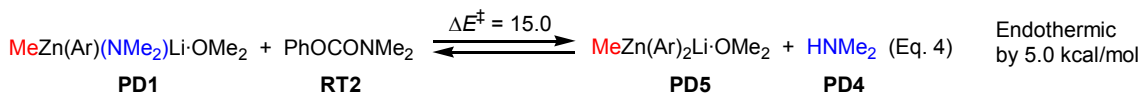
Stepwise ortho deprotonation; 1st step



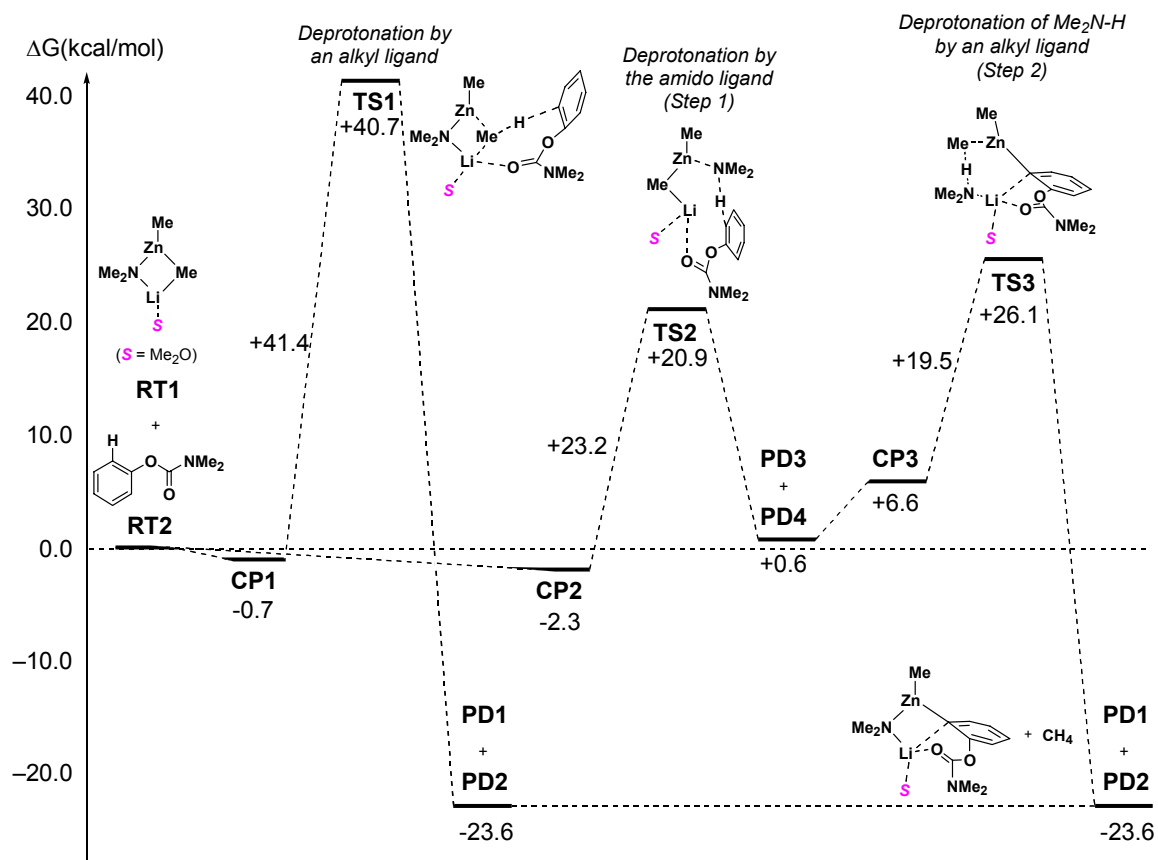
Step-wise ortho deprotonation; 2nd step



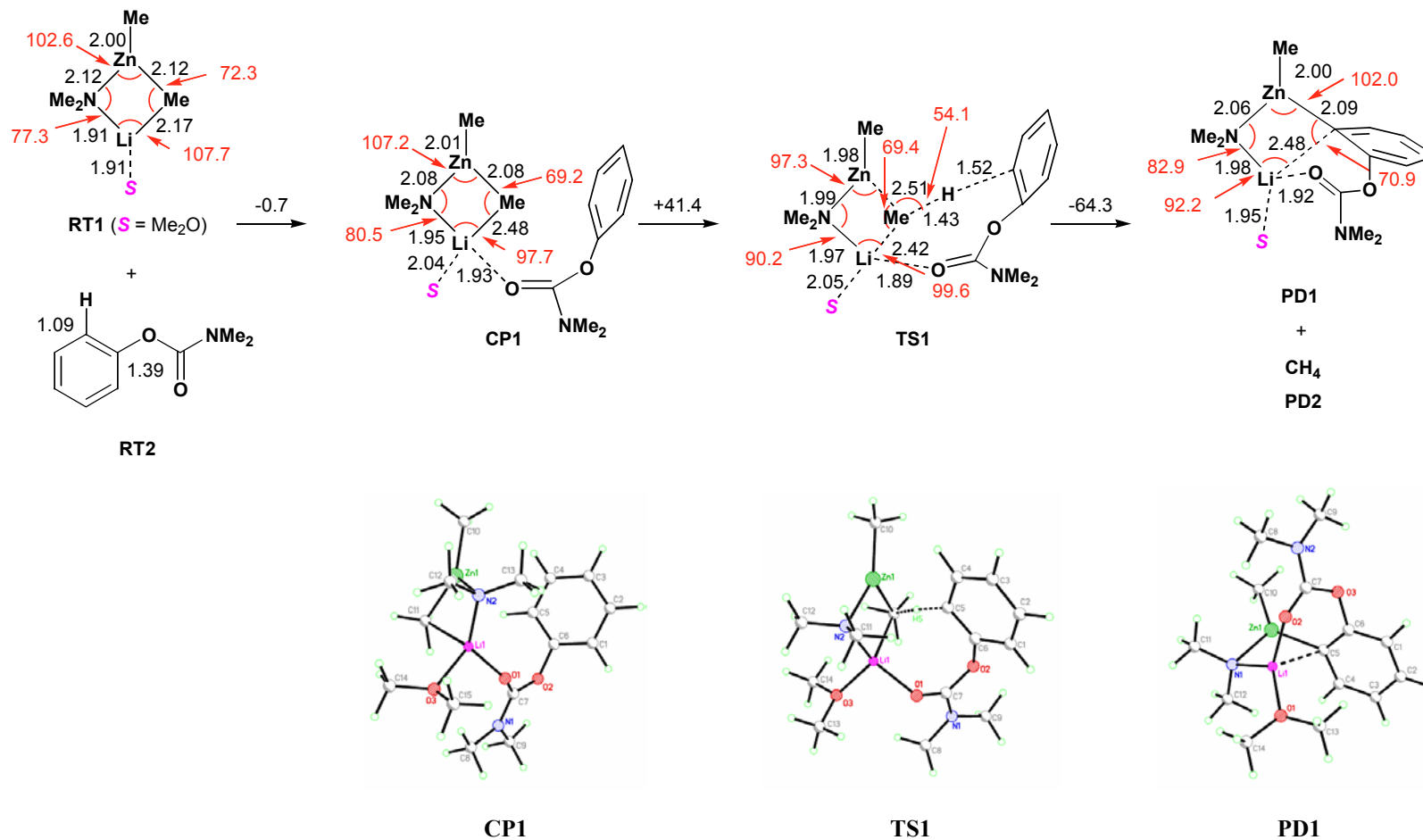
Step-wise ortho deprotonation; 3rd step



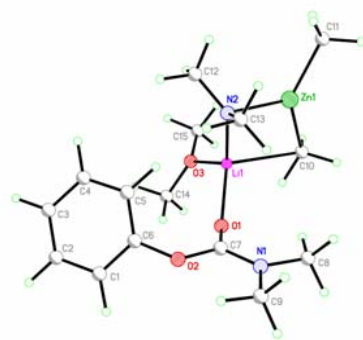
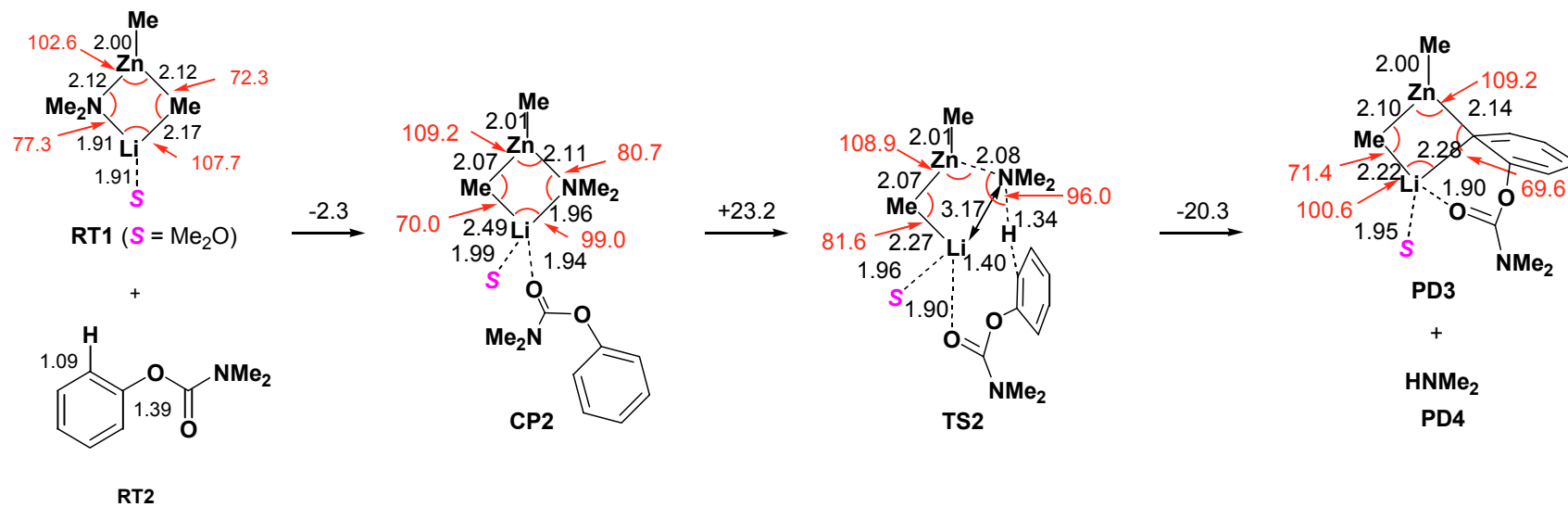
Scheme S2. Summary of plausible reaction pathways modelled using DFT calculations (ΔG^\ddagger kcal/mol). Optimization carried out at B3LYP level using 6-31G* basis set for H, C, N, O atoms, and SVP for Zn atoms. Single point energy calculations were performed at B3LYP 6-31++G**/SVP level.



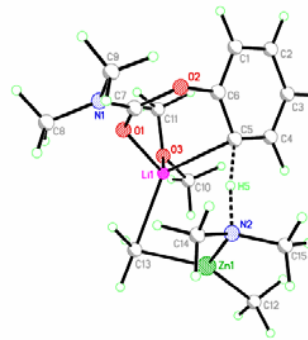
Scheme S3. Calculated structures of the reactants, transition states, products, and Gibbs free energy changes for kinetically unfavourable single-step *ortho* deprotonation (Eq. 1). Bond lengths, angles (red) and energy changes at the B3LYP/631SVPs level are shown in Å, degrees, and kcal/mol, respectively.



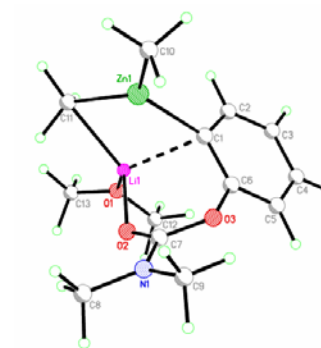
Scheme S4. Calculated structures and energy changes (B3LYP/631SVPs level) for step 1 (amine elimination) in step-wise *ortho* deprotonation (Eq. 2).



CP2

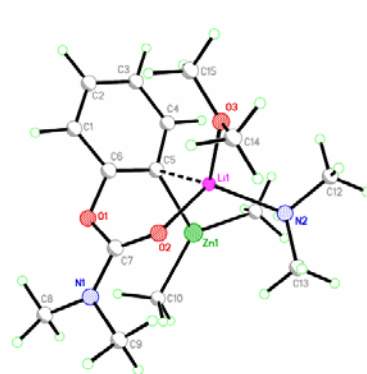
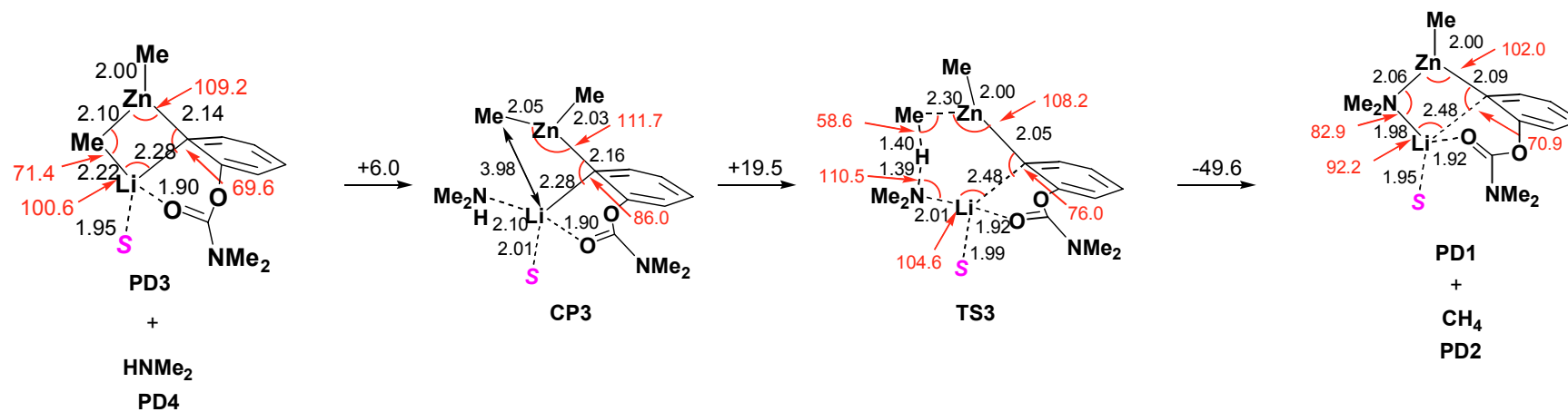


TS2

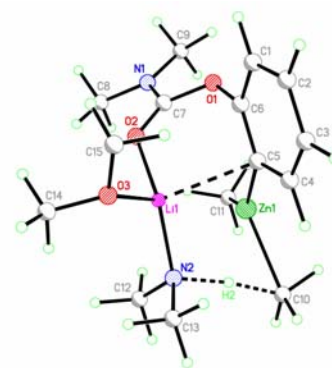


PD3

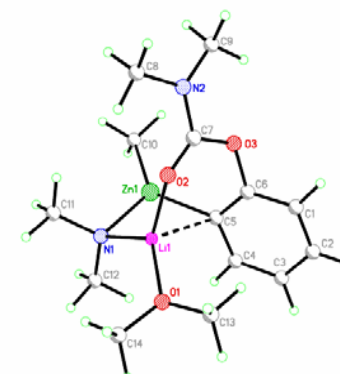
Scheme S5. Calculated structures and energy changes (B3LYP/631SVPs level) for step 2 (amine re-coordination/alkane loss) in step-wise *ortho* deprotonation (Eq. 3).



CP3

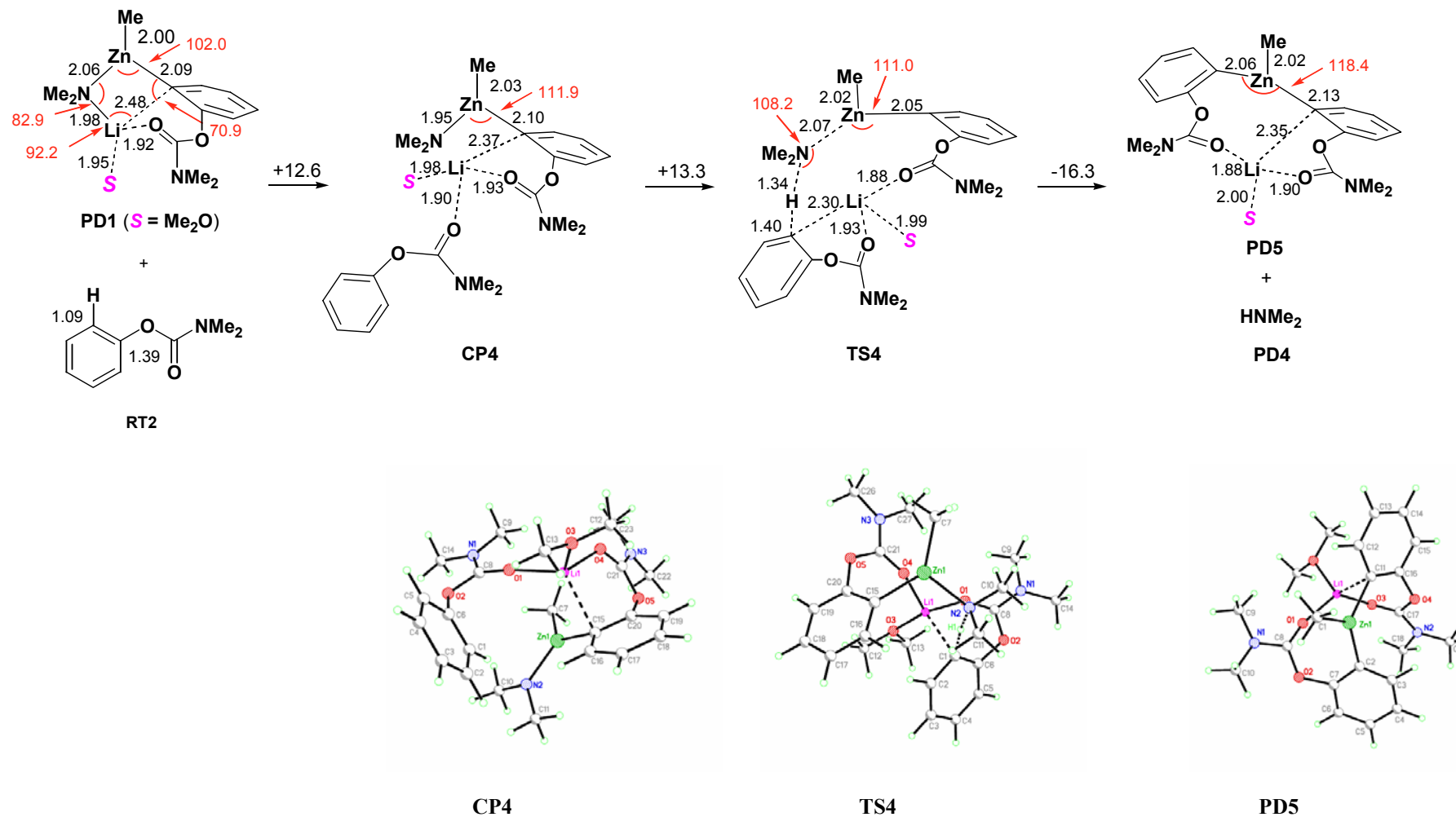


TS3

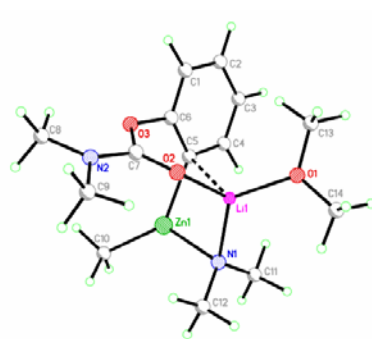
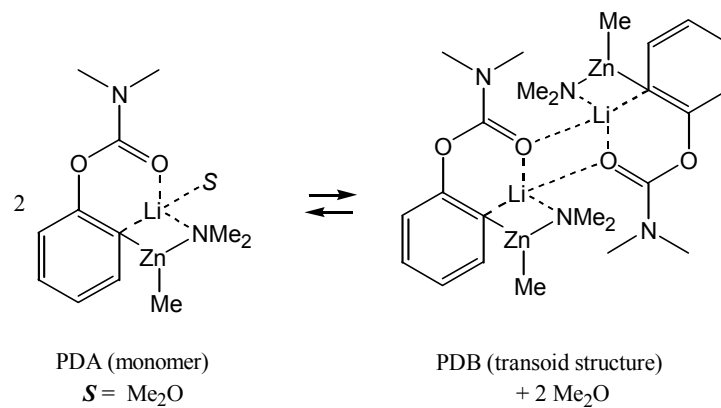


PD1

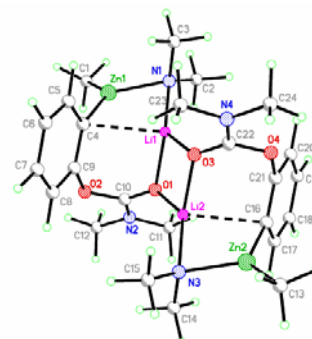
Scheme S6. Calculated structures and energy changes (B3LYP/631SVPs level) for step 3 (dibasic action/amine elimination) in step-wise *ortho* deprotonation (Eq. 4).



Scheme S7. Calculated structures and energy changes (B3LYP/631SVPs level) for dimerization and loss of solvent. The forward process (dimerization) is exothermic by 0.4 kcal/mol.



PDA



PDB

Thermodynamic deprotonation (alkyl basicity)

RT1 (MeZn(Me)(NMe₂)Li-OMe₂)

SCF Done: E(RB+HF-LYP) = -2156.228893 A.U. after 1 cycle

Atom	x	y	z
Li	-0.962274	-0.193896	0.004074
Zn	1.529156	-0.567754	-0.000625
C	3.522689	-0.474504	-0.005349
C	0.078507	-2.092517	0.004961
C	0.620809	1.990656	1.190305
N	0.353117	1.189944	0.002270
C	0.614639	1.988836	-1.188360
C	-3.744245	-1.318692	-0.001831
O	-2.875204	-0.188460	0.001312
C	-3.567148	1.060412	-0.001953
H	3.900913	-0.029696	0.924480
H	3.889977	0.153578	-0.827247
H	3.995050	-1.458568	-0.109528
H	0.687902	-3.002700	0.006675
H	-0.574177	-2.196491	-0.882432
H	-0.572663	-2.192112	0.894017
H	0.434400	1.404677	2.102733
H	-0.022937	2.890268	1.246562
H	1.665636	2.352706	1.245321
H	0.422899	1.401688	-2.098973
H	1.659400	2.350117	-1.249739
H	-0.028842	2.888772	-1.242365
H	-3.112012	-2.208455	0.001271
H	-4.375561	-1.316983	-0.900089
H	-4.383108	-1.316109	0.891060
H	-2.806436	1.843167	0.000679
H	-4.198508	1.152071	0.891515
H	-4.191472	1.151311	-0.900437

RT2 (PhOCONMe₂)

SCF Done: E(RB+HF-LYP) = -554.8204813 A.U. after 1 cycle

Atom	x	y	z
C	-1.784154	1.246346	-0.418255
C	-3.164198	1.051010	-0.481897
C	-3.725351	-0.144478	-0.028927
C	-2.897935	-1.141334	0.493246
C	-1.516598	-0.956852	0.569728
C	-0.971940	0.241472	0.106019
O	1.074607	-1.465227	-0.628550
C	1.333130	-0.372375	-0.161129
O	0.381434	0.549892	0.218216
C	3.728627	-0.699786	-0.332890
N	2.590126	0.113312	0.064546
C	2.890140	1.442266	0.575025
H	-1.326323	2.167223	-0.765875
H	-3.797875	1.834420	-0.888604
H	-4.799401	-0.298642	-0.081570
H	-3.327762	-2.074190	0.848008
H	-0.871754	-1.730688	0.965733

H	4.291358	-0.211092	-1.140192
H	3.366912	-1.666192	-0.680673
H	4.405277	-0.846168	0.518875
H	3.361578	2.060755	-0.201968
H	3.588540	1.365388	1.418269
H	1.979920	1.931070	0.913334

CPI

SCF Done: E(RB+HF-LYP) = -2711.066885 A.U. after 1 cycle

Atom	x	y	z
C	-3.266171	-1.571818	1.209336
C	-3.001818	-2.904708	1.532176
C	-2.080422	-3.639621	0.783685
C	-1.422525	-3.044278	-0.296014
C	-1.684465	-1.714856	-0.633759
C	-2.599620	-0.997746	0.132071
O	-0.945953	1.134754	0.468811
C	-2.043049	1.308313	-0.061384
O	-2.953012	0.313108	-0.227392
C	-1.665040	3.687691	-0.393278
N	-2.492966	2.495990	-0.531374
C	-3.822128	2.697744	-1.097524
Li	0.962539	0.889954	0.293533
Zn	1.845951	-1.209556	-0.981496
C	2.215834	-3.113951	-1.503461
C	1.584905	-1.506050	1.983965
N	2.066584	-0.561610	0.987242
C	3.474699	-0.285723	1.229832
C	1.812418	3.054207	2.015043
O	1.682939	2.771280	0.624077
C	2.751024	3.312608	-0.147878
H	-3.978974	-0.980990	1.775910
H	-3.516394	-3.364386	2.371346
H	-1.872656	-4.674052	1.041249
H	-0.696354	-3.606381	-0.874606
H	-1.585472	4.191364	-1.363772
H	-0.669767	3.409124	-0.050604
H	-2.116674	4.386792	0.323598
H	-3.733228	3.184607	-2.075824
H	-4.421359	3.344159	-0.442796
H	-4.328997	1.744045	-1.219650
H	1.526952	-3.485569	-2.274643
H	2.153810	-3.800217	-0.648774
H	3.226968	-3.224698	-1.920318
H	0.520059	-1.718499	1.828222
H	1.693880	-1.114779	3.015464
H	2.120676	-2.475934	1.962112
H	3.871762	0.405582	0.470901
H	4.114589	-1.191220	1.205366
H	3.651631	0.180940	2.221077
H	0.952818	2.602899	2.514575
H	1.810428	4.139478	2.188859
H	2.737097	2.621142	2.417606
H	2.579902	3.013774	-1.183290
H	3.718234	2.919376	0.191527
H	2.761120	4.409144	-0.074161

C	1.312460	0.449814	-2.119086
H	0.797091	1.351237	-1.743500
H	2.235683	0.817698	-2.594342
H	0.679865	0.089463	-2.942869
H	-1.182540	-1.240822	-1.471770

TS1

SCF Done: E(RB+HF-LYP) = -2710.998854 A.U. after 1 cycle

Atom	x	y	z
C	-0.017189	3.608492	0.791618
C	-1.278615	4.055957	1.183340
C	-2.400998	3.312808	0.818697
C	-2.248519	2.129945	0.085715
C	-0.994195	1.612911	-0.311080
C	0.077391	2.419837	0.070185
O	1.665759	0.235436	0.801036
C	2.116635	1.120411	0.058145
O	1.407610	2.156143	-0.399348
C	4.295277	0.047578	0.015441
N	3.399140	1.120407	-0.393279
C	3.998403	2.236247	-1.116257
Li	0.472612	-1.131763	0.273904
Zn	-2.169518	-0.779496	-0.610286
C	-3.678337	-0.597856	-1.872327
C	-1.651189	-1.006649	2.247916
N	-1.332231	-1.628174	0.960614
C	-1.645529	-3.055129	1.017989
C	2.167364	-3.176029	1.476391
O	1.759549	-2.719050	0.190162
C	1.721747	-3.761066	-0.778515
H	0.880585	4.175491	1.024015
H	-1.379108	4.978855	1.748452
H	-3.395646	3.656262	1.095130
H	-3.161410	1.607489	-0.199522
H	4.997493	-0.155632	-0.799843
H	3.717087	-0.851608	0.222497
H	4.871696	0.321764	0.910225
H	4.494508	1.865732	-2.020925
H	4.748573	2.741683	-0.492620
H	3.229541	2.950427	-1.399935
H	-3.506275	0.241807	-2.554491
H	-4.632294	-0.425626	-1.360162
H	-3.793314	-1.502497	-2.481966
H	-1.428983	0.064376	2.217278
H	-1.053886	-1.452497	3.064278
H	-2.712394	-1.125003	2.536966
H	-1.419988	-3.541781	0.059489
H	-2.706577	-3.263826	1.250824
H	-1.051417	-3.568507	1.796894
H	2.181425	-2.304970	2.134484
H	3.173885	-3.614662	1.428391
H	1.465463	-3.924565	1.867669
H	1.401678	-3.311517	-1.720269
H	1.012197	-4.546838	-0.484935
H	2.718517	-4.206248	-0.904700
C	-0.097622	-0.601764	-2.016391

H	0.997492	-0.609975	-1.884569
H	-0.402915	-1.648444	-2.190804
H	-0.289271	-0.078588	-2.961038
H	-0.608400	0.409044	-1.145282

PD1 (MeZn(Ar)(NMe₂)Li·OMe₂)

SCF Done: E(RB+HF-LYP) = -2670.561573 A.U. after 1 cycle

Atom	x	y	z
Li	-0.927876	0.360000	0.879828
Zn	0.305528	1.345707	-1.276556
C	1.829191	2.269811	-2.185764
C	-0.268494	3.287392	0.886493
N	-0.905079	2.198175	0.158578
C	-2.165943	2.665940	-0.403928
C	-3.264718	0.485248	2.664505
O	-2.475571	-0.348301	1.825022
C	-2.732114	-1.737136	2.000770
C	-0.404329	-0.619667	-1.340060
C	-1.624444	-0.968558	-1.962762
C	-2.073879	-2.287651	-2.090282
C	-1.307303	-3.336530	-1.577683
C	-0.099561	-3.049991	-0.938738
C	0.302329	-1.718214	-0.842921
O	0.726463	-0.373698	1.507851
C	1.695666	-0.838664	0.889655
O	1.588190	-1.534664	-0.256808
C	3.267388	0.051197	2.516845
N	2.976750	-0.715750	1.313564
C	4.127496	-1.208248	0.565624
H	1.478613	2.867065	-3.038269
H	2.573104	1.563844	-2.574767
H	2.347620	2.961885	-1.509540
H	0.680521	2.951677	1.324418
H	-0.901060	3.656150	1.718819
H	-0.044484	4.167905	0.253578
H	-2.668344	1.857852	-0.953587
H	-2.050475	3.518579	-1.102647
H	-2.871966	3.012554	0.377891
H	-2.994848	1.516756	2.431339
H	-3.060865	0.278086	3.724593
H	-4.334418	0.331882	2.466475
H	-2.104895	-2.273097	1.286603
H	-3.788471	-1.960777	1.798533
H	-2.485096	-2.052311	3.024199
H	-2.248698	-0.179605	-2.381616
H	-3.014965	-2.497457	-2.593707
H	-1.639472	-4.366856	-1.674726
H	0.528636	-3.838557	-0.533482
H	3.868422	-0.553066	3.207245
H	2.332679	0.331635	2.998555
H	3.832467	0.958207	2.265626
H	4.751790	-1.830386	1.218653
H	4.733094	-0.367484	0.203839
H	3.796843	-1.798931	-0.284851

PD2 (CH₄)

SCF Done: E(RB+HF-LYP) = -40.5253644 A.U. after 1 cycle

Atom	x	y	z
C	0.000171	0.000031	0.000122
H	-0.143589	-0.828733	-0.698622
H	-0.614651	-0.162954	0.889407
H	1.053055	0.054985	0.288904
H	-0.295839	0.936518	-0.480422

Kinetic deprotonation step 1 (amido basicity)**CP2**

SCF Done: E(RB+HF-LYP) = -2711.068063 A.U. after 1 cycle

Atom	x	y	z
C	-4.324589	-0.079056	-0.058068
C	-4.867618	-1.332699	-0.346475
C	-4.095809	-2.298088	-0.996523
C	-2.778773	-2.005519	-1.360313
C	-2.222437	-0.754145	-1.085188
C	-3.010421	0.191356	-0.430679
O	-0.795040	0.788753	1.062408
C	-1.415561	1.701272	0.511372
O	-2.553617	1.497153	-0.204745
C	0.118084	3.410905	1.308565
N	-1.070710	3.006508	0.565248
C	-1.815487	4.078986	-0.086002
Li	0.665899	-0.398637	0.594955
C	1.262910	-3.077973	1.823062
O	0.263534	-2.111094	1.525323
C	-0.934810	-2.307942	2.267577
Zn	3.162133	0.007414	-0.172659
C	4.857883	-0.001393	-1.243937
C	2.725435	0.274359	1.829790
C	1.158244	0.830599	-2.097099
N	1.365929	-0.325335	-1.236601
C	1.470367	-1.519099	-2.063219
H	-4.906327	0.689259	0.441562
H	-5.893491	-1.550335	-0.062826
H	-4.519522	-3.272559	-1.222220
H	-2.173778	-2.750363	-1.869480
H	-1.193648	-0.530257	-1.351833
H	0.817460	3.927025	0.640314
H	0.606523	2.534119	1.728988
H	-0.161795	4.096297	2.118160
H	-1.168931	4.596766	-0.804816
H	-2.151927	4.806232	0.663388
H	-2.679574	3.677155	-0.608680
H	2.142814	-2.830064	1.227442
H	0.913971	-4.087143	1.563663
H	1.529174	-3.049729	2.888600
H	-1.622912	-1.514881	1.975717
H	-0.735830	-2.249519	3.347139
H	-1.376266	-3.286784	2.034934
H	5.572653	0.760170	-0.905944
H	4.670884	0.178144	-2.310714

H	5.375384	-0.968078	-1.171718
H	3.186435	1.236199	2.100318
H	3.273802	-0.485821	2.405478
H	1.716114	0.307274	2.272273
H	1.087270	1.751240	-1.497746
H	0.222667	0.760045	-2.690015
H	1.972335	0.985600	-2.832510
H	1.628702	-2.409299	-1.437652
H	2.304169	-1.479212	-2.790637
H	0.551882	-1.704070	-2.657876

TS2

SCF Done: E(RB+HF-LYP) = -2711.033349 A.U. after 1 cycle

Atom	x	y	z
C	2.154833	2.327927	-1.425492
C	1.317893	3.378566	-1.807305
C	-0.065235	3.181139	-1.840134
C	-0.593800	1.931117	-1.498286
C	0.206563	0.837604	-1.109064
C	1.573926	1.105970	-1.091142
O	1.681119	-0.187399	1.326218
C	2.472818	-0.509438	0.426268
O	2.508876	0.072996	-0.784663
C	3.488956	-2.222567	1.824347
N	3.407734	-1.478842	0.574544
C	4.346769	-1.866682	-0.470849
Li	-0.160625	0.238524	1.124844
C	-1.982782	2.397886	2.047526
O	-0.655462	1.879319	2.080309
C	0.331905	2.896917	2.230597
Zn	-2.472736	-1.133527	0.223405
C	-4.340713	-0.610797	-0.286196
C	-1.495204	-1.349915	2.035054
C	-0.223574	-2.654330	-1.120985
N	-1.135064	-1.531631	-1.313342
C	-1.694093	-1.547699	-2.663571
H	3.234478	2.448265	-1.394208
H	1.746654	4.339030	-2.081361
H	-0.722463	3.992919	-2.144426
H	-1.674931	1.793159	-1.551732
H	-0.416863	-0.413583	-1.167000
H	3.305477	-3.288993	1.642295
H	2.743556	-1.841323	2.519529
H	4.488215	-2.112423	2.264008
H	4.188115	-2.916342	-0.748574
H	5.375977	-1.757925	-0.106111
H	4.209195	-1.241246	-1.349159
H	-2.656918	1.548651	1.922126
H	-2.106195	3.094184	1.207490
H	-2.213659	2.915881	2.988138
H	1.300646	2.396075	2.259110
H	0.171132	3.447005	3.167773
H	0.302257	3.593803	1.383238
H	-4.828585	-1.397115	-0.878482
H	-4.359998	0.296769	-0.906581
H	-4.983196	-0.416870	0.582038

H	-2.021664	-2.254810	2.376269
H	-1.699113	-0.599667	2.812068
H	-0.429808	-1.620245	2.106456
H	0.203071	-2.621602	-0.111215
H	0.610801	-2.640230	-1.846384
H	-0.727959	-3.628219	-1.234577
H	-2.364853	-0.693175	-2.799475
H	-2.277049	-2.462171	-2.859488
H	-0.906901	-1.489780	-3.436371

PD3 (MeZn(Me)(Ar)Li·OMe₂)

SCF Done: E(RB+HF-LYP) = -2575.872153 A.U. after 1 cycle

Atom	x	y	z
Li	-0.878103	0.704310	0.824444
Zn	0.360778	1.672676	-1.147695
C	1.885817	2.129406	-2.367294
C	-3.017561	1.301070	2.816038
O	-2.531293	0.420187	1.809533
C	-3.085399	-0.890679	1.892690
C	-0.590901	-0.240974	-1.224531
C	-1.845018	-0.373101	-1.863354
C	-2.454629	-1.606715	-2.119028
C	-1.824216	-2.787880	-1.719891
C	-0.593064	-2.718356	-1.065247
C	-0.030136	-1.462251	-0.842987
O	0.599605	-0.250100	1.546885
C	1.482966	-0.843898	0.907258
O	1.261989	-1.503911	-0.242063
C	3.185459	-0.216621	2.526377
N	2.772753	-0.914107	1.316505
C	3.832677	-1.551855	0.544418
C	-0.558961	2.844360	0.333093
H	2.200637	3.176757	-2.276390
H	1.632933	1.953551	-3.421137
H	2.767382	1.509738	-2.149573
H	-2.542826	2.270000	2.650188
H	-2.761895	0.929058	3.817910
H	-4.107708	1.409781	2.738104
H	-2.677559	-1.467655	1.061013
H	-4.179276	-0.847487	1.805403
H	-2.814860	-1.366258	2.845256
H	-2.367920	0.528013	-2.186629
H	-3.414032	-1.648376	-2.630039
H	-2.281636	-3.754598	-1.913819
H	-0.072579	-3.615207	-0.740325
H	3.704768	-0.911527	3.197511
H	2.306842	0.184674	3.027667
H	3.869399	0.605904	2.280025
H	4.372928	-2.264004	1.180095
H	4.544864	-0.799016	0.183050
H	3.410833	-2.078486	-0.307754
H	-0.326617	3.862043	-0.003202
H	-0.166018	2.794350	1.364359
H	-1.660569	2.809828	0.400182

PD4 (HNMe₂)

SCF Done: E(RB+HF-LYP) = -135.1788284 A.U. after 1 cycle

Atom	x	y	z
C	-1.213394	-0.222783	0.020527
C	1.213394	-0.222783	0.020527
N	0.000000	0.565647	-0.149965
H	-1.273841	-0.767661	0.982834
H	-1.276676	-0.968003	-0.782088
H	-2.090384	0.428315	-0.060817
H	1.273852	-0.767642	0.982844
H	2.090386	0.428308	-0.060845
H	1.276657	-0.968020	-0.782073
H	-0.000001	1.328567	0.523575

Kinetic deprotonation step 2 (amine coordination)**CP3**

SCF Done: E(RB+HF-LYP) = -2711.061456 A.U. after 1 cycle

Atom	x	y	z
Li	0.967131	-0.107195	0.755147
Zn	-0.371265	-1.391346	-1.644223
C	2.736572	2.274413	1.356526
O	2.302252	0.986158	1.786909
C	2.169995	0.903800	3.200738
C	-2.342491	-1.761276	-1.357923
C	3.091094	-2.247326	1.134622
N	1.653841	-2.088811	0.873905
C	0.836149	-2.967553	1.722669
C	0.291831	0.636859	-1.291633
C	1.413299	1.061052	-2.042275
C	1.701257	2.404372	-2.317436
C	0.861593	3.405025	-1.822958
C	-0.250924	3.049906	-1.057808
C	-0.494190	1.696144	-0.823119
O	-0.716751	0.271225	1.551473
C	-1.733147	0.689927	0.973889
O	-1.712448	1.449618	-0.133156
C	-3.191848	-0.437492	2.549641
N	-2.989871	0.477319	1.434683
C	-4.180334	0.848011	0.673986
H	2.773175	2.254740	0.267036
H	3.733616	2.495080	1.762363
H	2.032373	3.051687	1.682134
H	1.838085	-0.108841	3.438544
H	1.425971	1.623493	3.568077
H	3.134942	1.095564	3.690361
H	-2.969138	-0.920872	-1.686987
H	-2.589282	-1.948073	-0.300432
H	-2.676010	-2.649546	-1.910552
H	3.324199	-1.896312	2.145912
H	3.660009	-1.640862	0.424200
H	3.424065	-3.293951	1.050050
H	-0.211444	-2.891623	1.419010
H	0.915280	-2.647606	2.768359
H	1.145709	-4.023160	1.663995

H	2.074931	0.298702	-2.452945
H	2.565731	2.668875	-2.922962
H	1.063356	4.452780	-2.031307
H	-0.930486	3.801639	-0.665207
H	-3.947902	-0.025220	3.226983
H	-2.253699	-0.563426	3.087041
H	-3.536654	-1.417510	2.192842
H	-4.979230	1.102705	1.378186
H	-4.510950	0.017232	0.038446
H	-3.969461	1.711082	0.045975
C	1.142074	-2.567082	-2.366336
H	1.119609	-3.609183	-2.013657
H	0.983503	-2.632137	-3.454001
H	2.175817	-2.207256	-2.243871
H	1.482637	-2.344268	-0.103775

TS3

SCF Done: E(RB+HF-LYP) = -2711.025999 A.U. after 1 cycle

Atom	x	y	z
Li	0.893376	0.145609	0.928298
Zn	-0.112035	-1.505699	-1.112268
C	1.801291	2.894204	1.624555
O	1.919410	1.510879	1.941977
C	1.983651	1.271266	3.343265
C	-1.689732	-2.664428	-0.718165
C	3.199596	-1.410280	0.866696
N	1.760439	-1.661272	0.802489
C	1.400569	-2.723044	1.735989
C	0.294437	0.472931	-1.459332
C	1.470596	0.926114	-2.094742
C	1.669601	2.261168	-2.466001
C	0.678176	3.210393	-2.205783
C	-0.497591	2.817851	-1.562796
C	-0.647235	1.477593	-1.211184
O	-0.937475	0.557050	1.345581
C	-1.936025	0.648314	0.617057
O	-1.902056	1.147610	-0.636076
C	-3.371413	-0.351129	2.297522
N	-3.184055	0.301223	1.007893
C	-4.325372	0.278703	0.098663
H	1.762070	2.973842	0.537136
H	2.671304	3.447539	2.004124
H	0.884645	3.318393	2.057279
H	2.080057	0.192381	3.480739
H	1.072259	1.627727	3.843661
H	2.857681	1.772880	3.780589
H	-2.554039	-2.402315	-1.343496
H	-2.011094	-2.578930	0.329213
H	-1.466429	-3.722795	-0.897332
H	3.525195	-1.041816	1.856202
H	3.485102	-0.651431	0.126221
H	3.798405	-2.317305	0.657175
H	0.332018	-2.953535	1.652337
H	1.599240	-2.447752	2.789259
H	1.958061	-3.661199	1.550015
H	2.252995	0.204263	-2.321621

H	2.588095	2.557490	-2.967138
H	0.814179	4.247996	-2.499618
H	-1.289794	3.528813	-1.345662
H	-4.235446	0.089699	2.807352
H	-2.479072	-0.211463	2.904700
H	-3.550819	-1.426013	2.164558
H	-5.213788	0.630824	0.634171
H	-4.511521	-0.740772	-0.263007
H	-4.139607	0.929178	-0.752838
C	1.722262	-2.739963	-1.758224
H	1.696496	-3.815776	-1.547436
H	1.166866	-2.607710	-2.703271
H	2.757015	-2.459523	-1.995636
H	1.640252	-2.170693	-0.484214

Kinetic deprotonation step 3 (alkyl elimination)

CP4

SCF Done: E(RB+HF-LYP) = -3225.382288 A.U. after 13 cycles

Atom	x	y	z
C	-3.245000	0.235460	0.649200
C	-3.951740	1.417370	0.892375
C	-4.906402	1.884383	-0.015110
C	-5.164321	1.167426	-1.185707
C	-4.467524	-0.014446	-1.447646
C	-3.519932	-0.455797	-0.527245
Li	0.551332	0.428741	-1.195201
Zn	0.557787	-0.566789	1.707837
C	1.438214	-2.340513	1.269494
O	-0.953535	-0.717658	-1.382083
C	-1.629941	-1.736566	-1.212032
O	-2.913544	-1.699948	-0.777811
C	0.138422	-3.230199	-1.969068
N	-1.208953	-2.994500	-1.465604
C	-1.467097	-1.738318	3.496483
N	-0.925081	-0.506789	2.966868
C	-1.276236	0.600646	3.823723
C	1.201899	2.577782	-3.159920
O	0.175847	1.762232	-2.606185
C	-1.125757	2.314231	-2.775407
C	-1.996974	-4.187865	-1.175599
C	1.018714	1.338679	0.944874
C	0.117167	2.426003	1.025452
C	0.491287	3.755209	0.795433
C	1.813831	4.058879	0.463704
C	2.740723	3.023136	0.338365
C	2.310644	1.717204	0.568896
O	2.395199	-0.072065	-1.465405
C	3.269315	-0.122159	-0.584764
O	3.329497	0.726529	0.456610
C	5.204643	-1.177152	0.528116
N	4.293671	-1.009246	-0.599853
C	4.301236	-2.066418	-1.601336
H	-2.483942	-0.121858	1.350840
H	-3.754344	1.968134	1.807733
H	-5.452600	2.800667	0.192085

H	-5.909676	1.520274	-1.893315
H	-4.657533	-0.597504	-2.343820
H	1.978491	-2.378389	0.315063
H	0.706738	-3.161811	1.257277
H	2.163264	-2.597168	2.056546
H	0.735950	-3.758103	-1.218066
H	0.620192	-2.281016	-2.194910
H	0.083700	-3.838839	-2.880247
H	-1.158528	-2.592777	2.881685
H	-2.578253	-1.737075	3.524770
H	-1.141240	-1.950213	4.537159
H	-0.810208	1.529839	3.477301
H	-0.955741	0.451853	4.877006
H	-2.374049	0.777307	3.874114
H	2.145562	2.063618	-2.974842
H	1.218977	3.563988	-2.677797
H	1.050113	2.702074	-4.241599
H	-1.831429	1.606774	-2.339106
H	-1.348616	2.447988	-3.843444
H	-1.205903	3.283266	-2.264715
H	-1.492751	-4.789063	-0.409113
H	-2.096635	-4.794434	-2.084257
H	-2.985124	-3.910866	-0.818095
H	-0.918542	2.224184	1.288459
H	-0.241917	4.553347	0.890357
H	2.123734	5.088177	0.301263
H	3.776832	3.218068	0.074948
H	4.873527	-1.999011	1.176365
H	5.248421	-0.260957	1.112601
H	6.204392	-1.408825	0.145392
H	3.913695	-3.005149	-1.182562
H	5.328510	-2.231415	-1.943984
H	3.681122	-1.768456	-2.445157

TS4

SCF Done: E(RB+HF-LYP) = -3225.358313 A.U. after 13 cycles

Atom	x	y	z
C	1.546469	1.422960	-0.691229
C	0.988056	2.718460	-0.670439
C	1.722727	3.858099	-0.322306
C	3.071766	3.736637	0.022472
C	3.670321	2.474748	0.025229
C	2.891069	1.373908	-0.327052
Li	0.654169	0.229269	1.065019
Zn	-1.538159	-0.917076	-1.686021
C	-2.024109	-2.866122	-1.860049
O	2.276232	-0.806260	1.233029
C	3.210568	-0.877309	0.421222
O	3.602219	0.136491	-0.369504
C	3.649348	-3.197865	1.008157
N	3.969031	-1.991358	0.259401
C	1.240585	-1.482119	-2.546385
N	0.335592	-0.348933	-2.367149
C	0.288110	0.448441	-3.593338
C	-0.421814	2.423690	2.763729
O	0.514361	1.349604	2.707249

C	1.688822	1.607896	3.469811
C	5.043773	-2.104057	-0.718733
C	-2.589102	0.698957	-0.976679
C	-2.784497	1.933778	-1.629839
C	-3.476065	3.009195	-1.058478
C	-4.012013	2.890091	0.224760
C	-3.851510	1.689350	0.918950
C	-3.155302	0.652374	0.299487
O	-0.896701	-0.821998	0.974721
C	-2.026896	-1.243208	1.267360
O	-3.158692	-0.561918	1.053367
C	-3.565509	-3.017322	2.035752
N	-2.235894	-2.439865	1.868337
C	-1.109298	-3.342998	2.063520
H	0.893515	0.446125	-1.444686
H	-0.059552	2.837261	-0.946482
H	1.251955	4.839059	-0.331732
H	3.658420	4.614157	0.282536
H	4.718258	2.345984	0.283529
H	-1.234397	-3.535198	-1.488555
H	-2.191462	-3.144067	-2.910324
H	-2.948055	-3.120952	-1.322707
H	3.305898	-3.991219	0.331265
H	2.865190	-2.975313	1.729137
H	4.541007	-3.555842	1.537482
H	1.298929	-2.062806	-1.617719
H	2.262453	-1.151884	-2.809127
H	0.901749	-2.167179	-3.339234
H	-0.359047	1.319734	-3.446247
H	-0.100098	-0.124032	-4.451815
H	1.288197	0.821837	-3.877754
H	-1.283198	2.137790	2.157898
H	0.020434	3.343365	2.359229
H	-0.742181	2.595806	3.800862
H	2.340677	0.741722	3.349357
H	1.434665	1.739274	4.531059
H	2.201480	2.507283	3.103677
H	4.768633	-2.813012	-1.510485
H	5.951828	-2.472008	-0.225420
H	5.246829	-1.134292	-1.165939
H	-2.393073	2.066277	-2.637906
H	-3.601514	3.934847	-1.616215
H	-4.556415	3.713373	0.680088
H	-4.271456	1.546578	1.911269
H	-3.779974	-3.736886	1.234549
H	-4.318415	-2.232828	2.018760
H	-3.609005	-3.538698	2.998204
H	-1.090921	-4.114642	1.282446
H	-1.202277	-3.830341	3.040339
H	-0.180267	-2.776554	2.025705

PD5 (MeZn(Ar)₂Li·OMe₂)

SCF Done: E(RB+HF-LYP) = -3090.195218 A.U. after 13 cycles

Atom	x	y	z
Li	0.415393	-0.902394	0.963524
Zn	-0.596716	-0.308643	-1.623386

C	-1.813338	-1.493712	-2.720422
C	-1.050479	1.559447	-0.886541
C	-0.361409	2.746046	-1.213445
C	-0.713265	4.005878	-0.712932
C	-1.782607	4.127735	0.177555
C	-2.500160	2.986024	0.536197
C	-2.120369	1.762019	-0.011836
O	-1.462086	-0.788874	0.999640
C	-2.620224	-0.514947	0.645890
O	-3.032941	0.706647	0.292894
C	-3.310649	-2.832262	0.886558
N	-3.620224	-1.431304	0.634318
C	-4.941176	-1.154931	0.079370
C	1.317263	-1.125893	-1.195253
C	1.470439	-2.484825	-1.562503
C	2.707429	-3.134193	-1.634549
C	3.876783	-2.430713	-1.334851
C	3.787200	-1.091581	-0.955348
C	2.527738	-0.493152	-0.892342
O	1.587751	0.502804	1.466329
C	2.140667	1.270532	0.665055
O	2.563798	0.891607	-0.556923
C	1.841723	3.178506	2.134966
N	2.411540	2.567358	0.941020
C	3.051494	3.472704	-0.004189
H	-1.491761	-1.528246	-3.771093
H	-2.852227	-1.135969	-2.724694
H	-1.831603	-2.538014	-2.373593
H	0.482220	2.689243	-1.900974
H	-0.164316	4.892464	-1.025915
H	-2.068438	5.097570	0.576852
H	-3.352632	3.039804	1.207869
H	-4.056809	-3.256152	1.568561
H	-2.321039	-2.910110	1.332902
H	-3.324640	-3.403872	-0.050654
H	-5.698109	-1.648614	0.698903
H	-5.018923	-1.539948	-0.945886
H	-5.127556	-0.083740	0.071614
H	0.577863	-3.050001	-1.825505
H	2.761700	-4.177658	-1.937384
H	4.848653	-2.913664	-1.398307
H	4.675182	-0.511384	-0.719181
H	2.617916	3.743618	2.664307
H	1.452386	2.397569	2.785209
H	1.026141	3.859046	1.860365
H	3.798508	4.074670	0.526579
H	2.312354	4.147264	-0.453595
H	3.541803	2.905684	-0.792159
C	2.099953	-2.922034	2.295513
O	0.785131	-2.372568	2.261988
C	0.254409	-2.137399	3.561325
H	2.413079	-3.066882	1.260577
H	2.095929	-3.887785	2.819854
H	2.794965	-2.237041	2.800055
H	-0.735797	-1.699385	3.423876
H	0.890941	-1.440638	4.124749
H	0.168551	-3.080140	4.119591

Dimerization

PDA (monomer with solvating Me₂O)

SCF Done: E(RB+HF-LYP) = -2670.561573 A.U. after 1 cycle

Atom	x	y	z
Li	-0.927876	0.360000	0.879828
Zn	0.305528	1.345707	-1.276556
C	1.829191	2.269811	-2.185764
C	-0.268494	3.287392	0.886493
N	-0.905079	2.198175	0.158578
C	-2.165943	2.665940	-0.403928
C	-3.264718	0.485248	2.664505
O	-2.475571	-0.348301	1.825022
C	-2.732114	-1.737136	2.000770
C	-0.404329	-0.619667	-1.340060
C	-1.624444	-0.968558	-1.962762
C	-2.073879	-2.287651	-2.090282
C	-1.307303	-3.336530	-1.577683
C	-0.099561	-3.049991	-0.938738
C	0.302329	-1.718214	-0.842921
O	0.726463	-0.373698	1.507851
C	1.695666	-0.838664	0.889655
O	1.588190	-1.534664	-0.256808
C	3.267388	0.051197	2.516845
N	2.976750	-0.715750	1.313564
C	4.127496	-1.208248	0.565624
H	1.478613	2.867065	-3.038269
H	2.573104	1.563844	-2.574767
H	2.347620	2.961885	-1.509540
H	0.680521	2.951677	1.324418
H	-0.901060	3.656150	1.718819
H	-0.044484	4.167905	0.253578
H	-2.668344	1.857852	-0.953587
H	-2.050475	3.518579	-1.102647
H	-2.871966	3.012554	0.377891
H	-2.994848	1.516756	2.431339
H	-3.060865	0.278086	3.724593
H	-4.334418	0.331882	2.466475
H	-2.104895	-2.273097	1.286603
H	-3.788471	-1.960777	1.798533
H	-2.485096	-2.052311	3.024199
H	-2.248698	-0.179605	-2.381616
H	-3.014965	-2.497457	-2.593707
H	-1.639472	-4.366856	-1.674726
H	0.528636	-3.838557	-0.533482
H	3.868422	-0.553066	3.207245
H	2.332679	0.331635	2.998555
H	3.832467	0.958207	2.265626
H	4.751790	-1.830386	1.218653
H	4.733094	-0.367484	0.203839
H	3.796843	-1.798931	-0.284851

PDB (transoid dimer)SCF Done: E(RB+HF-LYP) = -5031.0369 A.U. after 14 cycles

Atom	x	y	z
Li	-1.059660	0.662969	-0.542667
Zn	-3.788213	0.531391	-0.549663
C	-5.531497	-0.297104	-1.071681
C	-2.452325	0.624723	-3.191630
N	-2.376069	1.236327	-1.870820
C	-2.426413	2.688486	-2.009326
C	-2.829292	0.778947	1.290652
C	-2.751789	2.038138	1.928916
C	-2.216372	2.217298	3.209856
C	-1.716821	1.121374	3.916910
C	-1.758213	-0.145350	3.331912
C	-2.303575	-0.261981	2.055961
O	-0.732639	-1.204611	0.045436
C	-1.600321	-1.965364	0.540108
O	-2.384661	-1.604692	1.557679
C	-1.026307	-3.756207	-1.008438
N	-1.821036	-3.212545	0.089264
C	-2.835478	-4.100243	0.653619
Li	1.060329	-0.651057	0.546164
Zn	3.790356	-0.534095	0.558671
C	5.534744	0.280122	1.098292
C	2.411397	-2.688952	2.009201
N	2.371122	-1.236088	1.875700
C	2.444794	-0.629881	3.199295
C	2.837782	-0.783878	-1.283941
C	2.758401	-2.043793	-1.920620
C	2.222036	-2.223732	-3.200992
C	1.723007	-1.128099	-3.909003
C	1.767109	0.139367	-3.325909
C	2.313879	0.256808	-2.050554
O	0.737061	1.213118	-0.052198
C	1.602661	1.972737	-0.552249
O	2.400448	1.600414	-1.554810
C	1.014276	3.777363	0.974852
N	1.807680	3.229742	-0.121821
C	2.821642	4.115706	-0.689897
H	-5.769423	-0.122367	-2.127710
H	-6.365591	0.093994	-0.475352
H	-5.520232	-1.384912	-0.917314
H	-2.411099	-0.469422	-3.111414
H	-1.611502	0.936345	-3.840751
H	-3.382207	0.876837	-3.736397
H	-2.370264	3.174116	-1.024202
H	-3.349706	3.053854	-2.500710
H	-1.584807	3.079315	-2.615263
H	-3.143709	2.916845	1.416819
H	-2.199467	3.207141	3.660744
H	-1.301741	1.244766	4.913278
H	-1.384579	-1.022194	3.852742
H	-0.451771	-4.622983	-0.660117
H	-0.342810	-2.997908	-1.385678
H	-1.692236	-4.079663	-1.816744
H	-2.356172	-4.990206	1.078652

H	-3.524040	-4.416485	-0.138033
H	-3.395145	-3.585167	1.430074
H	5.399445	1.032880	1.886304
H	6.051579	0.765332	0.261882
H	6.215914	-0.478519	1.505838
H	2.358144	-3.170678	1.022054
H	1.563750	-3.076809	2.608722
H	3.329384	-3.061760	2.504930
H	2.409130	0.464724	3.123211
H	3.370872	-0.888903	3.747145
H	1.599524	-0.939693	3.843596
H	3.149249	-2.922345	-1.407515
H	2.203700	-3.214083	-3.650722
H	1.306997	-1.252264	-4.904890
H	1.395322	1.016176	-3.848179
H	1.681053	4.106467	1.780327
H	0.333078	3.019678	1.357520
H	0.437440	4.641080	0.623056
H	3.528743	4.413473	0.092731
H	2.342099	5.016139	-1.091486
H	3.361283	3.607780	-1.484977

Me₂O

SCF Done: E(RB+HF-LYP) = -155.0389322 A.U. after 1 cycle

Atom	x	y	z
C	-1.170777	0.194875	-0.000003
O	0.000000	-0.589108	0.000037
C	1.170774	0.194873	-0.000004
H	-2.021683	-0.491794	-0.001962
H	-1.231683	0.840836	-0.892027
H	-1.233681	0.838147	0.893856
H	2.021684	-0.491796	-0.001474
H	1.233476	0.838494	0.893621
H	1.231910	0.840485	-0.892269

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