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Monomeric lithium and sodium silylbenzyl complexes: syntheses, structures, and C=O bond olefination†

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Herein we report the syntheses, structures and reactivity studies of two new monomeric alkali metal silylbenzyl complexes stabilised by a tetradentate amine ligand, tris[2-(dimethylamino)ethyl]amine (Me₆Tren). The two complexes, namely [MR'(Me₆Tren)] (R': CH(Ph)(SiMe₃)) (2-Li: M = Li; 2-Na: M = Na), exhibit significant different coordination modes according to their metal identity (Li: σ-coordination; Na: π-coordination). Reactivity studies of 2-Li and 2-Na reveal that they are efficient in promoting a widely-used class of organic functional group interconversion: C=O bond olefination of ketones, aldehydes and amides, to produce tri-substituted internal alkenes.

Organosodium and organolithium complexes play vital roles in synthetic chemistry.^{1,2} Due to the large ionic radii of Li⁺ and Na⁺ and the highly polarised M–C bond (M: Li, Na), these complexes commonly exist as aggregates in solution and solid-state.^{3–7} It has been long perceived that breaking the aggregates into corresponding monomers could enhance their reactivity.³ From a reaction mechanism perspective,³ the organosodium/organolithium monomers are considered as the key intermediates and the gateway to understanding mechanisms of the reactions mediated by these reagents, as the monomers remove the mingled aggregation and multimetallic effects.

For pursuing the enhanced reactivity (usually referring to Brønsted basicity) and understanding the reaction mechanisms, the coordination chemistry community has invested tremendous efforts in synthesising and characterising the organolithium monomers for decades, from sterically bulky alkyls such as LiCH₂SiMe₃^{8–11} and ^tBuLi,^{12,13} to the least bulky and the archetypical MeLi.¹⁴ These research efforts have encompassed the structural features of a number of organolithium monomers, including their essential metal-carbon bond lengths and the bonding characters (e.g., ionicity vs. covalence). Very recently,

this interest expanded into organosodium chemistry, represented by an organosodium monomer ([Na(CH₂SiMe₃)(Me₆Tren)], 1-Na) reported by the Hevia¹⁵ and our¹⁶ groups, simultaneously and independently, in 2023, which exhibited not only enhanced but also unique reactivity.

In comparison with the relatively well-documented synthesis and structural studies, the reactivity of organolithium/organosodium monomers is less studied, and almost all the reported reactivity studies (bar for 1-Na¹⁶) focused on Brønsted basicity (deprotonation) (e.g., ref. 9–11) and the follow-up nucleophilic substitution (such as arylation¹⁵). Recently, we reported a rare non-deprotonation reactivity pattern, where [Na(CH₂SiMe₃)(Me₆Tren)] (1-Na) conducted C=O bond methylenation.¹⁶ This case highlighted the hitherto largely unexplored versatile reactivity scope of the organolithium and organosodium monomers.

To unlock the exciting chemical space, it is essential to expand the alkyl group scope of the organolithium/organosodium monomers. Herein, we introduce silylbenzyl, namely [CH(SiMe₃)Ph][–] (R'), into organolithium/organosodium monomer chemistry (despite that phenyl-substituted silyl benzyls are known in Group-1/2 chemistry^{17–23}), reporting syntheses of the monomers [MR'(Me₆Tren)] (M = Li: 2-Li; M = Na: 2-Na), which exhibit diversified coordination modes between the metal cation and the R' alkyl. Moreover, 2-Li/Na can convert the C=O bond in ketones, aldehydes and amide into C=C(H)(Ph) bond, i.e., conducting the C=O bond olefination. These results are communicated herein.

The target monomers, 2-Li and 2-Na, can be synthesised by treating their corresponding [M(CH₂SiMe₃)(Me₆Tren)] monomer precursors (1-M; M = Li,¹¹ Na¹⁶) (formed *in-situ* by treating [MCH₂SiMe₃]_n with one equivalent of Me₆Tren; See ESI† for more details) with PhCH₂SiMe₃, respectively (Scheme 1). Single crystals suitable for X-ray diffraction studies were grown from their hexane/benzene mixed solutions under –35 °C, and their SCXRD molecular structures are displayed in Fig. 1.

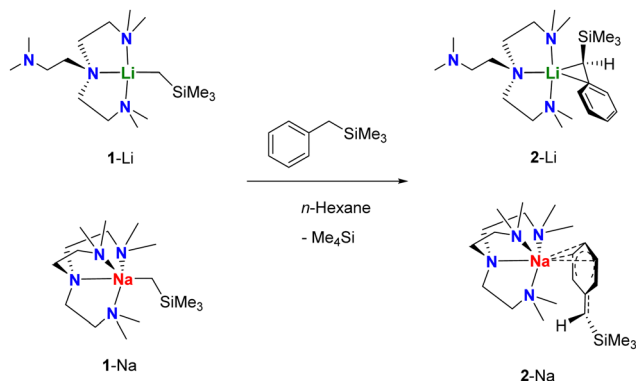
The salient structural feature of 2-Li and 2-Na is their different coordination modes of the silylbenzyl (R') group. In 2-Li, the R' group bonds to Li⁺ mostly through the benzylic

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Scheme 1 Syntheses of lithium and sodium silylbenzyl monomers **2-Li** and **2-Na**.

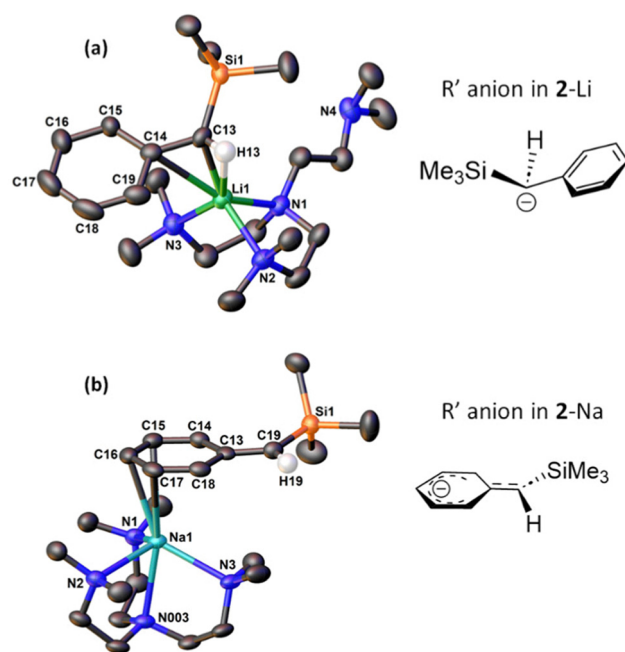


Fig. 1 Single-crystal X-ray diffraction (SCXRD) molecular structures of **2-Li** (a) and **2-Na** (b) measured at 150 K. Protons (except the benzylic protons) and solvent molecules in the lattice are omitted for clarity. Schematic representations of their R' anion are displayed next to the corresponding SCXRD structure. Key bond distances (Å): **2-Li**: Li1–C13 2.219(3); Li1–C14 2.759(3); Li1–N1 2.182(3); Li1–N2 2.197(3); Li1–N3 2.090(3); Li1–H13 2.322(17); C13–C14 1.437(2); C13–H13 0.940(17). **2-Na**: Na1–C15 3.0017(15); Na1–C16 2.8179(15); Na1–C17 2.9066(15); Na1–N1 2.5949(12); Na1–N2 2.5834(12); Na1–N3 2.4849(12); Na1–N003 2.5466(12); C13–C14 1.429(2); C14–C15 1.372(2); C15–C16 1.399(2); C16–C17 1.392(2); C17–C18 1.383(2); C18–C13 1.4469(19); C13–C19 1.4038(19).

carbon atom (C13) via a η^1 -C coordination, with a Li1–C13 bond length of 2.219(3) Å. This is significantly shorter than the Li–C^{benzylic} bond length (2.352(3) Å) in a benzyl lithium monomer [Li(η^1 -CH₂Ph)(Me₆Tren)] reported by Robertson, Mulvey and co-workers.²⁴ We also observed a relatively weak interaction between the *ipso*-carbon (C14) and Li⁺ (Li1–C14 2.759(3) Å). The bond length between the benzylic-carbon

(C13) and *ipso*-carbon (C14) is 1.437(2) Å, indicating a typical C–C single bond. Correspondingly, the geometry of the benzylic carbon C13 is best described as a distorted tetrahedron, with a sum of angles ($\Sigma \{ \angle \text{Si1–C13–C14, C14–C13–H13, H13–C13–Si1} \}$) of 349.5°.

On the other hand, in **2-Na**, the R' group bonds to Na⁺ through three carbon atoms (C15, C16, C17) in the phenyl ring, rendering the coordination mode to be η^3 -C₃. The Na–C bond lengths are relatively short (2.8 to 3.0 Å): they are at least 0.2 Å shorter than the Na–C^{*ipso*} distance (3.183(1) Å) in Robertson/Mulvey's benzyl sodium monomer [Na(η^2 -CH₂Ph)(Me₆Tren)],²⁴ where the Na–C^{*ipso*} interaction was reported to be pronounced. Hence, we conclude here that, in **2-Na**, the R' silylbenzyl group coordinates to Na⁺ through three strong Na–C^{Ph} bonds. It is intriguing to investigate more structural details of the R' group in **2-Na**. The C–C bond lengths in the phenyl ring exhibit a relatively wide distribution, and divide into two groups: one group is close to the expected value for delocalised arenes (~1.39 Å, C14–C15; C15–C16; C16–C17; C17–C18), while the other group features significantly longer carbon-carbon bonds (1.43–1.44 Å, C13–C14; C18–C13). Meanwhile, the C^{*ipso*}–C^{benzylic} bond length (C13–C19 1.4038(19) Å) is in the C=C double bond regime, and the C^{benzylic} (C19) features an alkene-type planar geometry ($\Sigma \Delta = 360^\circ$).

It is well known that different alkali metal cations prefer different σ - or π -coordination modes. The σ - or π -affinities are best demonstrated in benzyl or substituted benzyl complexes, since the anions offer both σ - (the benzylic carbon) and π - (phenyl) sites. In general, the light alkali metal cations Li⁺ and Na⁺ are more likely to adopt the σ -coordination mode, *i.e.*, the metal cation coordinates to the benzylic carbon, possibly accompanied by weak interaction(s) with the *ipso*-carbon. On the other hand, heavier alkali metal cations (K⁺, Rb⁺, Cs⁺) are more likely to adopt the π -coordination mode, *i.e.*, the metal cation coordinates to the phenyl ring. The trend can be clearly seen in the 2011 systematic study of alkali metal benzyl complexes²⁴ by Mulvey, Robertson and co-workers, and a 2022 follow-up from the same groups, expanding the anion scope into relevant ditopic arylmethyl anions such as diphenyl methyl and fluorenyl.²⁵ In comparison with the generally similar Li⁺/Na⁺ coordination mode in literature (especially compared with the Robertson/Mulvey's [Li/Na(CH₂Ph)(Me₆Tren)] monomers²⁴), in **2-Li** and **2-Na** the Li⁺ and Na⁺ exhibit entirely different coordination modes, which we attribute to the increased steric congestion of the silyl benzyl R' compared with benzyl. It should be noted that the σ - or π -preference trend of alkali metal cations is not rigid and there are exceptions where Li⁺/Na⁺ adopt π -coordination mode (*e.g.*, with fluorenyl²⁵) and K⁺/Rb⁺/Cs⁺ adopt σ -coordination mode (*e.g.*, with -NMe₂ substituted silyl benzyl¹⁸), usually caused by overriding electronic (*e.g.*, for the fluorenyl) or steric (*e.g.*, for the -NMe₂ substituted silyl benzyl) factors.

From a reactivity perspective, converting C=O bond into C=C bond, *i.e.*, carbonyl olefination, is an essential class of organic functional group interconversions.²⁶ The popular olefination methods include Wittig,²⁷ Tebbe,²⁸ Julia²⁹/Julia-Kociencki,³⁰ Peterson³¹ and so on. All these methods require hazardous/











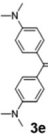
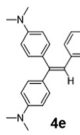
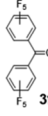
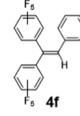












expensive reagents (*e.g.*, phosphorus ylide for Wittig, sulfones for Julia, titanium for Tebbe, cerium for modified Peterson) and/or conditions (*e.g.*, strong acids/bases for Peterson/modified Peterson).

We recently reported that the $-\text{SiMe}_3$ group in **1-Na** can serve as the leaving group, enabling the $\text{NaCH}_2\text{SiMe}_3$ to act as a $[\text{CH}_2]$ feedstock for $\text{C}=\text{O}$ bond methylenation.¹⁶ We are intrigued to expand this methodology to internal alkenes, utilising **2-Li/Na** as $[\text{CHPh}]$ feedstock, realising $\text{C}=\text{O}$ bond olefination to produce internal alkenes. Moreover, most traditional olefination methods perform less well for sterically congested substrates (especially for Wittig reagents due to their four-membered ring transition state). Since we observed a preference of the steric-bulky substrates in our previous methylenation work,¹⁶ expanding the methodology into constructing sterically congested internal alkenes would be attractive.

1 : 1 Reactions between **2-Li/Na** and nine ketones/aldehydes/amides (**3a–i**) were studied, and the results are summarised in Table 1. In eight out of the nine cases, **2-Li/Na** promoted smooth olefinations under mild conditions. Unlike our previous methylenation report,¹⁶ we do not observe different reaction patterns between **2-Li** and **2-Na**, despite their structural distinction. We attribute the same reaction pattern of **2-Li** and **2-Na** to their increased steric congestion compared with the $-\text{CH}_2\text{SiMe}_3$ (**R**) counterparts **1-Li/Na**.¹⁶ In the previous report,¹⁶ DFT reaction pathway calculations suggested that the key step, *i.e.*, intramolecular $-\text{SiMe}_3$ elimination, prefers sterically bulky environment. The bulky $\text{CH}(\text{Ph})\text{SiMe}_3$ (**R'**) group would likely facilitate the key $-\text{SiMe}_3$ elimination step to a level that both Li and Na's kinetic barriers are low enough for the olefination to proceed.

Table 1 **2-Li/Na** promoted $\text{C}=\text{O}$ bond olefinations

				
Olefination product(s)		Conditions	2-Li Conversion (%); <i>E/Z</i> ratio	2-Na Conversion (%); <i>E/Z</i> ratio
 3a	 4a	60 °C 2 hours	> 95%	> 95%
 3b	 E-4b  Z-4b	R. T. 30 min	> 95% 2 : 3	> 95% 1 : 1
 3c	 4c	RT 30 min	> 95%	> 95%
 3d	 E-4d  Z-4d	RT 30 min	> 95% 2 : 3	> 95% 1 : 1
 3e	 4e	RT 20 hours	> 95%	> 95%
 3f	 4f	RT 30 min	Intractable mixture	Intractable mixture
 3g	 E-4g  Z-4g	RT 30 min	> 95% 3 : 2	> 95% 1 : 1
 3h	 E-4h  Z-4h	60 °C 2 hours	> 95% 1 : 2	> 95% 1 : 3
 3i	 E-4i  Z-4i	RT 30 min	> 95% 2 : 3	> 95% 2 : 3



As a preliminary Communication, we do not aim to cover a comprehensive substrate scope here. Nevertheless, 2-Li/Na perform well with a range of ketones, aldehydes and an amide (Table 1). *tri*-Substituted internal alkenes, such as **4a-i**, are challenging targets for traditional olefination methods such as Wittig²⁷ and Julia-Kociński^{29,30} reagents, which prefer steric less bulky substrates. In contrast, 2-Li/Na promote olefinations of these steric bulky substrates with high conversions under mild conditions, providing a valuable route to synthesise the *tri*-substituted internal alkenes. Interestingly, mild *E/Z* selectivity was observed for **4b**, **4g**, **4h** and **4i**, which implies an interesting possibility of using chiral ligands to manipulate the selectivity.

In conclusion, we reported the syntheses and characterisations of lithium and sodium silylbenzyl monomers 2-Li and 2-Na, revealing their pronounced structural differences regarding the coordination modes of the silylbenzyl (R') group. While Li⁺ coordinates to R' via an unsurprising σ -interaction, Na⁺ behaves unexpectedly and adopts an entire π -coordination. Reactivity studies of 2-Li/Na towards organic carbonyl substrates demonstrate their capabilities to deliver olefinations, converting the C=O bond into *tri*-substituted internal alkenes. The olefination reactivity complements our previous report on NaCH₂SiMe₃-mediated ketone/aldehyde methylenation and provides a less hazardous alternative for the traditional olefination reagents such as Wittig, Tebbe, Julia/Julia-Kociński, Peterson and so on.

This work demonstrates the immense potential of Group-1 metal organometallic chemistry beyond the well-perceived deprotonation/nucleophilic/metal-exchange reactivity scope. Further work is underway in our group, focusing on exploiting the olefination reactivity and our recently reported ligand catalysis strategy,¹⁶ aiming at realising organo-alkali metal-mediated *E/Z* selective olefination catalysed by feasible chiral amine ligands.

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Conflicts of interest

The authors declare no conflict of interest.

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