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Monodentate coordination of the normally chelating chiral diamine (*R*,*R*)-TMCDA†

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After isolating an unusual binuclear, but monosolvated NaHMDS complex [{(*R*,*R*)-TMCDA}·(NaHMDS)$_2$]$_\infty$ which polymerises *via* intermolecular electrostatic Na···Me$_{HMDS}$ interactions, further (*R*,*R*)-TMCDA was added to produce the discrete binuclear amide [{κ^2-(*R*,*R*)-TMCDA}·(NaHMDS)$_2${κ^1-(*R*,*R*)-TMCDA}], whose salient feature is the unique monodentate coordination of one of the chiral diamine ligands.

Chiral diamine ligands, for example (−)-sparteine, its (+)-sparteine surrogate and *N*,*N*,*N*′,*N*′-(1*R*,2*R*)-tetramethylcyclohexane-1,2-diamine [(*R*,*R*)-TMCDA] have attracted considerable attention in asymmetric synthesis in a whole host of transition metal catalysed methodologies.[1] From an s-block perspective, when paired with an organolithium reagent it can be envisaged that 'chiral carbanions' are created, which can be used in subsequent enantioselective syntheses.[2] Focusing particularly on the C_2-symmetric ligand (*R*,*R*)-TMCDA, it has come to prominence recently as the availability of the historically more widely utilised diamine (−)-sparteine, has been unreliable over the past few years.[3] In terms of its coordination chemistry, (*R*,*R*)-TMCDA has worldwide interest and has been well studied. Over 50 metal complexes containing its ligated form have been reported, spanning both the s- (Li,[4] Na,[4e] K,[4e] and Mg,[5]) and d-block metals (Cu,[6] Zn,[7] Ru,[8] Pd,[9] Pt[10] and Hg[11]). Within s-block chemistry and germane to this work, Strohmann has comprehensively studied (*R*,*R*)-TMCDA complexes of synthetically important organolithium reagents (such as ^{t}BuLi,[4a] MeLi,[4b] ^{i}PrLi,[4b] ^{s}BuLi,[4b] ^{n}BuLi,[4c] BH$_3$P(Ph)(Me)CH$_2$Li,[4d] MeLi,[4g] PhLi,[4h] (allyl)Li[4h] and (benzyl)Li[4i] derivatives). An all-encompassing feature of all known structures is that the chiral diamine ligand adopts exclusively a κ^2-bidentate chelating mode. Due to the less flexible, fixed bite angle in (*R*,*R*)-TMCDA, with respect to that of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA),[12] it is a stronger chelating ligand than the latter,[13] with a recent study noting that it 'displays no tendency to bind as a monodentate ligand.'[14] This has been attributed to the κ^1 (or by implication η^1) form of (*R*,*R*)-TMCDA inducing severe steric strain due to the juxtaposition of the metal–NMe$_2$ with the uncoordinated NMe$_2$ group. The structural chemistry of alkali metal amide complexes continues to be an important topic of research.[15] We have recently discovered that lithium and sodium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS and NaHMDS) can capture alkali metal halide salts in the presence of donor ligands to form ion pair metal anionic crown (MAC) complexes, for example [Li{(*R*,*R*)-TMCDA}$_2$]$^+$[Li$_5$HMDS$_5$Cl]$^-$.[4f,16] A key starting material which remained hitherto elusive in our studies involving sodium is the (*R*,*R*)-TMCDA–solvated NaHMDS complex. Crystallisation of other donor ligated [*e.g.*, Me$_6$TREN[17] and (−)-sparteine[18]] NaHMDS complexes has proven difficult, although the polymeric TMEDA [(μ-TMEDA)·(NaHMDS)$_2$]$_\infty$[19] and *N*,*N*,*N*′,*N*′-tetramethylpropanediamine (TMPDA) [(μ-TMPDA)·(NaHMDS)$_2$]$_\infty$[20] complexes, which propagate *via* the non-chelating diamine ligand, are known (Fig. 1). These have similar structural motifs to Williard's lithium diisopropylamide (LDA) complex [(μ-TMEDA)·(LDA)$_2$]$_\infty$.[19]

In an effort to prepare the (*R*,*R*)-TMCDA complex of NaHMDS, an equimolar mixture of NaHMDS and (*R*,*R*)-TMCDA was combined in *n*-hexane medium and left to stir at ambient temperature for 1 hour (Scheme 1). The reaction mixture was then cooled to −33 °C and crystals suitable for X-ray crystallographic analysis deposited after 48 hours (27% non-optimised, crystalline yield; maximum yield 50% based on (*R*,*R*)-TMCDA consumption). X-ray data reveal the mono-(*R*,*R*)-TMCDA, binuclear [{(*R*,*R*)-TMCDA}·(NaHMDS)$_2$]$_\infty$ **1** (Fig. 2a). There are six crystallographically distinct but essentially chemically

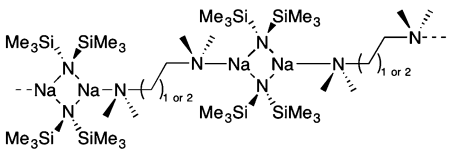

Fig. 1 Structures of previously known polymeric [(μ-TMEDA)·(NaHMDS)$_2$]$_\infty$ and [(μ-TMPDA)·(NaHMDS)$_2$]$_\infty$.

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† Electronic supplementary information (ESI) available: General synthetic procedures, crystal structure determinations and NMR spectroscopic data. CCDC 1501992 and 1501993. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc07190b

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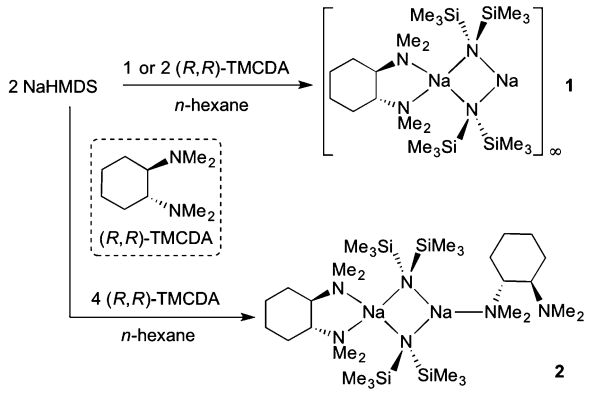

Scheme 1 Syntheses of $[\{(R,R)\text{-TMCDA}\}\cdot(NaHMDS)_2]_\infty$ **1** and $[\{\kappa^2\text{-}(R,R)\text{-TMCDA}\}\cdot(NaHMDS)_2\{\kappa^1\text{-}(R,R)\text{-TMCDA}\}]$ **2**.

equivalent molecules of $[\{(R,R)\text{-TMCDA}\}\cdot(NaHMDS)_2]$ in the structure of **1**, thus for brevity only one is discussed here. Interestingly, the empirical formula of **1**, *i.e.*, $[(\text{donor})\cdot(NaHMDS)_2]$ is identical to that for the aforementioned TMEDA and TMPDA derivatives; however, in keeping with previously known (*R*,*R*)-TMCDA complexes, the diamine adopts a chelating bonding mode, and with respect to the N donor atoms, renders one Na metal centre (Na1) four-coordinate in a distorted tetrahedral arrangement (bond angles range from 68.70(9) to 151.55(10)°, see ESI† for full details). Additionally, Na1 has two long Na···Me interactions with a methyl group from each HMDS ligand [Na1···C12 2.987(4) and Na1···C22 2.987(4) Å]. The second Na metal centre (Na2) remains only two-coordinate with respect to the bridging amido N atoms. To satisfy this electron deficiency, Na2 engages a solitary intermolecular Na···Me($SiMe_2$) [Na2···C65 distance, 2.818(4) Å] electrostatic interaction (Fig. 2b), which is short in comparison to known literature examples [range Na···Me($SiMe_2$) 2.947–3.138 Å].[21] This sole intermolecular Na···Me interaction induces propagation of binuclear units in a zigzag polymer chain. This change in the coordination chemistry of (*R*,*R*)-TMCDA in **1** with respect to the bridging TMEDA and TMPDA ligands in the aforementioned polymeric sodium amides emphasises the propensity for the chiral 1,2-diamine to remain as a chelating ligand rather than binding in a monodentate fashion. As a consequence of this coordination mismatch, significantly shorter Na2–N_{HMDS} bonds (mean distance, 2.356 Å) are observed when compared with Na1–N_{HMDS} bonds (mean distance, 2.530 Å). Despite utilising a 1:1 ratio of NaHMDS:(*R*,*R*)-TMCDA in this synthesis, it is clearly evident that the ultimate ratio in **1** is 2:1. When this optimised ratio is used in the synthesis, **1** was again the sole product isolated (36% crystalline yield).

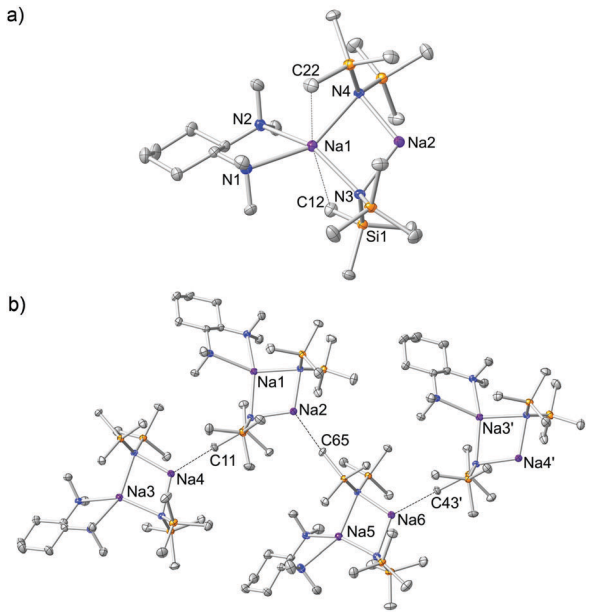

Fig. 2 (a) Molecular structure of $[\{(R,R)\text{-TMCDA}\}\cdot(NaHMDS)_2]_\infty$ **1** showing one molecule from the asymmetric unit. Hydrogen atoms omitted for simplicity and thermal ellipsoids are displayed at 35% probability. (b) Section of the zigzag polymeric chain of **1**. The dashed lines illustrate Na···Me($SiMe_2$) interactions. The symmetry operation used to generate the atoms labelled with ′ is $-x + 1, y + 1/2, -z + 1$.

Complex **1** is a rare example of a solvated sodium amide which contains an unsolvated Na site. Bochmann revealed the mono(tetrahydrofuran), mono(THF), complex $[(THF)\cdot(NaHMDS)_2]$ where one Na atom is two coordinate whilst the other binds to the ether to render it three coordinate.[22] Interestingly, seven years prior to this report Dehnicke published the bis(THF) analogue $[(THF)_2\cdot(NaHMDS)_2]$ where both Na atoms are three coordinate.[23] This begged the question: '*could the coordinatively unsaturated (Lewis acidic) Na atom in **1**, act as a host for another Lewis base*?'

A logical route to address this question would be to utilise monodentate donors such as THF and diethylether, in an attempt to saturate the deficient metal centre; but, it is highly likely that these strong σ-donors would also displace the chelating (*R*,*R*)-TMCDA ligand. Therefore to maintain synthetic simplicity, we repeated the preparation of **1** but employing an excess (two molar equivalents) of (*R*,*R*)-TMCDA with respect to NaHMDS in an attempt to coordinate a second molecule of the Lewis base ligand to the donor-free metal centre. High quality crystals (39% crystalline yield) were obtained by storing the resultant solution at −33 °C for 24 h, which were analysed by X-ray crystallography and were pleasingly found to be the target bis(solvated) derivative $[\{\kappa^2\text{-}(R,R)\text{-TMCDA}\}\cdot(NaHMDS)_2\{\kappa^1\text{-}(R,R)\text{-TMCDA}\}]$ **2** (Fig. 3). The distorted tetrahedral coordination sphere of Na1 in **2** (bond angles around Na1 range from 66.90(6) to 151.05(8), see ESI†) is essentially identical to that found in **1**, exhibiting additional long contacts with a methyl group from each HMDS amido ligand [Na1···C27 2.968(3) and Na···C24 2.976(3) Å]. However, the second sodium metal centre, Na2, is additionally coordinated to an extra molecule of (*R*,*R*)-TMCDA, giving rise to a distorted trigonal planar geometry. As such there are two distinct coordinated diamine ligands within the structure of **2**. Undoubtedly, the most eye-catching feature is that one (*R*,*R*)-TMCDA ligand adopts a previously unseen κ^1-coordination mode. To change from a κ^2- to a κ^1-coordination mode, it appears that inversion of the N1 atom of the (*R*,*R*)-TMCDA has occurred, no longer allowing the ligand to chelate to Na2 (Fig. 3).

Complex **2** is a discrete dimeric entity, despite the potential availability for N2 to coordinate further. In theory, this could be

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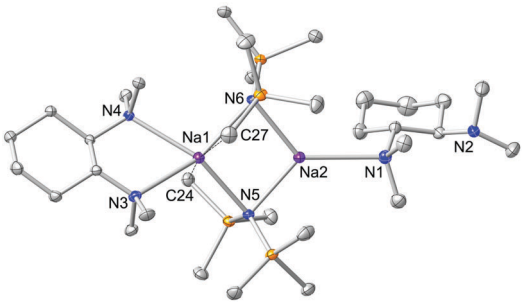

Fig. 3 Molecular structure of [{κ²-(*R*,*R*)-TMCDA}·(NaHMDS)₂{κ¹-(*R*,*R*)-TMCDA}] **2**. Hydrogen atoms and one disordered component of the mono-dentate (*R*,*R*)-TMCDA ligand are omitted for simplicity. Thermal ellipsoids are displayed at 35% probability.

achieved if this N atom could also invert thus allowing an additional *exo*-coordination site; however, it is unlikely that this would occur due to high steric strain (buttressing).[14] The κ^1-coordinated (*R*,*R*)-TMCDA is disordered over two domains, but its atomic connectivity and geometry are unequivocal. The κ^2- and the hitherto unseen κ^1-coordination mode (*R*,*R*)-TMCDA observed in **2** can be compared with DFT calculations (at the B3P86/6-311+G* level) performed for its diamine relative (−)-sparteine (Fig. 4).[24] It has been shown that when (−)-sparteine binds to a metal complex, it always adopts a chelating '*cis*' configuration. However, in the absence of a metal complex, it is actually slightly more stable (by 3.4 kcal mol^{-1}) in a ring-flipped '*trans*' configuration [akin to our κ^1-coordinated (*R*,*R*)-TMCDA] where the lone pairs of electron present on the N atoms are not adjacent to each other. We have performed similar DFT studies (ESI†) on (*R*,*R*)-TMCDA and have shown that there is negligible difference (less than 1 kcal mol^{-1}) between the potentially κ^1- and κ^2-coordination modes.

As **1** and **2** are both highly soluble in non-polar hydrocarbon and arene solutions, solutions of these compounds were studied by NMR spectroscopy. Using ^{1}H NMR spectroscopy, it was evident that the expected 1:2 and 2:2 (*R*,*R*)-TMCDA:HMDS ratios were observed respectively. For **1**, a single amido resonance (at δ 0.25) was observed and the (*R*,*R*)-TMCDA resonances (at δ 2.01, 1.90, 1.47 and 0.74) in C_6D_6 solution appeared to correspond to a metallo-coordinated ligand (see ESI† for full details). For **2**, the amido resonance appears at δ 0.31 in the same solvent. If the solid state structure of **2** was to be retained in solution, two unique sets of (*R*,*R*)-TMCDA resonances would be expected. In reality a single set of resonances (at δ 2.06, 1.99, 1.51 and 0.80 in C_6D_6 solution) is observed. This indicates that a single (*R*,*R*)-TMCDA environment exists at 300 K in arene solution, indeed, a variable temperature

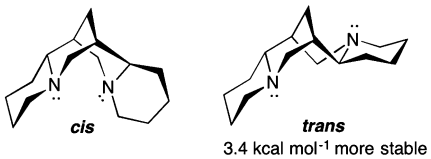

Fig. 4 Relative stabilities of *cis* and *trans* isomers of uncoordinated (−)-sparteine.[24]

NMR spectroscopic study of **2** in [D₈]-toluene solution unveiled that this situation was maintained even at low temperature (down to 206 K, see ESI†). In addition, ^{1}H and ^{13}C NMR spectra obtained in non-polar [D₁₂]-cyclohexane also reveal this situation (see ESI†). Therefore due to the steric bulk of the HMDS ligands within the molecule [thus precluding a dual κ^2-situation for the (*R*,*R*)-TMCDA ligands], it is likely that the spectra show a time-averaged situation between dynamic κ^1- and κ^2-coordinated (*R*,*R*)-TMCDA ligands.

In closing, we have shown that counter to previous studies, (*R*,*R*)-TMCDA can indeed bind to an alkali metal in a non-chelating κ^1-manner.

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