Supplementary Material (ESI) for Chemical Communications
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Supporting Information

Structural variations in bimetallic sodium-magnesium and sodium-zinc ketimides, and a sodium-zinc alkide-alkoxide-amide: connections to ring-stacking, ring-laddering, and inverse crown concepts[†]

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Experimental Section

General Methods.

General: All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. *n*,*s*-Dibutylmagnesium and *n*Bu_2Zn were purchased from Aldrich Chemicals as 1M solutions in heptane and hexane respectively. Butylsodium[1] and *t*Bu_2Zn[2] were prepared

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[1] Schade, C.; Bauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, *295*, C25.

[2] 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.

according to literature methods. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C.

Synthesis of [(Ph$_2$C=NH)$_2$(Ph$_2$C=N)$_6$Na$_2$Mg$_2$] (1): BuNa (0.16 g, 2mmol) was suspended in hexane (10 mL). Bu$_2$Mg (2 mL of a 1M solution in heptane, 2mmol) was introduced affording a white precipitate. Benzophenone imine (1.28 mL, 8 mmol) was then added dropwise. The reaction was exothermic and was accompanied by gas evolution, as an orange precipitate was obtained. The solution is heated until the entire solid is dissolved. Allowing this solution to cool slowly at room temperature produced a crop of orange crystals (Yield 1.05g, 68%). ^{1}H NMR (400 MHz, 25°C, C$_6$D$_6$): 8.75 (s, 2H, N*H*=C), 7.68 (m, 12H, Ph's), 7.37 (m, 6H, Ph's), 7.23 (m, 12H, Ph's), 7.01 (m, 12H, Ph's), 6.90 (m, 36H, Ph's), 6.82 (m, 6H, Ph's). ^{13}C{^{1}H} NMR (100.63 MHz, 25°C, C$_6$D$_6$): 178.17 (*C*=NH), 174.85 (*C*=N), 166.07 (*C*=N), 146.50, 146.24, 140.40, 138.35, 129.74, 128.34, 128.75, 128.27, 127.64, 127.85, 127.64 (Ph's).

Synthesis of [(Ph$_2$C=NH)$_2$(Ph$_2$C=N)$_4$(Bu)$_2$Na$_2$Zn$_2$] (2). BuNa (0.24 g, 3mmol) was suspended in hexane (10 mL). Bu$_2$Zn (3 mL of a 1M solution in heptane, 3mmol) was introduced affording a white precipitate. Benzophenone imine (1.50 mL, 9 mmol) was then added dropwise. The reaction was exothermic and was accompanied by gas evolution, and an orange oil was obtained. The mixture was stirred at room temperature for 4 hours affording an orange precipitate. At this stage toluene (5 mL) was introduced and the mixture was gently heated until all the orange solid had dissolved, affording a orange solution. Allowing this solution to cool slowly at room temperature produced a crop of orange crystals (Yield 1.48g, 72%). ^{1}H NMR (400 MHz, 25°C, C$_6$D$_6$): 8.72 (s, 2H, N*H*=C), 7.60 (m, 12H, Ph's), 7.22 (m, 48H, Ph's), 1.40 (m, 8H, C*H*$_2$'s, Bu), 1.02 (m, 6H, C*H*$_3$, Bu), -0.14 (m, 4H, Zn-C*H*$_2$, Bu).

Synthesis of [{(Me$_2$NCH$_2$CH$_2$O)(Bu^t)(TMP)NaZn}$_2$] (3). BuNa (2mmol, 0.16g) was suspended in hexane (10ml) and sonicated for 10 minutes to form a fine dispersion. TMPH (2mmol, 0.34ml) was added and the creamy, white suspension formed was allowed to stir for 1 hour. In a separate Schlenk tube, ^{t}Bu$_2$Zn (2mmol, 0.36g) was dissolved in hexane (10ml) then transferred via cannula to already prepared NaTMP. The solution was allowed to stir for around 1 hour before *N,N*-dimethylaminoethanol (1mmol, 0.1ml) was added. The solution immediately became transparent and was very pale yellow in colour. After stirring for 4 hours, some solvent was removed under vacuum and the Schlenk tube placed in the freezer (at -24°C) to aid crystallisation. A small crop of colourless crystals formed (0.12g, 8.02%).^{1}H NMR (400.1MHz, C$_6$D$_6$, 300K): δ 4.01 (1H, dd, CH_2 (adjacent to O)), 3.68 (1H, dd, CH_2 (adjacent to O)), 2.18 (2H, m, (adjacent to N)), 1.96, (s, γ-TMP), 1.92 (6H, s, NMe_2), 1.88 (s, β-TMP), 1.53 (9H, s, ^{t}Bu), 1.31 (3H, s, Me, TMP), 1.28 (3H, s, Me, TMP), 1.14 (3H, s, Me, TMP), 1.07 (3H, s, Me, TMP). ^{13}C NMR (100.6MHz, C$_6$D$_6$, 300K): δ 67.36(CH$_2$ (adjacent to N)), 60.98 (CH$_2$ (adjacent to O)), 52.29 (C$_\alpha$, TMP), 52.16 (C$_{\alpha'}$, TMP), 45.16 (NMe$_2$), 40.94 (C$_\beta$, TMP), 40.49 (C$_{\beta'}$, TMP), 39.42 (TMPH), 36.79 (CH$_3$, TMP), 36.33 (CH$_3$, TMP), 35.59 (CH$_3$, TMP), 35.23 (CH$_3$, TMP), 34.55 (C(CH$_3$)$_3$), 32.05 (TMPH), 21.30 (C$_\gamma$, TMP), 19.97 (TMPH), 19.49 (C(CH$_3$).

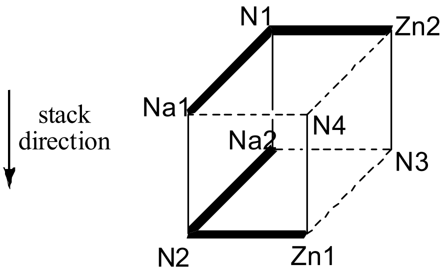
▬ short bond

—— intermediate bond

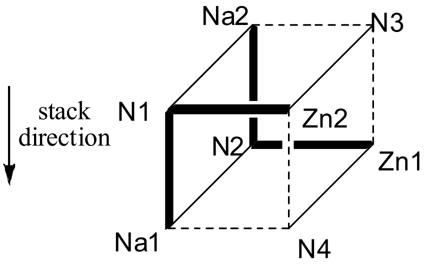
------ long bond

Zn2-N1	2.063(4)
Zn1-N2	2.058(4)
Na1-N1	2.377(4)
Na2-N2	2.398(5)
Zn1-N4	2.103(4)
Zn2-N3	2.111(4)
Na1-N2	2.403(4)
Na2-N1	2.402(4)
Zn1-N3	2.112(4)
Zn2-N4	2.139(4)
Na1-N4	2.548(4)
Na2-N3	2.448(4)

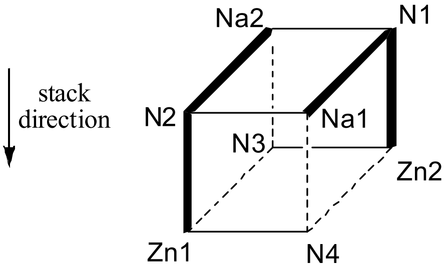
Esd's are not taken into consideration in this analysis



2A



2B



2C