Supporting Information

Transamination chemistry of sodium TMP-zincate: synthesis and crystal structure of a chiral amidozincate

David R. Armstrong,[a] William Clegg,[b] Sophie H. Dale,[b] Joaquín García-Álvarez,[a] Ross W. Harrington,[b] Eva Hevia,*[a] Gordon W. Honeyman,[a] Alan R. Kennedy,[a] Robert E. Mulvey,*[a] Charles T. O'Hara.[a]

[a]*WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.*
[b]*School of Natural Sciences (Chemistry), University of Newcastle, Newcastle upon Tyne NE1 7RU, U.K.*

For **2**: $C_{20}H_{48}N_3NaZn$, M = 419.0, monoclinic, space group $C2/c$, a = 27.7184(10), b = 9.8386(3), c = 19.6286(7) Å, β = 102.215(2)°, V = 5231.7(3) Å^3, Z = 8, T = 150 K; 34146 reflections measured, 5767 unique, R_{int} = 0.081; R (F, $F^2 > 2\sigma$) = 0.049, wR (F^2, all data) = 0.094. For **5**: $C_{58}H_{86}Li_2N_6Zn_2$, M = 1012.0, monoclinic, space group $P2_1/c$, a = 12.9978(13), b = 16.615(2), c = 15.8875(17) Å, β = 118.218(7)°, V = 3023.3(6) Å^3, Z = 2, T = 150 K; 21467 reflections measured, 5266 unique, R_{int} = 0.031; R (F, $F^2 > 2\sigma$) = 0.027, wR (F^2, all data) = 0.070. For **6**: $C_{52}H_{70}N_4Na_2Zn_2$, M = 927.8, orthorhombic, space group *Ibca*, a = 22.420(3), b = 22.883(3), c = 41.069(6) Å, V = 21069(5) Å^3, Z = 16, T = 150 K; 74668 reflections measured, 9282 unique, R_{int} = 0.054; R (F, $F^2 > 2\sigma$) = 0.053, wR (F^2, all data) = 0.165. Crystal data for **4**: $C_{22}H_{53}N_4NaZn$, M = 462.0, monoclinic, space group $C2/c$, a = 10.8591(9), b = 18.6245(16), c = 14.1986(12) Å, β = 100.5662(13)°, V = 2822.9(4) Å^3, Z = 4, T = 150 K; 7807 reflections measured, 1852 unique, R_{int} = 0.034; R (F, $F^2 > 2\sigma$) = 0.053, wR (F^2, all data) = 0.118. For **3**: $C_{26}H_{68}N_5NaSi_2Zn$, M = 595.4, triclinic, space group $P\bar{1}$, a = 9.3269(12), b = 10.649(2), c = 19.8598(12) Å, α = 81.740(10) β = 78.079(10), γ = 83.872(12)°, V = 1904.0(5) Å^3, Z = 2, T = 150 K; 29550 reflections measured, 8621 unique, R_{int} = 0.045; R (F, $F^2 > 2\sigma$) = 0.039, wR (F^2, all data) = 0.091. For **5**: $C_{29}H_{50}N_3NaZn$, M = 529.1, monoclinic, space

group $P2_1$, a = 8.9412(2), b = 17.3511(6), c = 20.8700(7) Å, β = 98.524(2)°, V = 3202.00(17) Å^3, Z = 4, T = 123 K; 42285 reflections measured, 11301 unique, R_{int} = 0.075; R (F, $F^2 > 2\sigma$) = 0.053, wR (F^2, all data) = 0.095, Flack absolute structure parameter = –0.008(10). Minor disorder of organic groups was resolved in all four structures. CCDC 660688, 660908–660910.

Computational Details

The geometry of the molecules was optimized using Gaussian 03.[1] Exploratory *ab initio* calculations at the Hartree Fock (HF) level were performed, utilising the 6-31G* basis set.[2] The resultant optimised geometries were subject to a frequency analysis and then refined by further density functional theory (DFT) calculations[3] using the B3LYP functionals[4][5] and the 6-311G** basis set.[6][7] The geometrical structural features from the DFT calculations are reported here while the total energy value from the DFT

[1]. Gaussian 03, Revision B.0.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

[2]. W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972). P. C. Hariharan and J. A. Pople, *Theo. Chim. Acta* **28**, 213 (1973).

[3]. W. Kohn, A. D. Becke and R.G. Parr, J. Phys. Chem., **1996**, *100*, 12974.

[4]. A.D. Becke, Phys. Rev. A, **1988**, *38*, 3098.

[5]. C.T. Lee, W.T. Yang and R.G.Parr, Phys.Rev. B, 1998, **37**, 785.

[6]. A. D. McLean and G. S. Chandler, J. Chem. Phys., **1980**, 72, 5639.

[7]. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., **1980**, *72*, 650.

calculation is adjusted by including the zero-point energy abstracted from the HF calculation modified by the factor 0.91.

TMEDA.Na(μ- Bu^t)(μ-TMP)Zn(Bu^t) + DAH → TMEDA.Na(μ-TMP)(μ-DA)Zn(Bu^t) + Bu^{t}H

ΔE=-22.95 kcal mol^{-1}

TMEDA.Na(μ- Bu^t)(μ-TMP)Zn(Bu^t) + DAH → TMEDA.Na(μ-DA)(μ- Bu^t)Zn(^{t}Bu) + TMPH

ΔE= -6.98 kcal mol^{-1}

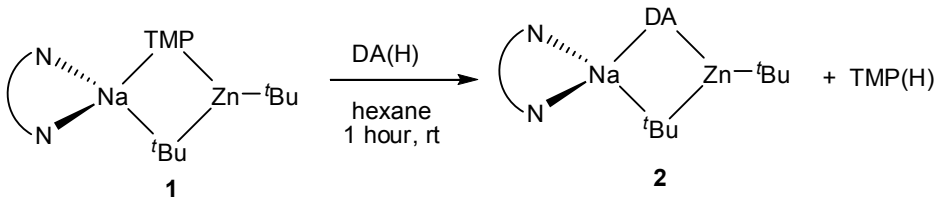
TMEDA.Na(μ- Bu^t)(μ-DA)Zn(Bu^t) + DAH → TMEDA.Na(μ-DA)$_2$Zn(^{t}Bu) + ^{t}BuH

ΔE= -16.84 kcal mol^{-1}

Experimental Section

General Methods. ^{1}H, ^{13}C NMR and ^{7}Li spectra were recorded on a Bruker DPX 400 MHz spectrometer. All ^{13}C NMR spectra were proton decoupled. Hexane and toluene were distilled from sodium-benzophenone. Butylsodium[8] and *t*Bu$_2$Zn[9] were prepared according to literature methods. All synthetic work was carried out under an inert argon atmosphere.

Synthesis of [(TMEDA)Na(DA)Zn(^{t}Bu)$_2$] (2)



1 2

A solution of *t*Bu$_2$Zn in hexane (2mmol) was added via canula to a solution of NaTMP in hexane [prepared *in situ* by reaction of BuNa(0.16 g, 2mmol) and TMP(H) (0.34 mL, 2 mmol)]. TMEDA (0.30 mL, 2mmol) was then introduced and the resulting pale yellow solution was allowed to stir for 15 minutes. Diisopropylamine (0.28 mL, 2mmol) was added and the mixture was allowed to stir at room temperature for one hour. The

8 C. Schade, W. Bauer, P. v. R. Schleyer, *J. Organomet. Chem.* **1985**, *295*, C25.

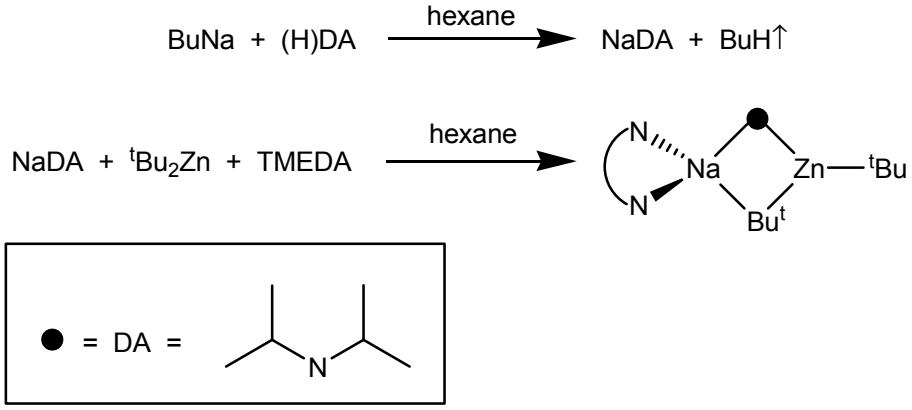
9 P. C. Andrikopoulos, D. R. Armstrong, H. R. L. Barley, W. Clegg, S. H. Dale, E. Hevia, G. W. Honeyman, A. R. Kennedy, R. E. Mulvey, *J. Am. Chem. Soc.* **2005**, *127*, 6184.

resulting pale yellow solution was placed in the refrigerator at -4°C. A crop of colourless crystals was deposited overnight; one of them was employed in an X-ray diffraction experiment. Yield: 0.32, 38%

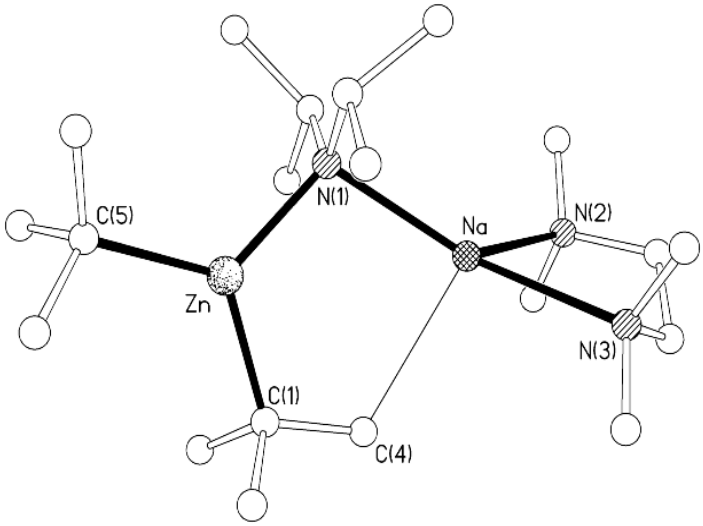
^{1}H NMR (C_6D_6): 0.97 and 1.24 (6H each, d, $^{3}J_{HH}$ = 5.5 Hz, C*H*$_3$-^{i}Pr of DA), 1.56 (18H, s, C*H*$_3$-^{t}Bu), 1.58 (4H, s, C*H*$_2$-TMEDA), 1.67 (12H, s, C*H*$_3$-TMEDA), 3.49 (2H, sept, 2H, $^{3}J_{HH}$ = 5.5 Hz, C*H*-^{i}Pr of DA).

^{13}C{^{1}H} NMR (C_6D_6): 22.66 (*C*(CH$_3$)$_3$ of ^{t}Bu), 26.48 and 27.32 (*C*H$_3$-^{i}Pr of DA), 35.88 (*C*H$_3$ of ^{t}Bu), 46.04 (*C*H$_3$-TMEDA), 49.83 (*C*H-^{i}Pr of DA), 57.12 (*C*H$_2$-TMEDA).

Alternative synthesis of 2:

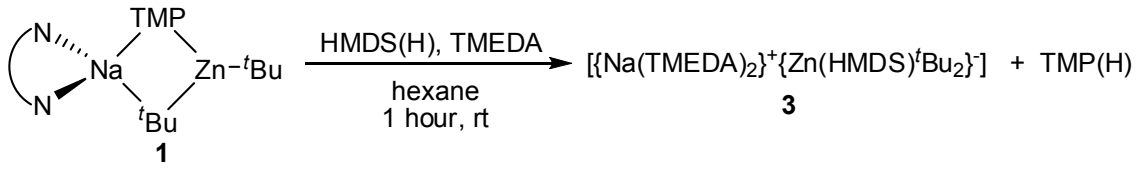


A Schlenk tube was charged with 2mmol (0.358g) of ^{t}Bu$_2$Zn which was dissolved in 10mL of hexane. In a separate Schlenk tube 2mmol of BuNa (0.16g) was suspended in 10mL of hexane and a molar equivalent of (H)DA (2mmol, 0.28mL) added via syringe. The resultant creamy white suspension was allowed to stir for an hour. After which, the hexane solution containing ^{t}Bu$_2$Zn was added via syringe. The suspension changed from creamy white to a clear solution. This was followed by the addition of a molar equivalent of TMEDA (2mmol, 0.30mL). The resultant solution was moved to the freezer to aid the crystallisation. A crop (0.33g, 39%) of colourless crystals formed in solution which were suitable for X-ray crystallographic analysis.



Molecular structure of **2** with hydrogen atoms omitted for clarity, showing the agostic Na…CH_3 contact as a thin line. Selected distances [Å]: Na-N1 2.345(2), Zn-N1 2.050(2), Na-C4 2.809(4), Zn-C1 2.065(3).

Synthesis of [{Na(TMEDA)$_2$}$^+${Zn(HMDS)^{t}Bu$_2$}$^-$] (3)

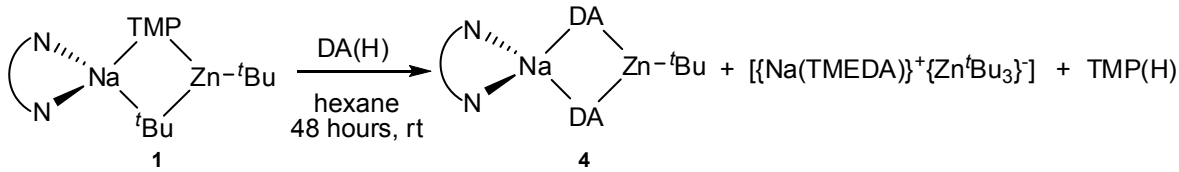


A solution of *t*Bu$_2$Zn in hexane (2mmol) was added via canula to a solution of NaTMP in hexane [prepared *in situ* by reaction of BuNa(0.16 g, 2mmol) and TMP(H) (0.34 mL, 2 mmol)]. TMEDA (0.30 mL, 2mmol) was then introduced and the resulting pale yellow solution was allowed to stir for 15 minutes. Hexamethyldisilazane (0.42 mL, 2mmol) was added and the mixture was allowed to stir at room temperature for one hour. The resulting pale yellow solution was placed in the refrigerator at -4^{o}C.to aid crystallisation. A crop (0.46 g, 39%, maximum possible yield 50%) of yellow crystals formed that were suitable for X-ray crystallographic analysis. When the reaction was repeated using an extra molar equivalent of TMEDA the yield of **3** was increased (0.68 g, 58%)

^{1}H NMR (C_6D_6): 0.34 (18H, s, HMDS), 1.49 (18H, s, C*H*$_3$-^{t}Bu), 1.67 (8H, s, C*H*$_2$-TMEDA), 1.95 (24H, s, C*H*$_3$-TMEDA).

^{13}C{^{1}H} NMR (C_6D_6): 6.33 (HMDS), 22.08 (*C*(CH$_3$)$_3$ of ^{t}Bu), 36.00 (*C*H$_3$ of ^{t}Bu), 46.48 (*C*H$_3$-TMEDA), 57.69 (*C*H$_2$-TMEDA).

Synthesis of [(TMEDA)Na(DA)$_2$Zn(^{t}Bu)] (4)



1 4

Following the same procedure described for compound **2**, one equivalent of diisopropylamide (0.28 mL, 2mmol) was added to a solution of **1** (2 mmol) prepared in situ. The reaction mixture was allowed to stir at room temperature for 48 hours and the resulting pale yellow solution was placed in the refrigerator at -4^{o}C for 24 hours affording a crop of colourless crystals; one of them was employed in an X-ray diffraction experiment. Yield: 0.30 g, 31% (maximum possible yield 50%).

^{1}H NMR (C_6D_6): 1.12, 1.27 (12H each, d, $^3J_{HH}$ = 6.4 Hz, C*H*$_3$-^{i}Pr of DA), 1.38 (9H, s, C*H*$_3$-^{t}Bu), 1.96 (16H, s broad, C*H*$_2$, and C*H*$_3$-TMEDA), 3.50, 3.17 (2H each, sept, $^3J_{HH}$ = 6.2 Hz, C*H*-^{i}Pr of DA).

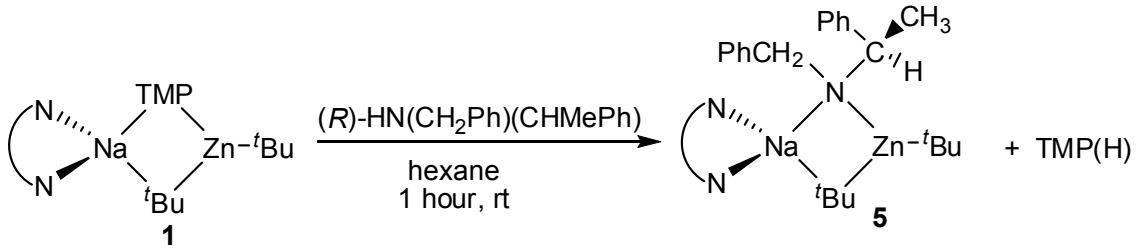
^{1}H NMR (d^8-THF):[10] 0.99 (9H, s, C*H*$_3$-^{t}Bu), 1.04 (24H, d, $^3J_{HH}$ = 6.2 Hz, C*H*$_3$-^{i}Pr of DA), 2.15 (4H, s, C*H*$_2$-TMEDA), 2.30 (12H, s, C*H*$_3$-TMEDA), 3.26 (4H, sept, $^3J_{HH}$ = 6.2 Hz, C*H*-^{i}Pr of DA).

^{13}C{^{1}H} NMR (C_6D_6): 21.87 (*C*(CH$_3$)$_3$ of ^{t}Bu), 26.69 and 27.87 (*C*H$_3$-^{i}Pr of DA), 33.54 (*C*H$_3$ of ^{t}Bu), 45.97 (*C*H$_3$-TMEDA), 49.44 and 49.86 (*C*H-^{i}Pr of DA), 57.55 (*C*H$_2$-TMEDA).

[10] When the ^{1}H NMR spectrum of **4** is carried out in a more polar solvent than benzene such as d^8-THF only one set of signals is observed for the isopropyl groups, suggesting the formation of a solvent-separated zincate which can be formulated as [{Na(THF)$_x$}$^+${Zn(DA)$_2$^{t}Bu}$^-$].

The ^{1}H NMR spectrum of the filtrate showed the presence of coordinated TMEDA and also a singlet at 1.45 ppm that could be attributable to the tBu group of the homoleptic zincate [(TMEDA)NaZn(tBu)$_3$], the other product resulting from the disproportionation of **2**.

Synthesis of [(TMEDA)NaZn(^{t}Bu)$_2${N(CH$_2$Ph)(CH(CH$_3$)Ph)}] (5)



A solution of *t*Bu$_2$Zn in hexane (2mmol) was added via canula to a solution of NaTMP in hexane [prepared *in situ* by reaction of BuNa(0.16 g, 2mmol) and TMP(H) (0.34 mL, 2 mmol)]. TMEDA (0.30 mL, 2mmol) was then introduced and the resulting pale yellow solution was allowed to stir for 15 minutes. One molar equivalent of the chiral amine (*R*)-*N*-benzyl-α-methylbenzylamine (2mmol, 0.42mL) was then introduced. On addition of this amine a purple solution was obtained which was allowed to stir at room temperature for one hour and then removed to the freezer to aid crystallisation. A crop (0.40g, 38.0%) of purple crystals were obtained, one of which was employed for X-ray crystallographic analysis.

^{1}H NMR (C_6D_6): 1.40 (18H, s, C*H*$_3$-^{t}Bu), 1.46 (3H, d, broad, NC*H*$_3$), 1.49 (s, broad, 16H, C*H*$_2$, and C*H*$_3$-TMEDA), 4.49 (1H, m, broad, NC*H*,), 4.35 (1H, m, broad, NC*H*H'), 3.84 (m, broad, NC*H*H'), 7.30-6.90 (overlapping multiplet, aromatic-H's, Ph groups)

^{13}C{^{1}H} NMR (C_6D_6): 23.60 (*C*(CH$_3$)$_3$ of ^{t}Bu), 26.081 (broad, NC*H*$_3$), 36.19 (*C*H$_3$ of ^{t}Bu), 45.92 (*C*H$_3$-TMEDA), 57.36 (*C*H$_2$-TMEDA), 60.23 (broad, NC*H*$_2$), 64.86 . (broad, NC*H*), 126.87, 126.96, 127.06, 127.59, 129.32, 129.84 (aromatics, Ph groups) 147.24, 151.86 (*C*$_{ipso}$, Ph groups).

The isolated crystalline product is the diastereomer (*R,R*)-**5** as only one set of signals for the amide, TMEDA and ^{t}Bu ligands is observed. Another possibility to consider is the formation of a solvent-separated species [{Na(TMEDA)(benzene}$_x$}$^+${Zn(*R*-amide)^{t}Bu$_2$}$^-$] with the consequent loss of the N as a steregenic centre. However we are less inclined to support this possibility as in all the amido-dialkyl zincates of type [(TMEDA)M(μ-NR$_2$)Zn(R')$_2$] the amide ligand still acts as a bridge between the two metals in solutions of non-polar solvents such as benzene or hexanes and a solvent-separated motif in solution only occurs when strongly coordinating ligands such as pyridine or THF are employed in the reaction solution.