Structurally-Defined Reactions of Sodium TMP-Zincate with Nitrile Compounds: Synthesis of a Salt-like Sodium Sodiumdizincate and Other Unexpected Ion Pair Products

General Techniques
All synthetic work was carried out under an inert argon atmosphere using standard Schlenk techniques. All solvents were distilled over sodium/benzophenone under a nitrogen atmosphere. The majority of reagents used were purchased from the Aldrich Chemical Co. including: \textsuperscript{8}BuLi (1.6M in hexane), \textsuperscript{t}BuLi (1.7M in pentane) and ZnCl\textsubscript{2} (1.0M in diethylether). Na\textsuperscript{t}Bu and TMEDA were purchased from Lancaster Chemicals and TMPH from Acros Organics. \textsuperscript{8}BuNa was prepared via a literature procedure (C. Schade, W. Bauer, P.v.R. Schleyer, \textit{J. Organomet. Chem.} \textbf{1985}, C25) as was \textsuperscript{t}Bu\textsubscript{2}Zn (P.C. Andrikopolous, D.R. Armstrong, H.R.L. Barley, W. Clegg, S.H. Dale, E. Hevia, G.W. Honeyman, A.R. Kennedy, R. E. Mulvey, \textit{J. Am. Chem. Soc.} \textbf{2005}, \textit{127}, 6184). Unless otherwise stated, other reagents used during this work were obtained from the Aldrich Chemical Co. at the highest purity available. Data for X-ray crystal structure determinations were obtained with a Nonius Kappa CCD using graphite monochromated Mo-K\textalpha\ radiation (? = 0.71073 Å) or a Bruker SMART 1K CCD diffractometer also using graphite monochromated Mo-K\alpha radiation (? = 0.71073 Å).

Synthesis of [(3-Me-C\textsubscript{6}H\textsubscript{4}CN)\textsubscript{2}Na(TMEDA)\textsubscript{2}]\textsuperscript{+} [{6-Zn(\textsuperscript{t}Bu)\textsubscript{2}-3-Me-C\textsubscript{6}H\textsubscript{3}CN}\textsubscript{2}Na (TMEDA)\textsubscript{2}]\textsuperscript{-} (1)
BuNa (2 mmol, 0.16 g) was suspended in hexane (10 ml) and sonicated for 10 minutes to form a fine dispersion. TMPH (2 mmol, 0.34 ml) was added and the creamy, white suspension formed was allowed to stir for 1 hour. \textsuperscript{t}Bu\textsubscript{2}Zn (2 mmol, 0.36 g) in hexane was then added followed by TMEDA (0.3 ml, 2 mmol) to give a yellow solution which was allowed to stir for around 45 minutes before meta-tolunitrile (2 mmol, 0.24 ml) was introduced. The solution became red in colour and slightly cloudy. Approximately 5ml toluene was added to give a red/orange homogeneous solution. Crystallisation occurred at -24°C (orange crystals, yield 0.39 g, 29.3%).
Consideration of the crystal structure led to the synthesis being repeated with a change in stoichiometry to try to improve the yield of the crystalline product. Thus, the amount of TMEDA was increased to 2 equivalents (0.6 ml, 4 mmol) in addition to 2 equivalents of meta-tolunitrile (4 mmol, 0.48 ml). Again a red precipitate formed immediately and hexane was removed in vacuo. 7ml of toluene were added to give a dark red solution. Crystallisation occurred at -24°C (new yield, 0.65g, 48.9%), mp.: 77.4°C. Anal. Calcd for C$_{72}$H$_{126}$N$_{12}$Na$_2$Zn$_2$: C, 67.40; H, 9.50; N, 12.58. Found: C, 67.40; H, 9.86; N, 12.51%.

NMR Spectroscopic Data for Compound 1

$^1$H NMR (400.1 MHz, C$_6$D$_6$, 300K): δ8.38 (2H, d, A$_3$), 8.29 (trace, d, unknown), 7.63 (s, 2H, A$_1$), 7.58 (trace, s, unknown), 7.44 (2H, s, B$_1$), 7.40, (2H, d, A$_2$), 7.37 (trace, s, unknown), 7.28 (trace, d, unknown), 7.23 (2H, d, B$_2$), 7.01 and 6.96 (4H, overlapped d, B$_4$ and t, B$_3$), 2.46 (6H, s, Me, A), 2.23 (50H, s, CH$_3$, TMEDA), 2.19 (19H, s, CH$_2$, TMEDA), 2.08 (6H, s, Me, B), 2.03 (36H, s, $^{1}$Bu).

![Figure S-1: Numbering scheme for the $^1$H NMR spectrum of compound 1.](image)
Figure S-2: Compound 1 $^1$H NMR spectrum – aromatic region (C$_6$D$_6$, 400.1MHz, 300K).

$^{13}$C NMR (100.63 MHz, C$_6$D$_6$, 300K): d184.8 (A$_2$), 139.8 (A$_3$), 139.3 (unknown), 133.6 (B$_2$), 132.6 (A$_5$), 131.8 (B$_3$), 131.5 (unknown), 130.9 (A$_4$), 130.7 (A$_6$), 129.3 (B$_4$), 129.2 (B$_1$), 128.9 (B$_6$), 119.3 (B$_5$), 118.9 (A$_1$), 112.0 (CN A$_1$ and B$_1$), 56.6 (CH$_2$ TMEDA), 45.4 (CH$_3$ TMEDA), 35.2 (C(CH$_3$)$_3$), 22.5 (C(CH$_3$)$_3$), 20.3 (Me A), 19.9 (Me B).

Figure S-3: Numbering scheme for Compound 1 $^{13}$C NMR.
Figure S-4: Compound 1 $^{13}$C NMR spectrum (C$_6$D$_6$, 100.63MHz, 300K).

Analysis of NMR Data
The NMR spectra of 1 can be almost fully assigned using COSY and HMQC 2-D NMR experiments. However, there is a trace amount of a species having four small resonances in the aromatic region which cannot be unambiguously identified. It is likely that this minor unknown secondary product could be associated with the remaining $^1$Bu$_2$Zn linkage of the base undergoing further reaction with the meta-tolunitrile to generate $^1$BuZn(di-ortho-deprotonated nitrile) species. Such behaviour of this sodium zincate reagent is preceded in reactions with aromatic ethers (see W. Clegg, S. H. Dale, A. M. Drummond, E. Hevia, G.W. Honeyman, R. E. Mulvey, *J. Am. Chem. Soc.*, 2006, 128, 7434) and also appears to be the case in the synthesis of compound 2. This hypothesis is supported by the fact that the unidentified resonances appear to be systematically further upfield than those associated with 2. NMR analysis of the filtrate shows predominantly unreacted meta-tolunitrile and a small amount of free TMEDA. Additionally, the presence of a characteristic resonance at 1.06 ppm confirms the presence of eliminated TMPH.
Synthesis of [(TMEDA)$_2$Na.(2-Zn(‘Bu)$_2$-1-CN-C$_{10}$H$_6$] (2)

BuNa (2 mmol, 0.16 g) was suspended in hexane (10 ml) and sonicated for 10 minutes to form a fine dispersion. TMPH (2 mmol, 0.34 ml) was added and the creamy, white suspension formed was allowed to stir for 1 hour. ‘Bu$_2$Zn (2 mmol, 0.36 g) in hexane was then added followed by TMEDA (0.6 ml, 4 mmol) to give a yellow solution which was allowed to stir for around 45 minutes before 1-cyanonaphthalene (2 mmol, 0.3 g) was introduced. The solution became red and a dark precipitate formed almost immediately. Hexane was removed from the mixture in vacuo and 7 ml of toluene was added to give a dark red solution which was stirred for around 45 minutes. A dark red crystalline solid formed (0.45 g) at -24°C which was used for the NMR analysis and the X-ray crystallographic study. No absolute yield can be given as this solid contained more than one metallo product (see NMR analysis), mp of mixture.: 123.3°C. For a mixture of 64% compound 2A and 36% 2B Anal. Calcd for C$_{31}$H$_{56}$N$_5$NaZn: C, 64.67; H, 8.91; N, 12.08. Found: C, 64.67; H, 8.84; N, 11.94%.

$^1$H NMR (400.1 MHz, C$_6$D$_6$, 300K): d8.36 (1H, d, A$_1$), 8.26 and 8.23 (1.2H, overlapped d, B$_1$ and overlapped d, B$_6$), 8.10 (1H, d, A$_6$), 7.68 (0.6H, overlapped d, B$_2$), 7.65 (1H, overlapped d, A$_3$), 7.61 (1.6H, overlapped d, A$_2$ and B$_3$), 7.47 (1H, t, A$_5$), 7.39 (0.6H, t, B$_3$), 7.24 and 7.21 (1.8H, overlapped t, A$_4$ and overlapped t, B$_4$), 1.91 (40H, s, CH$_3$ TMEDA), 1.85 and 1.84 (17H, overlapped s, CH$_2$ TMEDA and overlapped s, ‘Bu [{C$_{10}$H$_7$CN}$_2$.Zn(‘Bu)$_2$]), 1.71 (24H, broad s, ‘Bu).

Figure S-5: Numbering scheme for compounds 2A and 2B used in the $^1$H NMR interpretation.
Figure S-6: Compound 2 $^1$H NMR spectrum – aromatic region (C$_6$D$_6$, 400.1MHz, 300K).

Figure S-7: Compound 2 $^1$H NMR spectrum – aliphatic region (C$_6$D$_6$, 400.1MHz, 300K).

$^{13}$C NMR (100.6MHz, C$_6$D$_6$, 300K): d210.0 (B Zn-\( \equiv \)), 197.4 (A Zn-\( \equiv \)), 137.6 (A$_3$), 136.4 (A$_5$/A$_{10}$), 133.8 (B$_3$/B$_{10}$), 132.0 (A$_5$/A$_{10}$), 131.9 (B$_3$/B$_{10}$), 129.6 (A$_9$), 129.2 (overlapped B$_4$/B$_6$), 126.8 (B$_8$), 126.3 (A$_1$), 126.1 (B$_1$), 126.0 (A$_8$), 124.7 (B$_7$), 124.0
(A\textsubscript{7}), 123.4 (B\textsubscript{9}), 122.7 (A\textsubscript{9}), 114.9 (B CN), 114.3 (A CN), 56.7 (CH\textsubscript{2} TMEDA), 42.5 (CH\textsubscript{3} TMEDA), 34.9 (A C(CH\textsubscript{3})\textsubscript{3}), 34.5 (B C(CH\textsubscript{3})\textsubscript{3}), 31.2 (A C(CH\textsubscript{3})\textsubscript{3}), 29.50 (B C(CH\textsubscript{3})\textsubscript{3}).

**Figure S-8:** Numbering scheme for compounds 2A and 2B used in the $^{13}$C NMR interpretation.

**Figure S-9:** Compound 2 $^{13}$C NMR – aromatic region (C\textsubscript{6}D\textsubscript{6}, 100.63MHz, 300K).
Analysis of NMR Data
From the NMR analysis of isolated 2, it was apparent that two major distinct compounds were present in solution. These represent the zincated mono(1-cyanonaphthalene) complex 2, here labeled 2A and an additional second zincated 1-cyanonaphthalene species (Zn-C bonds give a characteristic chemical shift close to 8 ppm and a second set of resonances were observed in this region) labeled 2B. From $^1$H, $^{13}$C and variable temperature spectra, EXSY experiments and 2-dimensional HSQC and COSY experiments as well as carrying out the reaction under different conditions (see later), 2B can be confidently assigned as [(TMEDA)$_2$Na{Zn(t-Bu)CN-C$_{10}$H$_6$}]$_2$, that is a monoalkyl-biscyanonaphthyl zinc species. The $^1$H NMR spectra show two comparable sets of resonances both indicative of ortho-zincation in the 2-position (see table S-1).

Table S-1: Comparison of $^1$H NMR aromatic shifts for Compound 2 with assignments of A and B

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In the aliphatic region a broad signal at 1.71 ppm was observed for the 'Bu groups indicative of either a dynamic process or exchange. Variable temperature NMR spectra showed that this broad signal de-coalesced to two sharp peaks (at 1.82 and 1.44ppm at 238K) indicating the presence of two distinct exchanging 'Bu groups (see figure S-10).

Figure S-10: Compound 2 $^1$H NMR variable temperature spectrum (238K) – aliphatic region (toluene-d$_8$, 400.1MHz).

This confirmed the presence of two distinct zincated species and highlighted exchange between the complexes. However, a VT NMR spectrum obtained at 238K (figure S-10) also revealed a third minor species (at 1.74 ppm). This small resonance corresponds to a protic impurity or minor product which, as yet, is unidentified. However, other possible side products, $^1$Bu$_2$Zn.(1-cyanonaphthalene), $^1$Bu$_2$Zn, $^1$Bu$_2$Zn.TMEDA and (Bu$_3$Zn) can be ruled out on comparing this chemical shift with those of authentic samples. There are also precedents for the cleavage of neutral zinc Lewis acid-Lewis base complexes from closely related bimetallic alkali metal alkyl-amidozincates (for example, see H. R. Barley, W. Clegg, S. H. Dale, E. Hevia, G.W. Honeyman, A. R. Kennedy, R. E. Mulvey, Angew. Chem. Int. Ed., 2005, 44, 6018
To confirm the presence of three cyanonaphthyl species, the $^1$H NMR was obtained in THF-d$_8$. This allows the complex aromatic region of the spectra to be expanded and the overlapped resonances to be better resolved.

**Figure S-11**: Compound 2 $^1$H NMR spectrum – aromatic region (THF-d$_8$, 400.1MHz, 300K).

This NMR confirmed the presence of three distinct cyanonaphthyl species (2A, 2B and the aforementioned minor product).

To confirm the identity of the two main species 2A and 2B, a number of changes were made to the stoichiometry of the initial reaction in addition to changes to some of the reaction parameters.
Changing the stoichiometry of the reaction producing 2 proved insightful. The reaction was repeated using a zincate base:1-cyanonaphthalene ratio of 1:2. The $^1$H NMR spectrum of the orange crystalline product obtained from this reaction is shown in figure S-12.

**Figure S-12:** Aromatic region of the $^1$H NMR spectrum of mixed product 2A/2B made via a 1:2, zinc base:1-cyanonaphthalene ratio (C$_6$D$_6$, 400.1MHz, 300K).

This spectrum shows a significant increase in the amount of compound 2B, i.e. altering the ratio of products A:B from 66:34 to 32:68, as would be expected from the change in the stoichiometry of the reaction. To gain more information, the reaction was then carried out using a zincate base:1-cyanonaphthalene ratio of 2:1, that is, with a deficiency of the nitrile. This provided no further insight as the ratio of products was the almost identical to that in the 1:1 (zincate base:1-cyanonaphthalene) reaction.
Lastly, to explore the kinetics of this reaction, the original procedure was repeated without stirring for 45 minutes, that is, after the addition of toluene, the Schlenk tube was placed immediately in the freezer. It was envisaged that this would slow down the second metallation and thus reduce the formation of \textbf{2B}. This was duly confirmed from a $^1$H NMR spectrum which, from relative integrals, showed a \textit{A:B} ratio of 2.27:1, compared to 1.27:1 for the original stirred 1:1 reaction.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FigureS13.png}
\caption{Aromatic region of the $^1$H NMR spectrum of mixed product 2A/2B made via a 1:1, zinc base:1-cyanonaphthalene ratio without stirring (C$_6$D$_6$, 400.1MHz, 300K).}
\end{figure}

Note that quantities of \textbf{2B} were always found in samples of \textbf{2A} even when a ratio of 1:<1 (base: 1-cyanonaphthalene) was employed. Moreover, the ratio of \textit{A:B} was very similar to that observed in the original product. This indicates that complex \textbf{2} reacts faster with 1-cyanonaphthalene than the original sodium TMP-zincate reagent. A case where kinetic factors lead to \textit{ortho}-zincated mono- and di- derivatives of the same functionalised aromatic molecule is precededent in the reactions of anisole (see W. Clegg, S. H. Dale,

**Synthesis of \([\{t\text{BuCN}\}_2\text{Na(TMEDA)}_2]\)\(^+\)\([t\text{Bu}_3\text{Zn}]^-\) (3)**

BuNa (2 mmol, 0.16 g) was suspended in hexane (10 ml) and sonicated for 10 minutes to form a fine dispersion. TMPH (2 mmol, 0.34 ml) was added and the creamy, white suspension formed was allowed to stir for 1 hour. \(t\text{Bu}_2\text{Zn}\) (2 mmol, 0.36 g) in hexane was then introduced followed by two molar equivalents of TMEDA (0.6 ml, 4 mmol) to give a yellow solution which was allowed to stir for around 45 minutes before cooling to -20°C. At this point tert-butylcyanide (2 mmol, 0.18 ml) was added to the solution. The solution became orange/red in colour and a dark precipitate formed immediately. The solution was allowed to come to room temperature slowly (over 2 hours). 10 ml of toluene were added to give a dark red solution with some fine precipitate. Some solvent was removed *in vacuo* and the precipitate dissolved leaving a dark red/orange solution. A large crop (0.45 g, 35%) of small, red, needle like crystals formed overnight (at room temperature) which were employed for the XRD analysis and characterized by NMR spectroscopy. Upon isolation from solution, the crystals became opaque and sticky, and thus a melting point could not be obtained. Anal. Calcd for C\(_{34}\)H\(_{77}\)N\(_6\)NaZn: C, 62.03; H, 11.79; N, 12.76. Found: C, 62.40; H, 11.64; N, 11.81.

^1\text{H NMR (400.1MHz, C}_6\text{D}_6, 300K): d2.05 and 2.03 (32H, s, s CH\(_3\) and CH\(_2\) TMEDA), 1.45 (15H, broad s, \(^1\text{Bu [Zn}\text{Bu}_3\text{]}\), 0.84 (19H, s, \(^1\text{Bu[CN]}\)). The spectrum shows resonances between 1.50 and 1.68 ppm caused by protic impurities.
**Figure S-14**: Compound 3 $^1$H NMR spectrum – aliphatic region (C$_6$D$_6$, 400.1MHz, 300K).

$^{13}$C NMR (100.6MHz, C$_6$D$_6$, 300K): δ125.7 (CN), 57.5 (CH$_2$ TMEDA), 46.1 (CH$_3$ TMEDA), 35.7 (ZnC(CH$_3$)$_3$), 34.8 (ZnC(CH$_3$)$_3$), 27.4 (CNC(CH$_3$)$_3$), 24.3 (CNC(CH$_3$)$_3$).
Analysis of NMR Data

Using $^1$H and $^{13}$C NMR spectroscopy, compound 3 was fully characterised. The $^1$H NMR spectrum revealed four distinct signals. Two overlapped singlets at 2.05 and 2.03 ppm show coordinated TMEDA, in this case bound to the Na atom. Additionally, the $^t$Bu group adjacent to the CN functionality has shifted upfield to 0.84 ppm (from 0.94 ppm) indicating coordination to the sodium. The remaining broad singlet can be attributed to the $^t$Bu groups bonded to the Zn atom. It is likely that the broadness of this singlet is due to exchange between the three $^t$Bu groups.
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\(^1\)H NMR Spectrum of 1 in C\(_6\)D\(_6\)
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**13C NMR Spectrum of 1 in C6D6**
\(^1\)H NMR Spectrum of 2 in C\(_6\)D\(_6\)
$^{13}$C NMR Spectrum of 2 in C$_6$D$_6$
$^1$H NMR Spectrum of 3 in C$_6$D$_6$
$^{13}$C NMR Spectrum of 3 in C$_6$D$_6$