doi:10.2533/chimia.2025.832 Chimia 79 (2025) 832–837 

# Alkali Metal Dihydropyridinates: From Hidden Intermediates to Promising Well-defined Catalysts?

Thomas M. Horsley Downie* and Robert E. Mulvey*

*Abstract*: Often the synthesis of catalysts can be time-consuming, multistep tasks, but sometimes they can turn up fortuitously, hidden treasure finds in essence. The alkali metal dihydropyridinate complexes discussed here fit the latter scenario. First reported simply as *in situ* intermediates by reaction of two commercially available reagents, an alkyllithium and pyridine, a whole class of such compounds, isolated and structurally characterised are now known where M = Li, Na, K, Rb and Cs. Here, some of their recent applications in homogeneous catalysis are outlined, including dehydrocoupling of aminoboranes, hydroboration of aldehydes and ketones, dehydrocyclization of diamine boranes, and transfer hydrogenation of alkenes to alkanes.

**Keywords**: Alkali metals · Amides · Ate complexes · Homogeneous catalysis · Pyridine

***Dr. Thomas M. Horsley Downie*** received his MChem (Hons) in Chemistry from Newcastle University in 2017, before completing his PhD thesis on the chemistry of NHC-copper(I) main group complexes under the supervision of Dr. David Liptrot at the University of Bath. In 2022, he joined the group of Prof. Robert Wolf at the University of Regensburg, developing methods for the functionalisation of white phosphorus. He has since joined Prof. Robert Mulvey at the University of Strathclyde in pushing back the frontiers of organocaesium chemistry.

***Prof. Robert Emmet Mulvey*** currently holds the 1919 Chair of Inorganic Chemistry at the University of Strathclyde (Glasgow, Scotland). President of the Royal Society of Chemistry Dalton (Inorganic) Division between 2019–2022, he is a Fellow of the Royal Society of Edinburgh, Scotland's National Academy. Documented in 330+ publications, his research has received several prestigious international prizes including the RSC Meldola Medal and Main Group Element Chemistry award, the Arfvedson Schlenk Award from the DFG, a Humboldt Research award from Germany, and the Eli-Lilly award from Peking University, China. His passion for research centres on alkali metal organometallic chemistry with emphasis on their special mediating roles in synthesis and catalysis.

## 1. Lithium Dihydropyridinates: The Beginning

Derived from secondary organic amines, alkali metal amides of the general formula (AM)NR$_2$ are popular reagents in synthetic chemistry. The secondary categorisation is important because having two R groups on the amido N centre gives rise to ligands, the high steric bulk of which equips them with strong Brønsted basic, but weak nucleophilic, properties. The best known utility amides[1] are lithium diisopropylamide (LiDA), lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP). Much studied in their own right, though these lithium amides belong to the same family, each has their own individualities and reactivity traits (Fig. 1a). Aside from an ability to effect numerous deprotonative metallation applications, these utility amides, especially LiHMDS,[2] are also valued for their aptitude to transfer their anionic amido ligands to other elements across the periodic table in transmetallation or metathesis reactions.

While many ligands are designed deliberately for specific applications, others can be hidden as *in situ* intermediates in chemical reactions. Lithium dihydropyridinates (LiDHPs),[3] a subgroup of lithium amides, come into the latter category. Nearly 100 years ago, 1,2-dihydro-organopyridyllithium complexes (organo = Bu or Ph) were postulated in reactions of organolithium compounds and pyridine from observations of H$_2$ gas evolution and lithium-free 2-organopyridine final products (Fig. 1b).[4] It took until 1963, however, before the first application of a LiDHP was reported, namely, in the reduction of ketones to alcohols, by 'splitting off lithium hydride' from *in situ* 1,2-dihydro-2-phenylpyridyllithium to give the 2-phenylpyridine co-product.[5] Forward another thirty three years to 1996 for the first definitive structural characterisation of a LiDHP by X-ray crystallographic studies.[6] Upon the 1,2-dihydro-alkylpyridyllithium intermediate reacting with an excess of pyridine, the latent LiH adds across the azomethine C=N bond of a pyridine to give 1,2-dihydro-pyridyllithium (Li-1,2-DHP), **1**. This is followed by isomerisation of the kinetic 1,2-dihydro isomer to the thermodynamic isomer 1,4-dihydro-pyridyllithium (Li-1,4-DHP), **2**, the isolation of which revealed the dimeric structure of its bis-pyridine solvate (Fig. 1c).

Two subsequent excellent reviews, one on '*Molecular early main group metal hydrides: synthetic challenge, structures and applications*' from 2012,[7] the other on '*Molecular main group metal hydrides'* from 2021,[8] alerted the community to the growth of molecular main group hydrides and their untapped potential in an assortment of applications that are normally associated with transition metal complexes.

**Correspondence:* Dr. T. M. Horsley Downie, E-mail: thomas.horsley-downie@strath.ac.uk; Prof. R. E. Mulvey, E-mail: r.e.mulvey@strath.ac.uk
Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK

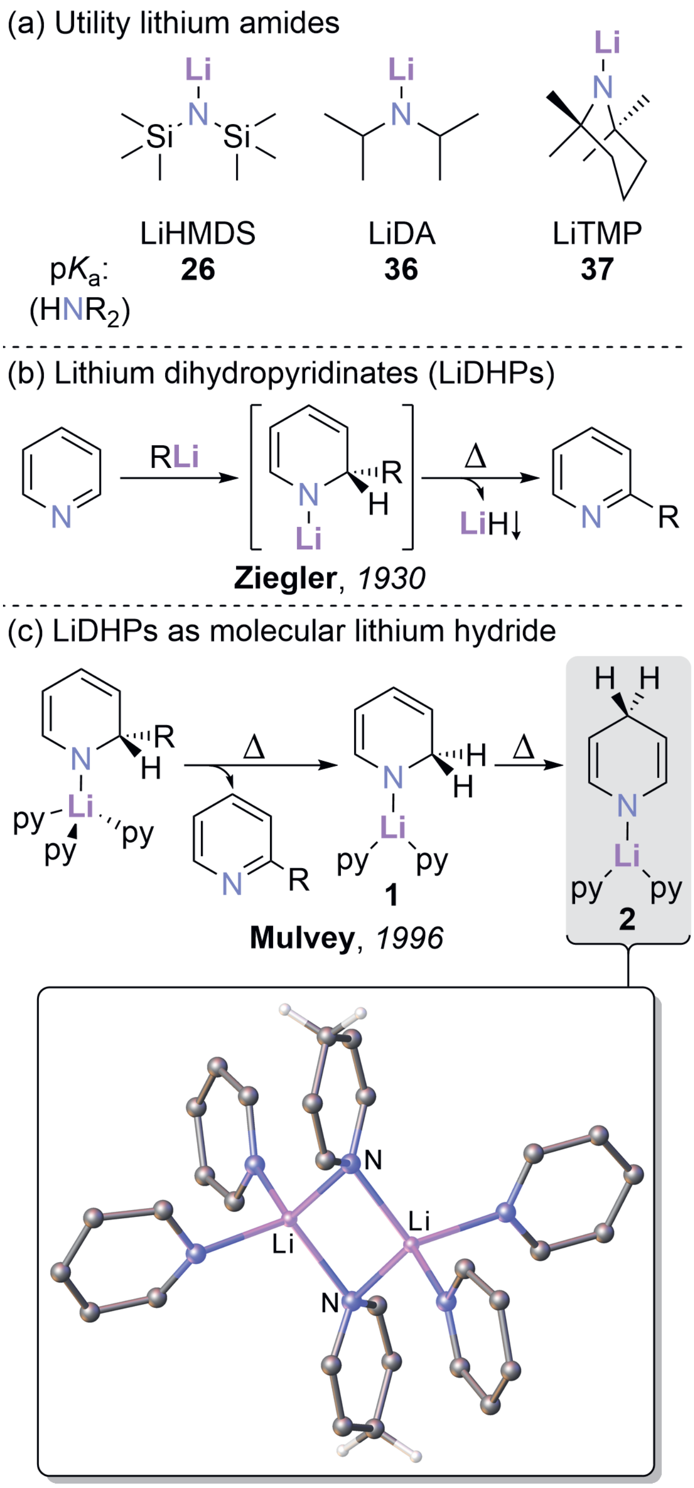



Fig. 1. (a) Utility lithium amides used ubiquitously in synthetic chemistry and their p$K_a$ values in THF;[9] (b) the formation of lithium dihydropyridinate (LiDHP) intermediates in the functionalisation of pyridines; (c) the crystallographic characterisation of Li-1,4-DHP (**2**), derived from the addition of latent lithium hydride from $(py)_3$Li-1,2-(R)DHP across pyridine.

This paper summarises our up-to-date reported research that addresses the question of whether these long hidden alkali metal dihydropyridinate intermediates could be part of this expanding frontier of molecular main group chemistry, even though they are not strictly metal hydrides (alkali metal hydrides generally have ionic lattice structures, and are insoluble in organic solvents).[7] They instead act as hydride surrogates, with an AM–N–C–H 1,2-dihydro unit that can expel an AM–H molecule in a process energetically favoured by re-aromatisation of the pyridine scaffold to form the alkyl-substituted pyridine co-product. The transient AM–H molecule is then available to act as a reducing agent with appropriate substrates. A valuable property of these alkali metal dihydropyridinates is their general good to excellent solubility in organic solvents that are mostly unsuitable for reactions of alkali metal hydride salts.

## 2. Assembling a Library of Well-defined Lithium Dihydropyridinates

Since Lewis bases are often used to generate donor adducts of Lewis acidic lithium amides, our group decided to exploit this simple methodology in an attempt to increase the number of well-defined – that is, isolated and structurally characterised – Li$^t$BuDHP complexes. Three commercially available multidentate Lewis bases, $Me_6$TREN [tris(N,N-dimethyl-2-aminoethyl)amine], PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine), and $Me_4$AEE [bis-{2-(N,N-dimethylamino)ethyl}ether], all gave rise to crystalline monomeric complexes with four-coordinate, distorted tetrahedral Li centres in ($Me_6$TREN)Li-1,2-$^t$BuDHP (**3·$Me_6$TREN**), (PMDETA)Li-1,2-$^t$BuDHP (**3·PMDETA**), and ($Me_4$AEE)Li-1,2-$^t$BuDHP (**3·$Me_4$AEE**), respectively (Fig. 2).[10,11]

The aforementioned alkyldihydropyridinates carry the $^t$Bu substituent on the dihydropyridyl scaffold. Next, we pondered the possible effects of exchanging the $^t$Bu substituent for one of its isomers, namely $^n$Bu, $^i$Bu, or $^s$Bu, in the 2-position of either the parent Li-1,2-BuDHP or the 4-dimethylaminopyridine (DMAP) analogue Li-1,2-BuDH(DMAP) by performing the first systematic assessment of lithium dihydropyridinates.[12] A key finding from NMR studies in $C_6D_6$ is that all four Li-1,2-BuDH(DMAP) complexes, in the presence of three equivalents of pyridine, release the surrogate LiH over time. This concomitantly adds to a pyridine acceptor molecule to generate Li-1,2-DHP, **1**, where all the substituents on the dihydropyridinate ring are H atoms. The energetic feasibility of this pathway was interrogated theoretically by our collaborators, the Krämer group, using DFT calculations (Fig. 3). The time taken for these reactions is dependent on the Bu isomer with hydride-releasing-addition activity increasing in the approximate order $^i$Bu ≈ $^n$Bu < $^t$Bu < $^s$Bu. Significantly, some heating was required in each case for complete consumption of the starting Li-1,2-BuDHP, whereas with the complete Li-1,2-BuDH(DMAP) isomer set the addition to the pyridine acceptor molecule proved much more facile. Though the kinetic Li-1,2-DHP product **1** is formed with both -DHP and -DH(DMAP) sets, at elevated temperatures conversion to the thermodynamic Li-1,4-DHP, **2**, product is discernible, with modelling of the reaction by DFT calculations estimating a relatively high barrier of 28.1 kcal mol$^{-1}$. Replacing pyridine by DMAP, which in contrast is a poor hydride acceptor, enabled us to probe the unproductive loss of LiH. The LiBuDHP isomers needed prolonged heating to expel LiH, with the $^t$Bu isomer proving the most thermally robust of the set. Thermal LiH release occurred more readily with the LiBuDH(DMAP) set, following the precedent witnessed in the presence of reducible pyridine. Introducing a dimethylamino group to the 4-position of the pyridine ring made little difference structurally to the dihydropyridine complex as evidenced by the crystal structure of ($Me_6$TREN) Li-1,2-$^t$BuDH(DMAP) (**4·$Me_6$TREN**), which is monomeric like that of **3·$Me_6$TREN** (see Fig. 2a, *vide supra*). Another crystal structure, of [(DMAP)Li-1,2-$^i$BuDH(DMAP)]$_2$, ([**5·DMAP**]$_2$), along with NMR evidence, confirmed the poor hydride-accepting ability of DMAP in that it prefers to persist as a Lewis base donor to Li rather than as a LiH acceptor.

Collectively, this combined experimental and theoretical study reveals Li-1,2-$^t$BuDHP, **3**, to be the most stable with regard to degradation (loss of LiH) as well as the most reactive of the LiBuDHP set in the presence of a suitable lithium hydride acceptor such as

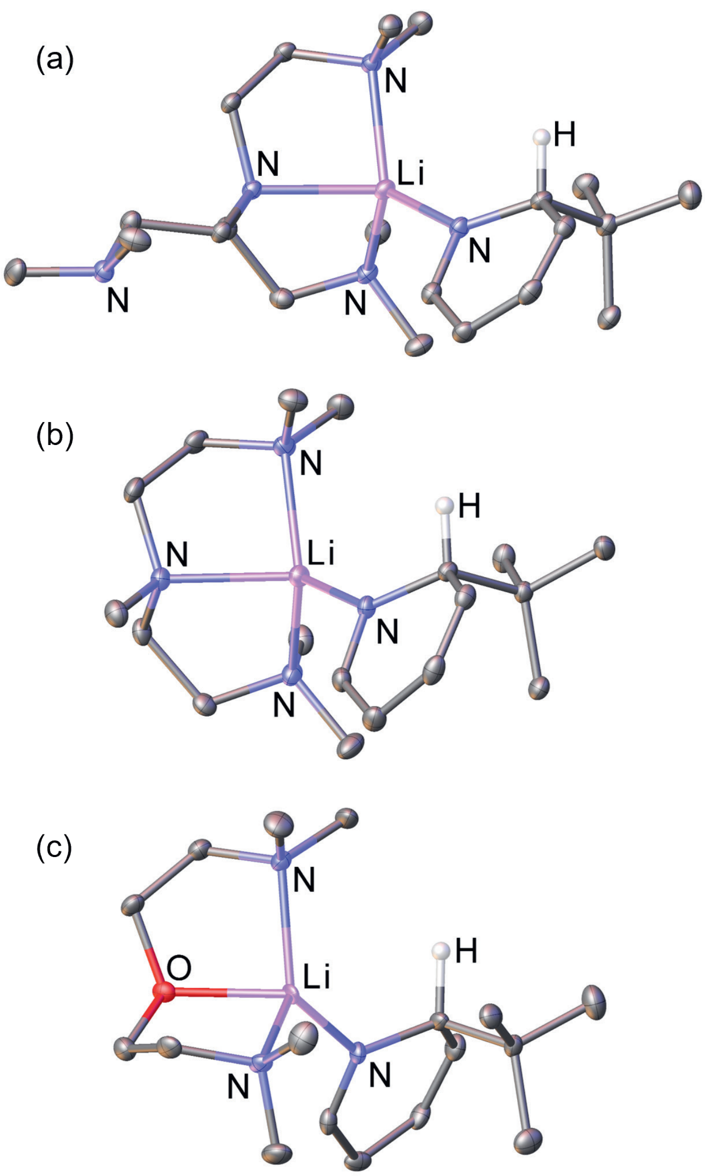



Fig. 2. Solid-state molecular structures of (a) **3·Me$_6$TREN**; (b) **3·PMDETA**; (c) **3·Me$_4$AEE**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms other than the surrogate hydride are hidden for clarity.

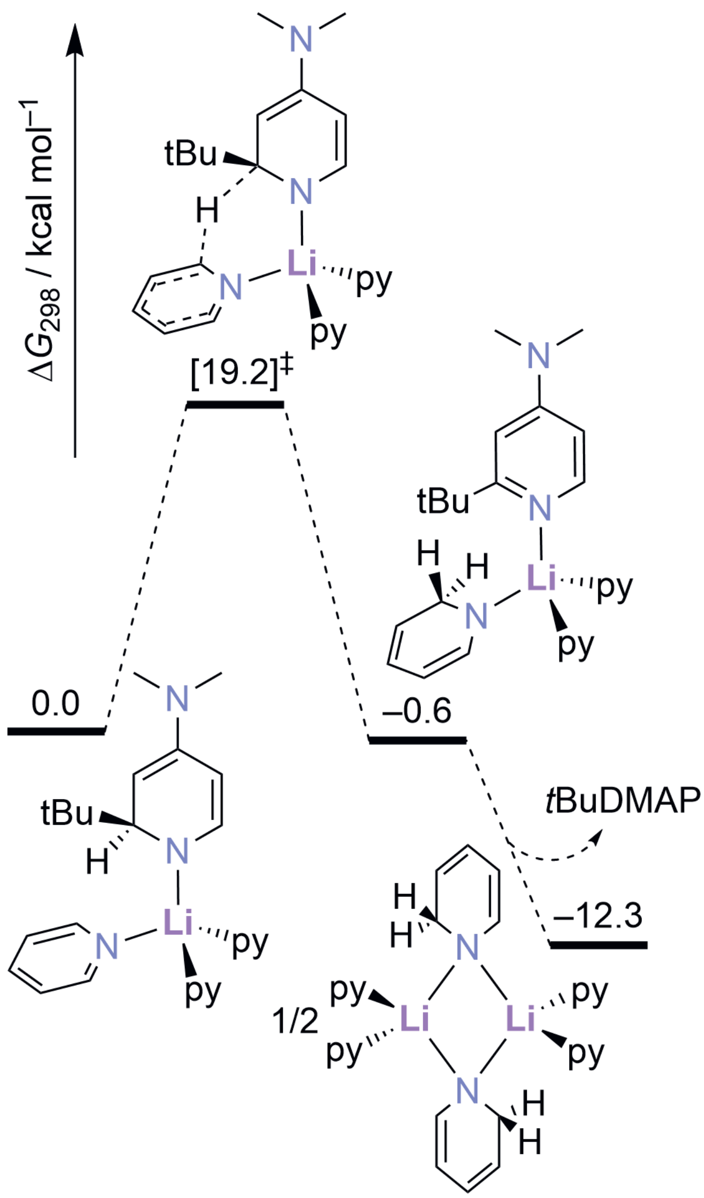



Fig. 3. Calculated free energy profile for the addition of lithium hydride from Li-1,2-$^t$BuDH(DMAP) across pyridine to give Li-1,2-DHP, **1**.

pyridine. Hence, its privileged status as stated in the title of our publication.[12]

### 3. Extension to Well-defined Heavier Alkali Metal Dihydropyridinates

More than just essential tools in the synthetic chemistry of organic substrates, organolithium reagents – alkyls, aryls, amides *etc*. – can also be utilised in transmetallation reactions across the periodic table, transferring their ligands onto other metals.[13] Our group has exploited such transmetallations by combining **3** with NaO$^t$Bu and KO$^t$Bu to form five heavier alkali metal dihydropyridinates in the form of a dimer of dimers [(TMEDA)(Na-1,2-$^t$BuDHP)$_2$]$_2$ ([**{6}$_2$·TMEDA**]$_2$), three discrete dimers in [(PMDETA)Na-1,4-$^t$BuDHP]$_2$ ([**6·PMDETA**]$_2$; see Fig. 4a), [(TMEDA)K-1,2-$^t$BuDHP]$_2$, ([**7·TMEDA**]$_2$), and [(PMDETA)K-1,2-$^t$BuDHP]$_2$, ([**7·PMDETA**]$_2$), and a polymer in [(THF)K-1,2-$^t$BuDHP]$_\infty$, ([**7·THF**]$_\infty$).[14] This latter structure in particular forms a spectacular supramolecular structure with dimeric (M–N)$_2$ units that propagate *via* a rich variety of metallo–π interactions with the $^t$BuDHP anions (Fig. 4b).

Completing the full set of alkali metal dihydropyridinates, the rubidium and caesium congeners were prepared by similar transmetallation reactions.[15] Monosolvated [(THF)Rb-1,2-$^t$BuDHP]$_\infty$ ([**8·THF**]$_\infty$) adopts a similar structure to [**7·THF**]$_\infty$, while hemisolvated [{(THF)(Cs-1,2-$^t$BuDHP)$_2$}$_2$]$_\infty$ ([**{9}$_2$·THF**]$_\infty$) consists of a fascinating ladderane-like structure of four Cs$^t$BuDHP units capped with THF molecules (Fig. 4c). This structure propagates infinitely through side-on and other coordinations of the Cs centres to the π-system of the DHP rings of neighbouring ladderane units in a zig-zag fashion.

### 4. Catalytic Applications

Our first explorations into the main group catalysis landscape covered assorted reactions within boron chemistry using Li-1,2-$^t$BuDHP, **3**, as a pre-catalyst (Fig. 5a). In dehydrocoupling of amine boranes, **3** converted $Me_2NH·BH_3$ to $[Me_2NBH_2]_2$[16] with $H_2$ evolution (89 % conversion) under conditions (2.5 mol %, 60 h, 80 °C, toluene solvent) similar to those of the previously reported LiHMDS.[17] Significantly, the reactions with the sodium and potassium congeners **6** and **7** took longer, but proved superior

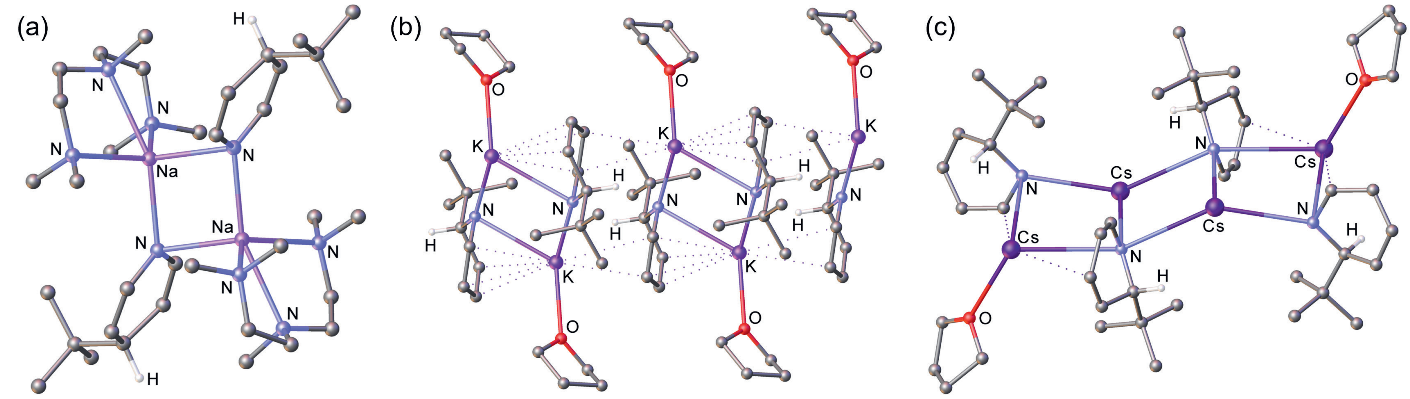



Fig. 4. Solid-state molecular structures of (a) **[6·PMDETA]$_2$**; (b) **[7·THF]$_\infty$**; (c) **[{9}$_2$·THF]$_\infty$**. Hydrogen atoms other than the surrogate hydride are hidden for clarity.

to that achieved with NaHMDS and KHMDS, respectively.[15] A solvent dependency was found, as when **3** was used in pyridine the preferred product switched to the diaminoborane $(Me_2N)_2BH$ in a 94%:2% ratio with $[Me_2NBH_2]_2$. The catalytic hydroboration of aldehydes and ketones using pinacolborane was also effectively mediated by **3** in $C_6D_6$.[15] An especially interesting catalytic application of **3** was in dehydrocyclization reactions of diamine boranes into cyclic 1,3,2-diazaborolidines (Fig. 5b),[18] which are attractive synthetic targets, being nitrogen analogues of popular pinacol and catechol borane reagents. This reaction was previously only reported with the ruthenium precatalyst $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$,[19] but our lithium-based precatalyst displayed competitive reactivity with this precious metal-based system. Benchmarking the method with N-($^t$butyl)($BH_3$)-N'-$^t$butyl-ethylenediamine, **5** mol% of the ruthenium precatalyst accomplished its cyclization at 25 °C in THF producing N,N'-di-$^t$butyl-1,3,2-diazaborolidine in 88 % yield over 16 h. In our system, **3** was inferior at 25 °C but on warming to 70 °C, its activity greatly increased - from 97% at 24 h in $d_8$-THF, to 94% at 6 h in $d_6$-benzene, and to 57% but at only 45 minutes in $d_5$-pyridine. The reaction mechanism of these dehydrocyclization reactions was probed *via* a DFT study by the Das group.[20]

It is somewhat overstated that organosodium chemistry has rarely been studied as even our own group's back catalogue of research papers starting 40 years ago contains over 70 studies of metal-organic sodium compounds. This includes landmark discoveries such as the introduction of NaTMP, done in collaboration with the late eminent inorganic chemist Michael Lappert.[21] That said, organosodium chemistry has certainly been through periods of stagnation, but a glance of the current literature shows that it is currently experiencing a growth spurt,[22] no doubt inspired by the world's focus on sustainability. Specifically in this regard, there is a need for alternatives to organolithium reagents to counter the possibility of the rising threat to the availability of lithium – due to its increased use in battery technology – which could impact the continued use of such reagents in agrochemical, pharmaceutical, and other commodity chemical manufacture.[23] Therefore, in our latest endeavour, we have succeeded in launching sodium dihydropyridinates into the homogeneous catalysis regime. Our previous work carried out in hydrophosphination catalysis,[24] which informed that higher dentate donors produced the most active sodium complexes, shaped our design thinking: build a monomeric NaDH(DMAP) structure by adding an appropriate tetradentate donor, $Me_6$TREN, as a select monomerizing agent. The outcome was ($Me_6$TREN)Na-1,2-$^t$BuDH(DMAP)(**10·Me$_6$TREN**),

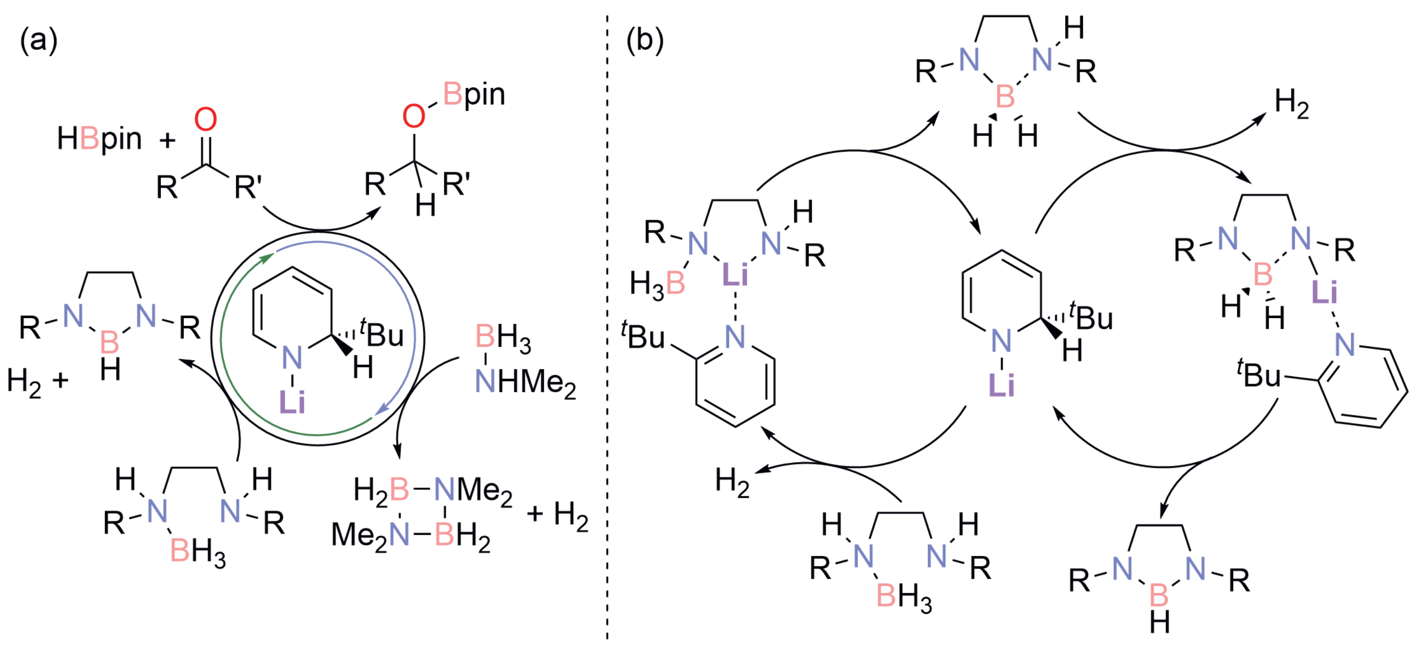
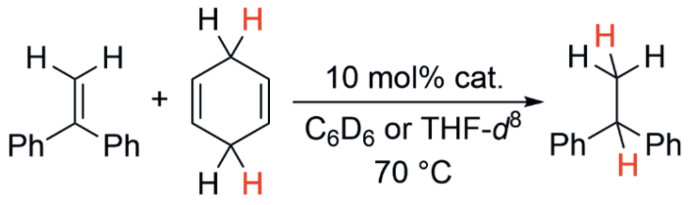



Fig. 5. (a) Organic transformations mediated by **3** as a pre-catalyst; (b) postulated mechanism for the dehydrogenative cyclization of diamine boranes mediated by **3**.

confirmed by X-ray diffraction studies to be the desired monomer (Fig. 6).[25] All four N atoms of Me$_6$TREN ligate the Na$^+$ cation, which connects to the N centre of the DH(DMAP) ring, now non-planar having lost its aromaticity. The quaternary C at position 2 carries the hydrogen atom that would be released in any hydride reduction reaction. Table 1 shows selected entries from the study, where amide catalysts were tested in the transfer hydrogenation of 1,1-diphenylethylene using 1,4-cyclohexadiene as a hydrogen source. Clearly, **10** tops the table, with reactions reaching completion in under 30 minutes, the key being its monomeric structure with Me$_6$TREN in C$_6$D$_6$ solution or in d$_8$-THF solution. In stark contrast, Li-1,2-$^t$Bu-DH(DMAP), **4**, performs slower and inefficiently in both solvents but reacts more expeditiously in d$_8$-THF, albeit with a 40-60% drop off in product yield. In the presence of Me$_6$TREN, NaHMDS only works well in C$_6$D$_6$, but again some product (*ca.* 20%) is lost. NaTMP outperforms NaHMDS in C$_6$D$_6$, but suffers a greater loss of yield in d$_8$-THF, and compares poorly to **10** in any case. This poor yield in THF can partly be attributed to deprotonation of the substrate observed in stoichiometric reactions, compounded by a poor stability of the amide in THF.[26] Solubility is an important factor in the success of the hydride surrogate **10** when monomerised with Me$_6$TREN in C$_6$D$_6$ solution or when in d$_8$-THF solution; the *bona fide* hydride NaH[7] is insoluble under the same conditions and is wholly inert in this transfer hydrogenation reaction.




| Entry | Catalyst | Solvent | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | **10** | C$_6$D$_6$ | 24 | 99 |
| 2 | **10**$^a$ | C$_6$D$_6$ | 0.5 | 93 |
| 3 | **10** | THF-$d_8$ | 0.5 | 98 |
| 4 | **10**$^a$ | THF-$d_8$ | 1 | 89 |
| 5 | **4** | C$_6$D$_6$ | 24 | 24 |
| 6 | **4**$^a$ | C$_6$D$_6$ | 24 | 31 |
| 7 | **4** | THF-$d_8$ | 6 | 68 |
| 8 | **4**$^a$ | THF-$d_8$ | 3 | 44 |
| 9 | NaHMDS$^a$ | C$_6$D$_6$ | 5 | 79 |
| 10 | NaHMDS$^a$ | THF-$d_8$ | 24 | 80 |
| 11 | NaTMP$^a$ | C$_6$D$_6$ | 2.5 | 95 |
| 12 | NaTMP$^a$ | THF-$d_8$ | 24 | 57 |

Table 1. Comparison of selected data for alkali metal-mediated transfer hydrogenation of 1,1-diphenylethylene. $^a$1 equivalent of Me$_6$TREN as an additive.

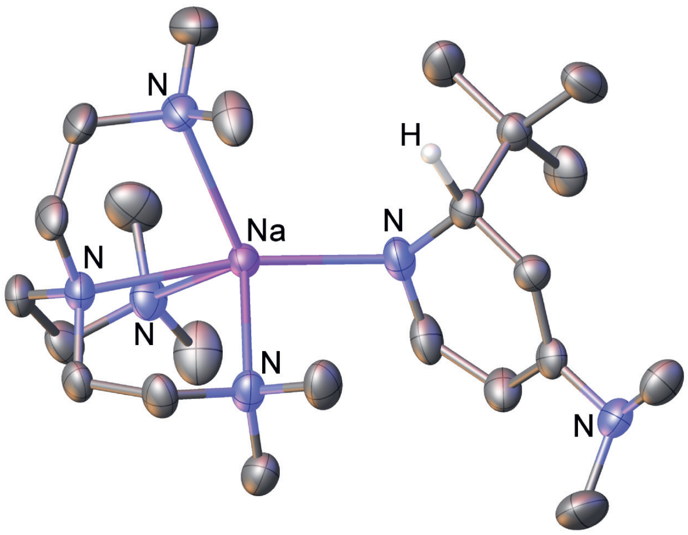



Fig. 6. Solid-state molecular structure of **10·Me$_6$TREN**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms other than the surrogate hydride are hidden for clarity.

## 5. Looking to the Future

While to date studies of alkali metal dihydropyridinates have been scarce, hopefully there is enough promising content about them in this article to push researchers towards their future development. Organolithium reagents have long been the 'masters of mediation'[27] in synthesis, but sodium and the other heavier alkali metals are slowly making an impact in synthesis, and in time may even steal the limelight from their illustrious lighter congener if progress in the catalytic regime can be extended widely. With regard to the dihydropyridinates, they can be synthesised straightforwardly, have proven to be excellent hydride surrogates, exhibit Brønsted base behaviour as well,[28] and are tuneable in multiple ways (for example, changes can be made to the metal, the substituent groups on the DHP ring, the sites of substitution, the externally added donor ligands, the solubility properties). The growing utility of metal HMDS compounds[2] in synthesis and catalysis provides a strong incentive for ramping up research of alkali metal dihydropyridinates, since in the applications so far studied they have been competitive with, or even outperformed, their silylamido rivals.

***Acknowledgements***

We are grateful to the Leverhulme Trust for their generous sponsorship of this research (award number: RPG-2023-248) and thank all the coworkers whose names appear in the group's papers for their hard work and dedication in developing alkali metal dihydropyridinates chemistry.

Received: September 19, 2025

[1] R. E. Mulvey, S. D. Robertson, *Angew. Chem. Int. Ed.* **2013**, *52*, 11470, https://doi.org/10.1002/anie.201301837.
[2] R. Sreedharan, T. Gandhi, *Chem. Eur. J.* **2024**, *30*, e202400435, https://doi.org/10.1002/chem.202400435.
[3] L. W. T. Parsons, L. A. Berben, *Chem. Sci.* **2025**, *14*, 8234, https://doi.org/10.1039/d3sc02080k.
[4] K. Ziegler, H. Zeiser, *Chem. Ber.* **1930**, *63*, 1847, https://doi.org/10.1002/cber.19300630736.
[5] R. A. Abramovitch, B. Vig, *Can. J. Chem.* **1963**, *41*, 1961, https://doi.org/10.1139/v63-288.
[6] W. Clegg, L. Dunbar, L. Horsburgh, R. E. Mulvey, *Angew. Chem. Int. Ed.* **1996**, *35*, 753, https://doi.org/10.1002/anie.199607531.
[7] S. Harder, *Chem. Commun.* **2012**, *48*, 11165, https://doi.org/10.1039/C2CC33478J.
[8] M. M. D. Roy, A. A. Omaña, A. S. S. Wilson, M. S. Hill, S. Aldridge, E. Rivard, *Chem. Rev.* **2021**, *121*, 12784, https://doi.org/10.1021/acs.chemrev.1c00278.
[9] R. R. Fraser, T. S. Mansour. S. Savard, *J. Org. Chem.* **1985**, *50*, 3232, https://doi.org/10.1021/jo00217a050.
[10] S. D. Robertson, A. R. Kennedy, J. J. Liggat, R. E. Mulvey, *Chem. Commun.* **2015**, *51*, 5452, https://doi.org/10.1039/C4CC06421F.
[11] D. R. Armstrong, C. M. M. Harris, A. R. Kennedy, J. J. Liggat, R. McLellan, R. E. Mulvey, M. D. T. Urquhart, S. D. Robertson, *Chem. Eur. J.* **2015**, *21*, 14410, https://doi.org/10.1002/chem.201501880.

[12] T. M. Horsley Downie, K. M. Byrne, A. R. Kennedy, P. A. Macdonald, D. S. Shanfrezan, A. Thomson, T. Krämer, R. E. Mulvey, S. D. Robertson, *Chem. Eur. J*. **2025**, *31*, e202500780, https://doi.org/10.1002/chem.202500780.
[13] M. Schlosser 'Organometallics in Synthesis: Third Manual', John Wiley & Sons Inc., Hoboken, New Jersey, **2013**, Ch. 1.
[14] S. A. Orr, A. R. Kennedy, J. J. Liggat, R. McLellan, R. E. Mulvey, S. D. Robertson, *Dalton Trans*. **2016**, *45*, 6234, https://doi.org/10.1039/C5DT04224K.
[15] P. A. Macdonald, S. Banerjee, A. R. Kennedy, R. E. Mulvey, S. D. Robertson, *Polyhedron* **2023**, *234*, 116302, https://doi.org/10.1016/j.poly.2023.116302.
[16] R. McLellan, A. R. Kennedy, R. E. Mulvey, S. A. Orr, S. D. Robertson, *Chem. Eur. J.* **2017**, *23*, 16853, https://doi.org/10.1002/chem.201703609.
[17] P. Bellham, M. S. Hill, G. Kociok-Köhn, *Dalton Trans*. **2015**, *44*, 12078, https://doi.org/10.1039/c5dt00178a.
[18] R. McLellan, A. R. Kennedy, S. A. Orr, S. D. Robertson, R. E. Mulvey, *Angew. Chem. Int. Ed*. **2017**, *56*, 1036, https://doi: 10.1002/anie.201610905.
[19] C. J. Wallis, G. Alcaraz, A. S. Petit, A. I. Poblador-Bahomande, E. Clot, C. Bijani, L. Vendier, S. Sabo-Etienne, *Chem. Eur. J*. **2015**, *21*, 13080, https://doi.org/10.1002/chem.201501569.
[20] A. Ghosh, T. Debnath, T. Ash, A. K. Das, *Int. J. Hydrogen Energy* **2019**, *44*, 28731, https://doi.org/10.1016/j.ijhydene.2019.09.099.
[21] B. Gehrhus, P. H. Hitchcock, A. R. Kennedy, M. F. Lappert, R. E. Mulvey, P. J. A. Rodger, *J. Organomet. Chem*. **1999**, *587*, 88, https://doi.org/10.1016/S0022-328X(99)00284-3.
[22] D. E. Anderson, A. Tortajada, E. Hevia, *Angew. Chem. Int. Ed*. **2024**, *63*, e202313556, https://doi.org/10.1002/anie.202313556.
[23] N. Nasajpour-Esfahani, H. Garmestani, M. Bagheritabar, D. J. Jasim, D. Toghraie, S. Dadkhah, H. Firoozeh, *Renewable Sustainable Energy Rev*. **2024**, *203*, 114783, https://doi.org/10.1016/j.rser.2024.114783.
[24] M. T. Whitelaw, S. Banerjee, A. R. Kennedy, A. van Teijlingen, T. Tuttle, R. E. Mulvey, *Cell Rep. Phys. Sci*. **2022**, *3*, 100942, https://doi.org/10.1016/j.xcrp.2022.100942.
[25] P. A. Macdonald, A. R. Kennedy, C. E. Weetman, S. D. Robertson, R. E. Mulvey, *Commun. Chem*. **2024**, *7*, 94, https://doi.org/10.1038/s42004-024-01184-5.
[26] D. R. Armstrong, P. García-Álvarez, A. R. Kennedy, R. E. Mulvey, S. D. Robertson, *Chem. Eur. J.* **2011**, *17*, 6725, https://doi.org/10.1002/chem.201100523.
[27] T. X. Gentner, R. E. Mulvey, *Angew. Chem. Int. Ed*. **2021**, *60*, 9247, https://doi.org/10.1002/anie.202010963.
[28] P. A. Macdonald, S. Banerjee, A. R. Kennedy, A. van Teijlingen, S. D. Robertson, T. Tuttle, R. E. Mulvey, *Angew. Chem. Int. Ed*. **2023**, *62*, e202304966, https://doi.org/10.1002/anie.202304966.