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# Synthesis, characterisation, and catalytic application of a soluble molecular carrier of sodium hydride activated by a substituted 4-(dimethylamino)pyridine



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Recently main group compounds have stepped into the territory of precious transition metal compounds with respect to utility in the homogeneous catalysis of fundamentally important organic transformations. Inspired by the need to promote more sustainability in chemistry because of their greater abundance in nature, this change of direction is surprising since main group metals generally do not possess the same breadth of reactivity as precious transition metals. Here, we introduce the dihydropyridylsodium compound, Na-1,2-*t*Bu-DH(DMAP), and its monomeric variant [Na-1,2-*t*Bu-DH(DMAP)]·Me<sub>6</sub>TREN, and demonstrate their effectiveness in transfer hydrogenation catalysis of the representative alkene 1,1-diphenylethylene to the alkane 1,1-diphenylethane using 1,4-cyclohexadiene as hydrogen source [DMAP = 4-dimethylaminopyridine; Me<sub>6</sub>TREN = tris(*N,N*-dimethyl-2-aminoethyl)amine]. Sodium is appealing because of its high abundance in the earth's crust and oceans, but organosodium compounds have been rarely used in homogeneous catalysis. The success of the dihydropyridylsodium compounds can be attributed to their high solubility and reactivity in organic solvents.

Throughout the two decades of the 21st century, main group chemistry has been developing in areas previously considered out of bounds for these elements<sup>1</sup>. Sometimes these developments have been described collectively as a renaissance, but they are probably more accurately described as new beginnings. Following his discovery of a germanium compound<sup>2</sup> able to break the strong covalent bond in H<sub>2</sub>, Power's vision of main group compounds imitating transition metal chemistry<sup>3</sup> was surely epiphanic in this regard. Since then, the number of main group compounds reported as catalysts or co-catalysts in reactions usually carried out by transition metal complexes has grown significantly, especially main group metal hydride compounds<sup>4,5</sup>. In another development the previously barren landscape of low valent aluminium (I) chemistry has been transformed into fertile land<sup>6,7</sup> often realised through alkali metal mediation<sup>8</sup>.

Drilling down the main group chemistry literature, one element that is attracting more recent attention is sodium. Synthetic chemists have rarely considered organosodium compounds as useful chemical reagents, probably because of the success of organolithium reagents that prompted their

commercial availability and the greater challenge in handling their perceived more reactive, but significantly less studied heavier sodium congeners. Motivation for the recent upsurge in the study of organosodium chemistry<sup>9</sup> has been attributed to the World's ever sharpening focus on sustainability, specifically in this case meaning finding a solution to the rising threat to supplies of lithium (and therefore to organolithium compounds that are ubiquitous in fine chemical manufacture) due to the escalating use of lithium in energy technology<sup>10</sup>. Plentiful in the earth's crust and oceans, and the sixth most abundant element overall, sodium, about 1500 times more abundant than lithium<sup>11</sup> is the obvious alternative to make up for any shortfall of lithium in the chemical industry. Therefore, different campaigns are underway to advance the chemistry of sodium organoamides, especially with diisopropylamide (DA), 1,1,3,3-hexamethyldisilazide (HMDS), and 2,2,6,6-tetramethylpiperidide (TMP), the so-called utility amides<sup>12</sup>, which have been so prolifically successful in their lithium form. Highlights include detailed studies of NaDA in synthesis<sup>13</sup>, unravelling solvent-modulated aggregation phenomena of NaHMDS<sup>14</sup> and their influences on reactivity<sup>15</sup>,

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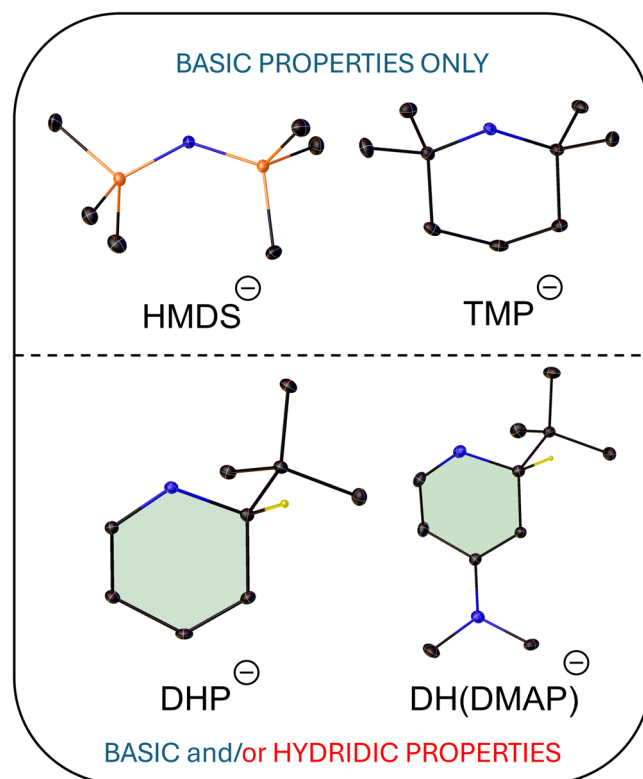
and establishing that NaTMP can catalyse perdeuteration of arenes via hydrogen isotope exchange when activated by *N,N,N',N'',N'''*-penta-methyldiethylenetriamine (PMDETA)<sup>16</sup>. Accessed using sodium dispersions and inexpensive arylchlorides, organosodium compounds have also proved effective transmetalating alternatives to organolithium compounds in transition metal catalysed cross-coupling reactions<sup>17</sup>. Remarkably, onward reactivity of intermediate organosodium compounds has even been achieved in reaction mixtures containing protic substances such as water, glycerol, deep eutectic solvents (DESs) or air, all generally nemeses of polar organometallic compounds<sup>18</sup>. A selection of these and other recent advances has been captured in a mini review<sup>19</sup>.

The original research we report herein intersects two important developmental aspects of organosodium chemistry. First, the necessity to expand the number of monomeric compounds within the area<sup>20,21</sup>, since such small molecular compounds can be highly reactive and second, to provide exemplars for new catalysts in fundamental organic transformations<sup>22</sup>. To meet these objectives, we have focused on establishing unique sodium dihydropyridyl compounds. Alkali metal dihydropyridyl compounds, in which the alkali metal and an anionic ligand such as an alkyl have added across the azomethine C-N bond to break the aromaticity of the N-heterocycle are appealing being simple to prepare, and versatile in their reactivity since they can exhibit both protic and (surrogate) hydridic behaviour<sup>23,24</sup>. Herein, we report the synthesis of Na-1,2-*t*Bu-DH(DMAP), **1** (we use DH(DMAP) as a trivial acronym for dihydro 4-dimethylamino pyridine), its solvated monomeric derivative [Na-1,2-*t*Bu-DH(DMAP)]·Me<sub>6</sub>TREN, **1**·Me<sub>6</sub>TREN and compare their performances with more common sodium reagents in the transfer hydrogenation catalysis of the model alkene 1,1-diphenylethylene using 1,4-cyclohexadiene (see Fig. 1). Unlike saline sodium hydride, which is generally insoluble in organic solvents, a significant limiting factor in its utilisation, **1**·Me<sub>6</sub>TREN possesses good solubility in both arene and ether solvents and so can be regarded as a soluble carrier of a molecular NaH unit, a beneficial factor exploited here in our catalytic studies.

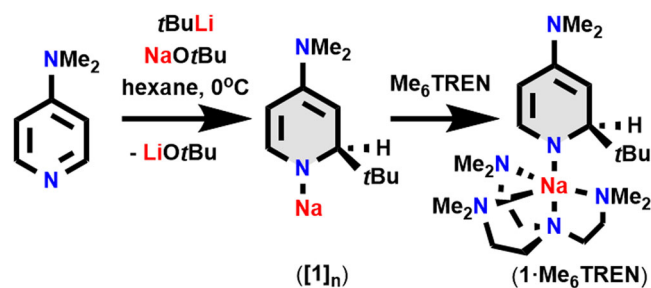
## Results and discussion

Since Davidson and Mahon et al. introduced Me<sub>6</sub>TREN to alkali metal chemistry in 2010 and reported a monomeric sodium complex in the aryloxide ArONa·Me<sub>6</sub>TREN (Ar is 2,6-*t*Bu<sub>2</sub>-4-MeC<sub>6</sub>H<sub>3</sub>)<sup>25</sup> then followed up by us introducing the first Me<sub>6</sub>TREN-complexed alkyl sodium monomers in ArCH<sub>2</sub>Na·Me<sub>6</sub>TREN (Ar is C<sub>6</sub>H<sub>5</sub> or 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sup>26,27</sup>, we decided to stick to this polyamine as the monomerizing agent in this study. Me<sub>6</sub>TREN is also an effective monomerizing agent for other reactive s-block species<sup>28</sup>. For a potential catalytically active sodium complex we selected a modified dihydropyridyl complex. In previous catalytic transfer hydrogenation studies of imines to amines<sup>24</sup> we have shown that 2-*t*BuC<sub>5</sub>H<sub>5</sub>NM, M(*t*BuDHP), complexes (M = alkali metal) can be effective pre-catalysts though results using M = sodium were disappointing in comparison to those of the heavier alkali metals. Therefore in this study we have synthesised [Na-1,2-*t*Bu-DH(DMAP)]·Me<sub>6</sub>TREN, in which a NMe<sub>2</sub> substituent replaces a hydrogen atom at the 4-position of the pyridyl ring, in an attempt to see if this group modified the reactivity. This was indeed prepared by an in situ transmetalation reaction of the lithium 1,2-*t*Bu-DH(DMAP) congener and the bulky alkoxide NaOtBu in hexane solution to yield **1**·Me<sub>6</sub>TREN (Fig. 2) and isolated in an 80% yield as yellow crystals after recrystallisation from hexane/Me<sub>6</sub>TREN. A direct route using *t*BuNa is not viable due to the instability of alkylsodium compounds as previously noted in M(*t*BuDHP) literature<sup>29</sup>.

Monomer **1**·Me<sub>6</sub>TREN has been characterised by solution NMR spectroscopic studies and single crystal X-ray diffraction (SCXRD) studies. Diagnostic of its asymmetric 2-substituted dihydro formulation and loss of aromaticity, resonances appear at 7.23, 4.69, 4.02 and 3.76 ppm in its <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub> solution (see Supplementary Fig. 5 for full details). Estimating the molecular weight of **1**·Me<sub>6</sub>TREN by diffusion ordered spectroscopy (DOSY) NMR studies<sup>30</sup> in C<sub>6</sub>D<sub>6</sub> solution strongly suggests that our target of a monomeric sodium complex has been successfully reached. The error in the DOSY data is low at either 4% or -5% assuming the



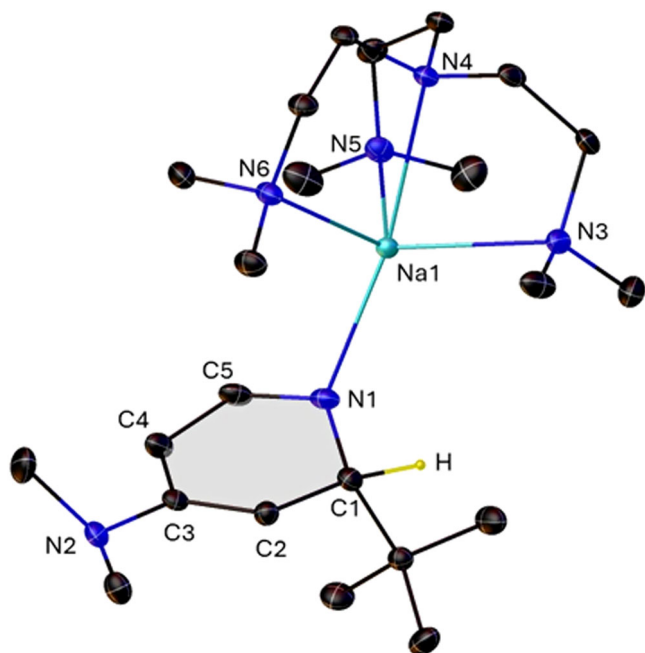
**Fig. 1** | Empirical structures of amides relevant to this catalytic study. Atoms in each molecule are represented by colours as follows: Carbon (black), nitrogen (blue), silicon (orange) hydrogen (yellow). Note the non-planar DHP rings are shaded in grey.



**Fig. 2** | Synthetic protocol to obtain dihydropyridylsodium complexes. Reaction of 4-DMAP with *t*BuLi/NaOtBu in hexane followed by monomerization using Me<sub>6</sub>TREN to yield the desired dihydropyridyl sodium complex.

molecule has a dissipated sphere and ellipsoid shape (DSE) or other shape (see the Supporting Information section 2 - Supplementary Figs. 13–16 and Supplementary Tables 2–9). Isolated as a white solid in a 90% yield, [1]<sub>n</sub>, made in the absence of Me<sub>6</sub>TREN also produced DOSY data consistent with a monomeric species but of formula **1**·(d<sub>8</sub>-THF)<sub>4</sub>, which seems logical from a coordination number perspective given the structure of **1**·Me<sub>6</sub>TREN.

While there are lithium examples in the literature<sup>23,31</sup>, complex **1**·Me<sub>6</sub>TREN represents the first monomeric dihydropyridyl sodium complex to be characterized crystallographically (Fig. 3). The Me<sub>6</sub>TREN ligates sodium via all four Lewis basic nitrogen atoms, consistent with all previously characterized Na/Me<sub>6</sub>TREN complexes<sup>32–34</sup>. The hydrogen atom on C1 could be located and refined, confirming its quaternary sp<sup>3</sup> nature. Bond lengths around the ring are consistent with loss of aromaticity and confirm the conjugated double bond system running through the C<sub>5</sub> unit as is typically the case in such DHP anions. Loss of aromaticity is further confirmed by the non-planar nature of the six-membered ring. The Na1-N1-C3 angle of 130.86(8)° is consistent with an anionic ligand which has the



**Fig. 3 | Molecular structure of 1-Me<sub>6</sub>TREN.** The molecular structure of 1-Me<sub>6</sub>TREN with ellipsoids shown at 50% probability and all hydrogen atoms except that on C1 and minor disordered components of Me<sub>6</sub>TREN ligand removed for clarity. Selected bond lengths and angles: Na1-N1, 2.344(2); Na1-N3, 2.557(2); Na1-N4, 2.564(2); Na1-N5, 2.484(2); Na1-N6, 2.528(2); N1-C1, 1.480(3); C1-C2, 1.513(3); C2-C3, 1.363(3); C3-C4, 1.425(3); C4-C5, 1.382(4); C5-N1, 1.317(4); C3-N2, 1.428(3); C1-N1-C5, 115.5(2); N1-C1-C2, 112.2(2); C1-C2-C3, 122.2(2); C2-C3-C4, 118.3(2); C3-C4-C5, 116.1(2); C4-C5-N1, 129.0(2); C2-C3-N2, 122.1(2); C4-C3-N2, 119.6(2).

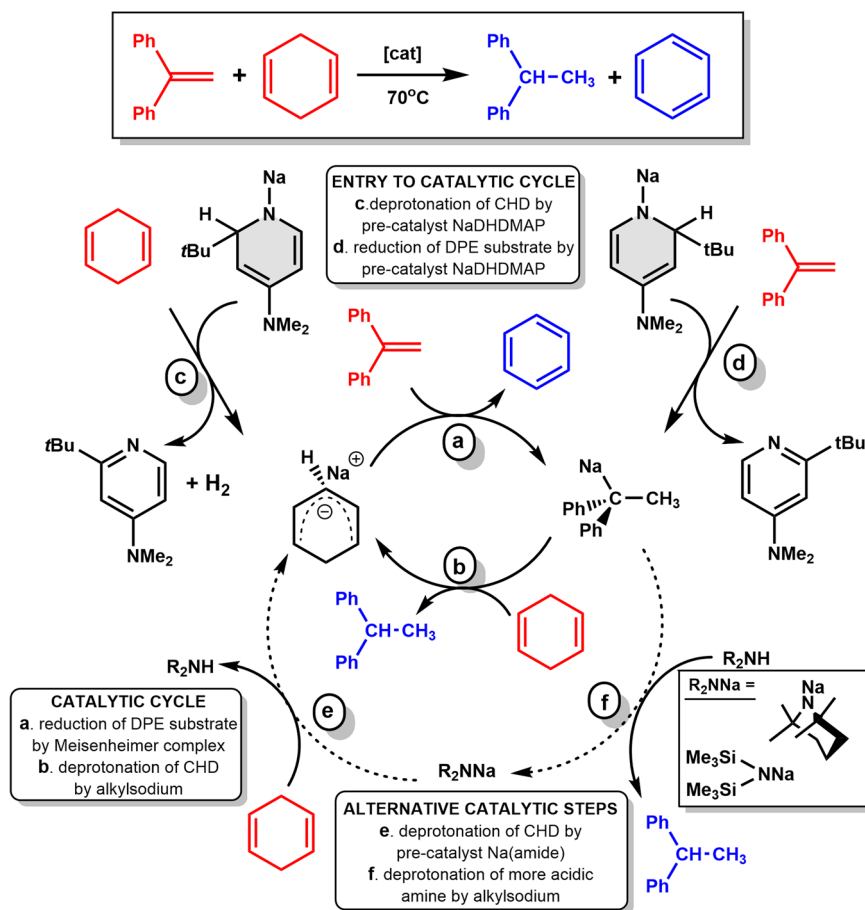
negative charge localized at the ring nitrogen rather than a neutral Lewis donating ring which would be expected to bind linearly. The description of the DH(DMAP) ligand as a secondary amide is further supported by the Na1-N1 bond distance of 2.344(2) Å, which is intermediate between that of monomeric (HMDS)Na-PMDETA [2.285(1) Å; 4-coordinate Na]<sup>35</sup> and Me<sub>6</sub>TREN solvated secondary amides generated via methyl deprotonation of picolines followed by relocalization of the negative charge on to the ring nitrogen [2.391(2) Å, 5-coordinate Na]<sup>36,37</sup>. Loss of aromaticity is further manifested through loss of planarity at the exocyclic NMe<sub>2</sub> group. Neutral DMAP has a planar NMe<sub>2</sub> on account of resonance stabilization experienced through lone pair donation into the ring and is exemplified by the average sum of bond angles in a recently reported [Li-4DMAP]<sup>+</sup> moiety of 359.55°<sup>38</sup>, in 1-Me<sub>6</sub>TREN this value is 342.97°, deviating considerably from trigonal planarity. The crystal structure of unsolvated **1** could not be determined due to its insolubility in non-Lewis-base donor solvents such as hexane. It is likely that this complex adopts a polymeric arrangement as is commonplace in unsolvated sodium amide chemistry. An infinite network made up of ionic Na-N bonds and non-covalent Na-π-DHP interactions, similar to those seen between alkali-metals and an Al-bound DHP ligand<sup>39,40</sup>, is likely.

To test whether monomeric sodium dihydropyridyl 1-Me<sub>6</sub>TREN showed any catalytic activity we chose the conversion of 1,1-diphenylethylene (DPE) to 1,1-diphenylethane as a representative reduction reaction (see inset reaction in Fig. 4). Previous studies<sup>41–43</sup> have established that 1,4-cyclohexadiene (CHD) is a convenient, easily handled liquid transfer hydrogenation reagent so it was employed as the hydrogen source. Alkali-metal-mediated reactions are often solvent dependent with some of the most distinct behaviours found between low-polarity arene and polar ether solvents, therefore C<sub>6</sub>D<sub>6</sub> and d<sub>8</sub>-THF respectively were investigated as the medium in this study with the temperature fixed at 70 °C and catalyst loading at 10 mol%. For **1**, in the absence of Me<sub>6</sub>TREN, the reaction took

24 hours in C<sub>6</sub>D<sub>6</sub> to reach quantitative (99%) conversion as measured by consumption of the alkene substrate 1,1-diphenylethylene with virtually quantitative yield of the product, 1,1-diphenylethane (Table 1, entry 1). However, in d<sub>8</sub>-THF, 99% conversion was accomplished in just 0.5 hours, with essentially no reduction in product yield (entry 3). Solubility is not an issue as **1** is fully soluble at 70 °C in both solvents though its solubility drops in C<sub>6</sub>D<sub>6</sub> at 25 °C. Analogous reactions with monomeric 1-Me<sub>6</sub>TREN reached full conversion in both solvents in less than one hour though there were small reductions of 6% and 10% in product yields (93% and 89%) in C<sub>6</sub>D<sub>6</sub> and THF-d<sub>8</sub> respectively (entries 2 and 4). These results strongly hint that the key factor in catalytic performance is the size of the molecular structure of the catalyst in solution with the aforementioned DOSY studies implicating monomeric structures for both 1-Me<sub>6</sub>TREN in C<sub>6</sub>D<sub>6</sub> (consistent with its solid-state structure) and **1** in d<sub>8</sub>-THF which is likely to be 1-(THF-d<sub>8</sub>)<sub>4</sub>. These values are far superior to their lithium counterparts demonstrating the importance of sodium in this catalysis. In benzene solution, complete conversion is not achieved after 24 h, with yields of only 24 and 31% witnessed in the absence and presence of Me<sub>6</sub>TREN respectively (entries 5 and 6). In THF solution, reactions reach 99% conversion after 6 hours (no Me<sub>6</sub>TREN, entry 7) and 3 hours (with Me<sub>6</sub>TREN, entry 8) but with inferior yields of 68 and 44%.

The next part of our study compared these catalytic performances with those of other related sodium compounds under the same conditions. These comprised NaDHP, [Na-1,2-*t*Bu-DHP], where the 4-substituent has switched from a dimethylamino group in **1** to a hydrogen atom, the aforementioned utility amides NaHMDS and NaTMP, an alkylsodium reagent (*n*BuNa) and the common bench reagent NaH. The most predictable outcome was the failure of the salt NaH (entries 9 and 10) to generate any product at all due to its insolubility in both organic solvents even in the additional presence of a molar equivalent of Me<sub>6</sub>TREN. We note that Chiba recently reduced 1,1-DPE using excess of a NaH/NaI mixture in 87% yield although this required a solvothermal process at 100 °C for one day<sup>44</sup>. Sterically more demanding NaTMP is known to be a stronger more reactive Brønsted base than NaHMDS<sup>12</sup>, which may give it an advantage in any initial deprotonation of cyclohexadiene (see mechanism discussion, *vide infra*) but the comparative data in Table 1, though in the expected order of reactivity, are not significantly different (see Supplementary Information section 3 - Supplementary Figs. 17–36, for all related spectra). In the presence of a molar equivalent of Me<sub>6</sub>TREN each amide performs well in C<sub>6</sub>D<sub>6</sub> with NaTMP having a slight edge in both reaction time and product yield (by 2.5 hours and 16%, respectively, entries 11 and 13), though significantly these reactions are slower than those with 1-Me<sub>6</sub>TREN which are complete within 0.5 hours (entry 2). The performances of NaHMDS and NaTMP fall off sharply in THF-d<sub>8</sub> (entries 12 and 14), taking 24 hours to reach completion (in the case of NaHMDS to only 85%) and a degree of decomposition is apparent with NaTMP reflected by a drop in product yield to 57%. Degradation of reaction mixtures of NaTMP in THF have previously been noted<sup>45</sup> and stoichiometric reaction of NaTMP with DPE shows deprotonative processes occur. NMR spectra show a number of unidentified resonances although some appear to be consistent with formation of 1,1,2-triphenylethane<sup>46</sup> and display no evidence for dimerization products as witnessed previously by Harder<sup>47</sup>. These substantially longer reaction times suggest that the mechanisms in bulk THF-d<sub>8</sub> medium for both NaTMP and NaHMDS with added Me<sub>6</sub>TREN differ substantially from those in C<sub>6</sub>D<sub>6</sub>. No such large solvent-dependent distinction was witnessed with 1-Me<sub>6</sub>TREN, implying that the mechanism/s of its reactions are likely to be similar, though the possibility of different mechanisms due to different aggregations/stabilities of these amides in the solvents employed cannot be ruled out. The strong alkyl base *n*BuNa was also tested, showing similar results to NaTMP. Specifically, conversion was complete within 3 h, with the yield of the desired product dropping from 96% in C<sub>6</sub>D<sub>6</sub> to 50% in THF (entries 15 and 16). Moving to the results for NaDHP, where the Me<sub>2</sub>N group has been removed from the dihydropyridyl ring, the trends observed seem more akin to those of NaDH(DMAP) than to those of the utility amides. Entry 17 bears some resemblance to that of entry 1 since in the

**Fig. 4 | Proposed catalytic mechanism for transfer hydrogenation of 1,1-diphenylethylene with 1,4-cyclohexadiene to yield 1,1-diphenylethane and benzene. All reactants are shown in red and final products are shown in blue.**



**Table 1 | Comparison of data for sodium-catalysed conversion of 1,1-diphenylethylene to 1,1-diphenylethane**

Entry	Catalyst	Equivalents of Me <sub>6</sub> TREN	Solvent	T [°C]	Time [h]	Conversion [%]	Yield [%]
1	NaDH(DMAP)	0	C <sub>6</sub> D <sub>6</sub>	70	24	99	99
2	NaDH(DMAP)	1	C <sub>6</sub> D <sub>6</sub>	70	0.5	99	93
3	NaDH(DMAP)	0	THF-d <sub>8</sub>	70	0.5	99	98
4	NaDH(DMAP)	1	THF-d <sub>8</sub>	70	1	99	89
5	LiDH(DMAP)	0	C <sub>6</sub> D <sub>6</sub>	70	24	30	24
6	LiDH(DMAP)	1	C <sub>6</sub> D <sub>6</sub>	70	24	80	31
7	LiDH(DMAP)	0	THF-d <sub>8</sub>	70	6	99	68
8	LiDH(DMAP)	1	THF-d <sub>8</sub>	70	3	99	44
9	NaH	1	C <sub>6</sub> D <sub>6</sub>	70	24	0	0
10	NaH	1	THF-d <sub>8</sub>	70	24	0	0
11	NaHMDS	1	C <sub>6</sub> D <sub>6</sub>	70	5	95	79
12	NaHMDS	1	THF-d <sub>8</sub>	70	24	85	80
13	NaTMP	1	C <sub>6</sub> D <sub>6</sub>	70	2.5	99	95
14	NaTMP	1	THF-d <sub>8</sub>	70	24	99	57
15	nBuNa	1	C <sub>6</sub> D <sub>6</sub>	70	3	99	96
16	nBuNa	1	THF-d <sub>8</sub>	70	3	99	50
17	NaDHP	0	C <sub>6</sub> D <sub>6</sub>	70	24	50	29
18	NaDHP	1	C <sub>6</sub> D <sub>6</sub>	70	3	99	99
19	NaDHP	0	THF-d <sub>8</sub>	70	3	99	80
20	NaDHP	1	THF-d <sub>8</sub>	70	3	99	81

Reactions all carried out with 10 mol% catalyst loading using 0.3 mmole scale reaction in 0.5 mL using 1.5 equivalents of 1,4-CHD. Conversions were calculated by depletion of 1,1-diphenylethylene (integration versus SiMe<sub>4</sub> standard) while yields were calculated on generation of 1,1-diphenylethane (also integration versus SiMe<sub>4</sub> standard).

absence of any Lewis base donor solvent catalytic reaction time is extended considerably in  $C_6D_6$  though the DH(DMAP) pre-catalyst is superior to its less substituted rival in both conversion (99% vs. 50%) and product yield (99% vs. 29%). On addition of monomerising agent  $Me_6TREN$ , NaDHP improved by orders of magnitude with 99% conversion achieved in only 3 h in both  $C_6D_6$  and THF- $d_8$  with product yields high (99% and 81%, entries 18 and 20), though as seen with NaDH(DMAP) some instability of the reaction solution is seen in bulk THF- $d_8$ . NaDHP also performs well in neat THF- $d_8$  without any  $Me_6TREN$  presence, exactly matching its performance in that donor solvent when an equivalent of  $Me_6TREN$  is present (entry 19). The data collected for NaDHP in entries 18–20, lie in the same ballpark as those for NaDH(DMAP) in entries 2–4, though in every case NaDH(DMAP) is modestly superior with reactions completed in about 1 hour compared to 3 hours in 93–99% compared to 80–99% product yields. A plausible empirical conclusion at this stage could be that NaDHP and NaDH(DMAP) could be operating in a similar way in these catalytic processes and that the relatively small differences between them could be due to the electronic and/or steric influences of the  $Me_2N$  substituent attached to the ring in the latter compound. This is corroborated by preliminary theoretical investigations, wherein comparison of the DHP and DH(DMAP) charge densities reveal minor subtle differences between the two ring systems. CHELPG charges highlight the effect of including an electron donating group, as a slight increase in the negative charge is seen on the nitrogen atom (NaDHP -0.986 vs NaDH(DMAP) -1.068) in line with the expected increase in nucleophilic character (see Supplementary Information section 5—Supplementary Figs. 40–41 and Supplementary Tables 10–13).

The development of catalysts and pre-catalysts for environmentally benign organic transformations including alkene to alkane transformation is a highly active area of research. Most literature catalysts to date feature transition-metal complexes<sup>48–51</sup>, but increasing emphasis is being placed on examples based on main-group elements for the reasons alluded to in the introduction. The specific reduction reaction of 1,1-diphenylethylene to 1,1-diphenylethane investigated here has been studied with several such main group element catalysts, since it is least prone to unwanted side reactions so is a good model alkene<sup>42,47,52–56</sup>. Most relevant to our present study are those based on sodium's nearest heavier congener potassium<sup>57</sup>. Guan found that KH (10 mol% loading) afforded less than 5% product when using direct hydrogenation via  $H_2$  at 6 bar in  $C_6D_6$  for 6 h at 60 °C, but this improved to a quantitative yield on mixing KH with KHMDS or  $M(HMDS)_2$  where  $M = Mg, Ca, \text{ or } Zn$  under the same conditions. We also used a bimetallic approach via the defined compound  $KMg(HMDS)_3$  (10 mol%) achieving quantitative yield in 1.5 hours at 75 °C using transfer hydrogenation from 1,4-cyclohexadiene<sup>8</sup>.

We are therefore able to propose a catalytic cycle, taking the above cited previous literature and our observations into account (Fig. 4). The principal catalytic cycle likely involves reduction of the DPE substrate by the sodium pseudo-Meisenheimer intermediate (step a) which generates 1,1-diphenylethylsodium with concomitant release of benzene. This substituted alkyl sodium can then operate as a Brønsted base in its own right, deprotonating CHD to reform the sodium pseudo-Meisenheimer complex and release the 1,1-diphenylethane product (step b). It is plausible that the variable results discussed above are a consequence of distinct entry points available to the sodium pre-catalysts. Dihydropyridyl complexes have access to two points of entry as they can act as conventional sodium amide bases, deprotonating CHD to generate the intermediate Na pseudo-Meisenheimer complex (path c) or alternatively as a molecular sodium-hydride induced reducing agent for the generation of the alkyl sodium intermediate (path d). Both paths c and d generate rearomatized 2-*t*butyl-4-dimethylaminopyridine, as witnessed in their  $^1H$  NMR spectra (see Supplementary Information section 4 - Supplementary Figs. 37–39). The possibility of **1** acting as a reducing agent is supported by its stoichiometric reaction with the unsaturated substrate, which after 2 hours at 70 °C in  $C_6D_6$  solvent results in essentially complete conversion to 1,1-diphenylethylsodium, as evidenced by generation of a singlet representing the methyl group, at 2.34 ppm. We also probed pathway c stoichiometrically and duly observed evolution of  $H_2$  at 4.55 ppm in the  $^1H$

NMR spectrum after one hour at 70 °C in THF- $d_8$  alongside rearomatization of the pyridine, confirming the viability of this alternative entry point. In contrast, the sodium utility amides can act as bases only, accessing the catalytic cycle by deprotonating CHD to give Na pseudo-Meisenheimer complex with concomitant formation of secondary amine (step e). This then introduces the possibility of this non-volatile by-product being preferentially deprotonated at a later stage by the ethylsodium (step f), forming the reduced organic product whilst reforming the sodium utility amide and introducing an alternative catalytic cycle with an additional step.

## Conclusions

In this research we have synthesised a target sodium amide complex, but a specialised type in that it is a DMAP-substituted dihydropyridyl complexed by the polydentate polyamine  $Me_6TREN$ . As planned for, the reported complex here is a monomer in the solid-state and from DOSY studies appears to retain this state in  $C_6D_6$  solution. The specialness of this sodium amide lies in its twofold reactivity as our observations show that it can act both as a conventional metal amide in performing deprotonating reactions and a molecular hydride source, whereas conventional metal amides only possess the former reactivity. This reactivity of **1- $Me_6TREN$**  has proved useful in the representative reduction reaction of the alkene  $Ph_2C=CH_2$  to the alkane  $Ph_2(H)C-CH_3$ , in which it has outperformed the common utility amides NaHMDS and NaTMP as well as the insoluble, inert sodium hydride which showed no catalytic reactivity at all (although stoichiometric reactivity is possible under extreme conditions). These results underline that with proper development compounds of earth abundant sodium could begin to join the elite compounds of scarce transition metals with regard to their usefulness in homogeneous catalysis of fundamentally important organic transformations. Future work will examine the scope of this reaction with a library of substrates, probe the mechanisms of the catalyses by theoretical calculations, and extend the use of this sodium amide monomer (and other related dihydropyridyl monomers yet to be synthesised) to other industrially important organic reactions.

## Methods

For general experimental procedures see Supplementary Information section 1 - Supplementary Methods, Supplementary Figs. 1–12 and Supplementary Table 1.

### Synthesis of Na-1,2-*t*Bu-DH(DMAP) (**1**)

DMAP (0.366 g, 3 mmol) was added to a Schlenk flask along with hexane (15 ml) and NaOtBu (0.288 g, 3 mmol). The solution mixture was cooled to 0 °C using an ice bath and then *t*BuLi (1.7 M in pentane, 1.76 ml, 3 mmol) was added dropwise via syringe. The resultant cloudy yellow solution was left to stir for 4 hours producing an off-white suspension. The solvent was then removed via cannula filtration and the white solid was dried under reduced pressure. The compound was then transferred into the glove box, weighed and stored at -20 °C in the freezer as a white powder material (0.55 g, 90% yield).

$^1H$  NMR [400.03 MHz, 300 K, THF( $d_8$ ):  $\delta$  0.82 (s, 9H, *t*Bu), 2.54 (s, 6H, NMe<sub>2</sub>), 3.10 (dd, 1H, C1-H), 3.45 (d, 1H, C2-H), 4.06 (dd, 1H, C4-H), 6.80 ppm (d, 1H, C5-H);  $^{13}C$  { $^1H$ } NMR [100.60 MHz, 300 K, THF( $d_8$ ):  $\delta$  152.00 (C5-H), 80.17 (C4-H), 69.59 (C1-H) 68.78 (C2-H), 39.61 (NMe<sub>2</sub>), 39.12 (quaternary [DH(DMAP)]), 24.70 ppm (*t*Bu).

### Synthesis of [Na-1,2-*t*Bu-DH(DMAP)]- $Me_6TREN$ (**1- $Me_6TREN$** )

Na-1,2-*t*Bu-DH(DMAP) (1 mmol, 0.202 g) was added to a vial of hexane (5 ml) in the glovebox.  $Me_6TREN$  (1 mmol, 0.26 ml) was subsequently added, and the suspension was left to stir for 5 minutes. The resultant yellow solution was placed into the freezer at -20 °C. After 24 hours transparent large block crystals had formed which were isolated and stored in the glovebox freezer (0.34 g, 80% crystalline yield).

$^1H$  NMR [400.03 MHz, 300 K,  $C_6D_6$ ):  $\delta$  1.45 (s, 9H, *t*Bu), 2.07 (s, 30H,  $Me_6TREN$ ), 2.95 (s, 6H, NMe<sub>2</sub>), 3.76 (dd, 1H, C1-H), 4.02 (d, 1H, C2-H), 4.70 (dd, 1H, C4-H), 7.23 ppm (d, 1H, C5-H);  $^{13}C$  { $^1H$ } NMR [100.60 MHz,

300 K, C<sub>6</sub>D<sub>6</sub>]:  $\delta$  153.00 (C5-H), 79.85 (C4-H), 71.79 (C1-H), 70.60 (C2-H), 56.60 (CH<sub>2</sub> Me<sub>6</sub>TREN), 50.88 (CH<sub>2</sub> Me<sub>6</sub>TREN), 44.58 (CH<sub>3</sub> Me<sub>6</sub>TREN), 42.68 (NMe<sub>2</sub>), 41.05 (quaternary [DH(DMAP)]), 25.40 ppm (tBu).

### Data availability

The datasets generated during and/or analysed during the current study are available in the PURE repository, <https://doi.org/10.15129/3fb4efe4-1841-4fa0-a326-cd0e3cbc866b>. The X-ray crystallographic coordinates for the structure reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 2327713. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). General experimental procedures, DOSY NMR spectroscopic details, NMR spectra from catalytic and stoichiometric reactions and computational details are provided in Supplementary Information and cif file for complex **1**·Me<sub>6</sub>TREN is available as Supplementary Data file 1.

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## Author contributions

Peter A. Macdonald - practical investigation – writing – construction of supporting information. Alan R. Kennedy – crystallographic data acquisition/curation. Robert E. Mulvey – writing – original draft, conceptualization, supervision, project administration, funding acquisition. Stuart D. Robertson – supervision, writing – review and editing. Catherine E. Weetman – theoretical data acquisition/curation.

## Competing interests

The authors declare no competing interests.

## Additional information

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