The Hydronaphthalide Monoanion: Isolation of the "red transient" Birch Intermediate from liquid Ammonia

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Birch reactions employing alkali metals in ammonia have been a well-established method for the reduction and functionalisation of aromatic compounds for nearly 100 years. Speculations regarding intermediates in the reaction pathway have been discussed since the beginning. We hereby report the isolation of NMe₄(HNaph) (1), a kinetically trapped intermediate of the Birch reaction of naphthalene and sodium in liquid ammonia. 1 has been fully characterised and has been shown to continue to react to 1,2/1,4-dihydronaphthalene – the Birch product of the reduction of naphthalene. The reactivity of 1 was investigated towards activity as an electron and hydride transfer agent with both, elements and small organic molecules. 1 demonstrates a tamed reduction potential which allows for controlled reactions such as the selective formation of hexasulphide and hexaselenide anions.

Introduction

The formation of alicyclic molecules *via* the reduction of aromatic compounds by metals has been widely applied for the functionalisation of benzene as well as of macrocycles.[1] First developed by Wooster and vastly extended by Birch,[2,3] the initial synthetic approach including alkali metals in liquid ammonia has meanwhile been expanded to other amines, various organic solvents, alkali metals in silica-gels, as well as metal-free photocatalytic reductions.[4–8]

The reduction of naphthalene in THF through the reaction with alkali metals was already reported in 1928.[9] Common reaction products resulted from the sodium naphthalene adducts acting as Lewis bases and undergoing nucleophilic reactions with, *e.g.*, proton sources, such as methanol, carbondioxide or chloridotrimethylsilane.[10,11] The active species, the naphthalide radical anion, is stabilised in solution *via* the alkali metal cation and the solvent. The salt of the naphthalide was first isolated and characterised as a solvent-separated solid in 1995.[12]

The addition of sequestering agents prevents the reduction of the alkali metal cation and facilitates the isolation of the salt as a solid.[13] Whilst both lithium and sodium were observed to form the naphthalide radical anion, due to the different reduction potentials of the metals, lithium was found to reduce the aromatic compounds more readily a second time, yielding dianionic reactive intermediates.[9,14,15] The dianion of naphthalene was described as a purple solution, and the salt was isolated as a solvent-stabilised solid in 2009.[14,16]

The observation of the reaction of sodium and naphthalene in liquid ammonia resulting in a red solution was first reported in 1939, contrary to the dark green solutions that are formed in organic ether.[17] Subsequent protonation led to 1,2/1,4-dihydro or 1,2,3,4-tetrahydronaphthalene. A mechanism was first proposed in 1965, suggesting a subsequent series of one-electron reductions and protonations of the naphthalene backbone proceeding through the formation of a carbanion (Scheme 1). The mechanism includes an intermediate described as a "red transient" species which to the best of our knowledge as of yet has never been isolated.[14]

We hereby present the isolation and full characterisation of the red transient Birch intermediate as an organic salt. Performing the reaction in liquid ammonia at low temperatures under strict exclusion of air and moisture next to tetramethylammo-
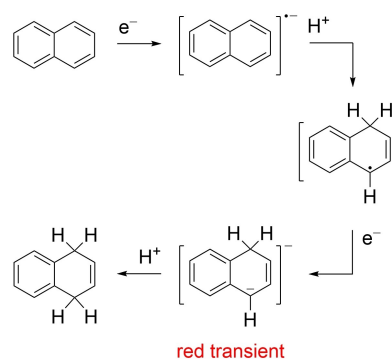
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Scheme 1. Proposed mechanism for the reduction of naphthalene to 1,4-dihydronaphthalene passing through a "red transient" species.[14]

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nium chloride allows us to kinetically trap this intermediate in a reliable pathway and in good yields.

Results and Discussion

Synthesis and Characterisation

The reaction of sodium, tetramethylammonium chloride and naphthalene at −60 °C in liquid ammonia results in a deep red solution and colourless solid. Within seconds, the reaction mixture progresses from dark blue indicating the dissolution of sodium under the formation of an electride solution,[18] over green, suggesting a naphthalide radical anion,[10,19] to an intense red colouring. The reaction mixture is left to stir for an hour to ensure complete conversion. Next to the formation of the soluble NMe$_4$(HNaph) (**1**) (Scheme 2), sodium chloride is eliminated (characterised *via* PXRD, Figure S10), acting as a driving force to the formation of **1**. After evaporation of the ammonia at −60 °C, the solids are extracted and filtered with cold (−60 °C) tetrahydrofuran (THF) in order to remove the sodium chloride, leading to a dark red solution of **1**. The organic salt was characterised by means of single crystal X-ray diffraction (XRD) analysis, UV-visible, NMR and Raman spectroscopy.

1 is soluble in several primary amines, such as ammonia, methylamine and (*iso*−)propylamine, slightly soluble in dimethylether and well soluble in THF, allowing for more facile handling of the compound. When stored at −75 °C, the solid of **1** is stable for >12 months, whilst a solution of **1** in THF starts to decompose within three days (Table 1).
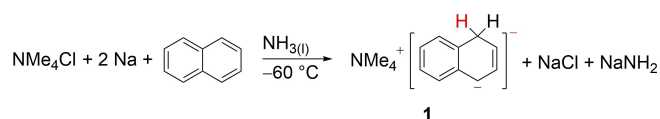
Contaminants such as traces of water, or protic solvents like ammonia are likely to act as the proton source for the naphthalene backbone. While the reaction pathway suggests the basicity of the naphthalide or naphthalene dianion is sufficient to deprotonate ammonia, the hydronaphthalide anion of **1** does not abstract a further proton to form dihydronaphthalene. When adding a more acidic source of protons such as methanol compared to the protophilic ammonia to **1**,[20] the mixture turns colourless instantly. The reaction products were

characterised by means of gas chromatography-mass spectrometry (GC-MS) confirming the expected formation of 1,2- and 1,4-dihydronaphthalene (Figure S8).

Investigating the dominant species in solution, the ^{1}H NMR spectrum of **1** was recorded at −75 °C in liquid ammonia (NH$_3$) under suppression of the ammonia signal. Compared to the planar naphthalene molecule or the radical naphthalide anion, protonation of the aromatic backbone results in a reduction of the symmetry which leads to an increase in the number of resonances for **1** in the ^{1}H NMR spectrum (Figure 1). The signals for the aromatic protons H7–H10 of the planar ring appear between 5.72–4.81 ppm, whereas the loss of planarity in the neighbouring ring causes a highfield shift of the resonances of the other five protons H2–H5. The integral ratios of the signals support the formation of an aliphatic carbon centre, with the resonance at 2.59 ppm being assigned to H2A and H2B. The chemical shifts of all atoms were assigned unambiguously by means of ^{1}H, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H COSY and ^{13}C{^{1}H} NMR spectra (see Supporting Information for more details). The signals of the aromatic protons H7–H10 display ^3J-coupling constants of 7.2–7.8 Hz, which is in the typical range for a fully delocalised aromatic system.[21] The ^3J-coupling constant between H5 and H4 appears to be slightly smaller at 6.8 Hz. The NMR spectra show unreacted naphthalene (2%) with two resonances at 7.22 and 6.83 ppm.

Single crystals suitable for X-ray diffraction (XRD) analysis were obtained from a concentrated reaction mixture in liquid ammonia layered with diethylether and stored at −75 °C for 48 hours. Crystal selection was carried out under a nitrogen atmosphere at −60 °C. The compound crystallises with one molecule of ammonia in the space group $P2_1$ (Figure 2) and four formula units in the unit cell.[22] With exception of the tetramethylammonium cations, hydrogen atoms were assigned from residual electron density and confirm two hydrogen atoms connected to atom C2.

The loss of planarity and thus symmetry through the introduction of a tetrahedrally coordinated carbon centre, which was observed in the solution of **1**, is confirmed in the solid state. The idealised bond angle for a sp^2-hybridised carbon atom is 120°, whereas ideal tetrahedral centres display bond

Scheme 2. Synthesis of **1**.

Figure 1. ^{1}H NMR spectrum of **1** (400 MHz, NH$_3$, −75 °C).

Table 1. Thermal decomposition studies of **1**.

Temperature	Time until decomposition
23 °C	Within minutes[a]
0 °C	~1 hour[a]
−27 °C	<48 hours[a]
−75 °C	>12 months,[a,b] ~3 days[c]

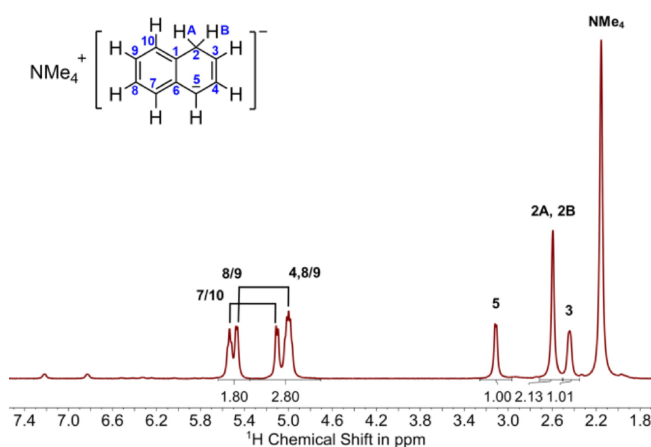[a] In the solid state [b] Reaction mixture in ammonia [c] In THF.

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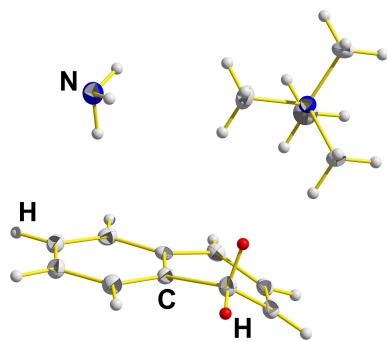European Chemical
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Figure 2. Excerpt of the molecular structure of **1**·NH$_3$ in the solid state. Thermal ellipsoids are shown at 50% probability level.

angles of 109.5°.[23,24] Table 2 shows a comparison of selected bond lengths and angles of **1** determined from the experimental data and from density functional theory (DFT) calculations. All DFT calculations within the scope of this work were performed with Turbomole 7.3[25] using resolution of identity (RI) methods,[26] def2-TZVP basis set,[27] B3-LYP functional,[28,29] and solvent simulation according to the conductor like screening model (COSMO, $\varepsilon = \infty$)[30] level of theory. The experimentally determined H2 A–C2–C3 angle of the molecular structure in the solid state is 108(3)°, which is in good agreement with the expected angle from DFT calculations (110.048°) and confirms a tetrahedrally coordinated carbon atom. The bond lengths span from 1.365(4)–1.519(4) Å, showing a clear distinction between connectivities: Bond lengths of 1.519(4) Å (C1–C2) and 1.510(4) Å (C2–C3) are within the expected range for a carbon-carbon single bond, whereas the bond lengths of 1.365(4) Å (C3–C4), 1.416(4) Å (C4–C5) and 1.425(4) Å (C5–C6) are in line with (conjugated) carbon-carbon double bonds.[31]

Mulliken electron population analysis of **1** was used to calculate the atomic populations from the total electron density and compared to those of the naphthalene dianion.[32,33] With 48.3% of the total charge, C5 in **1** displays the highest charge density (−0.48262, Table S6) indicating a localisation of the negative charge. In comparison, C2 displays a distinctly lower negative charge of −0.05889 compared to −0.47108 as was found for the analogous atom in the naphthalene dianion (Table S6). A comparison of the spatial orientation of the HOMO in **1** and the naphthalene dianion support the localised charge

at C5 in **1** compared to the delocalised electron density in the naphthalene dianion (Figure 3).

The energetic separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) can be applied as an indicator for the chemical reactivity and kinetic stability of a molecule.[34] Examining the HOMO-LUMO gap of naphthalene, the naphthalide ion, the dianion of naphthalene, hydronaphthalene and the hydronaphthalide anion in **1**, can provide insight into the lability of these polycyclic hydrocarbons (Figure 3). Compared to the highly reactive naphthalide radical with the smallest HOMO-LUMO gap and the energetically high-lying HOMO of the naphthalene dianion, the anion of **1** exhibits a large HOMO-LUMO gap of 3.568 eV (Table S7). Additionally, the HOMO of **1** appears to be 1.217 eV lower in energy than that of the naphthalide, which suggests **1** displays a tamed reduction potential compared to that of naphthalide. Whether the reaction pathway to the intermediate of **1** follows subsequent reduction and protonation of naphthalene,[14] or the formation of a dianion which is protonated,[35] cannot be concluded without further investigations.

For deeper understanding of the present system, UV-visible spectra were recorded of different reaction mixtures of alkali metals and naphthalene in THF as well as of **1**. Solutions of **1** at −60 °C were measured without cooling during the measurement restricting measurement time and data resolution (see SI for more information). The UV-visible spectrum of a green solution of sodium and naphthalene added in equal equivalents shows an absorbance maximum at 367 nm and a broad absorbance from 750–850 cm^{-1} (Figure 4) attributed to the naphthalide radical, which is in good agreement with the literature.[14] The addition of two equivalents of lithium to naphthalene in THF lead to the formation of a coloured solution of the dianion of naphthalene, with an absorbance maximum of 428 nm.[14] The intense red colour of **1** resembles that of the
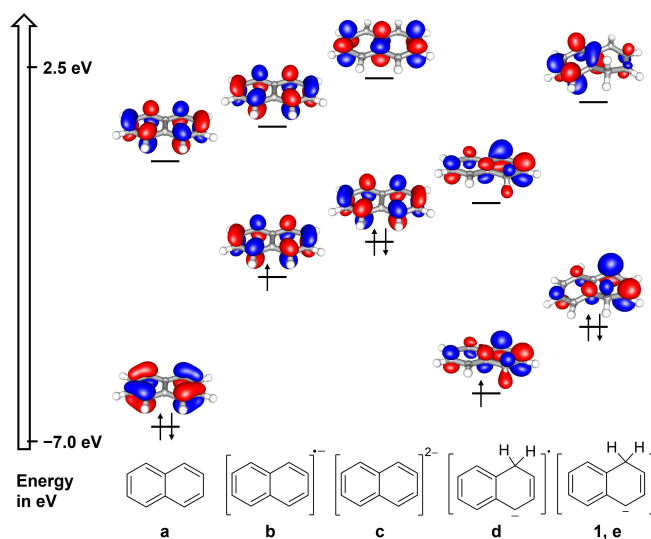
Table 2. Selection of experimentally determined bond lengths and angles (determined *via* DFT calculations) of **1**.[a]

Atoms	Bond Lengths in Å/Angles in °
C1–C2	1.519(4) (1.518)
C2–C3	1.510(4) (1.511)
C3–C4	1.365(4) (1.366)
C4–C5	1.416(4) (1.423)
C5–C6	1.425(4) (1.423)
H2A–C2–C3	108(3) (110.048)

[a] DFT calculations were performed with Turbomole 7.3, def2-TZVP, B3-LYP, COSMO ($\varepsilon = \infty$).

Figure 3. Schematic representation of the frontier orbitals of naphthalene (a), the naphthalide ion (b), the dianion of naphthalene (c), hydronaphthalene (d) and the anion of **1** (e). DFT calculations were performed with Turbomole 7.3, def2-TZVP, B3-LYP, COSMO ($\varepsilon = \infty$), threshold = 0.05 e$^-$/Å^3.

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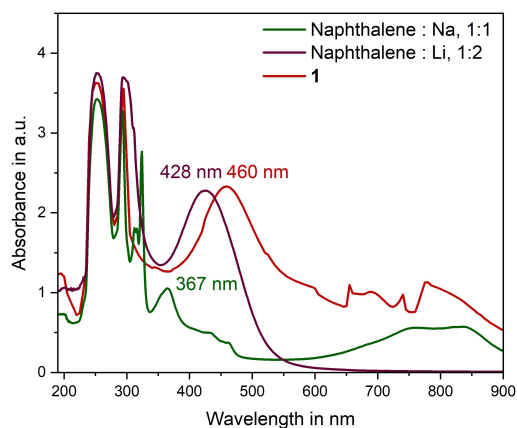**Chemistry Europe**
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Figure 4. UV-visible spectra of naphthalene and sodium (1:1) (green), of naphthalene and lithium (1:2) (purple) and of **1** (red) in THF.

naphthalene dianion, however, the UV-visible spectrum of **1** displays an absorbance maximum at 460 nm. The increased HOMO-LUMO gap of 1.373 eV of **1** compared to that of the naphthalene dianion (Figure 3) would suggest an absorbance at a lower wavelength for **1**. The bathochromic shift of 32 nm between **1** and the dianion of naphthalene could be a result of the harder lithium ions forming stronger contact ion pairs with the naphthalene dianion compared to the tetramethylammonium cation in **1**. All the compounds show a strong absorbance at lower wavelengths (220–320 nm) due to the naphthalene backbone.

Raman spectra of a solution of **1** in THF at $-50\,°C$ reveal the expected bands for the (a)symmetric stretching and deformation frequencies of polycyclic aromatic hydrocarbons with a naphthalene backbone (Figure S7).[36,37] Due to an overlap of wavenumbers of the indicative bands, it is not possible to unambiguously differentiate the formation of the tetrahedrally coordinated carbon atom C2 (2900–3050 cm^{-1}) from a sp^2-hybridised carbon centre (3000–3100 cm^{-1}).[38]

Reactivity

The transient nature of **1** suggests the anionic moiety might display properties as an electron or a hydride transfer agent. We thus investigated the reactivity of **1** towards electron accepting elements such as sulphur or selenium, as well as towards hydride transfer reactions with the organic compounds benzaldehyde and 2-cyclohexen-1-one, which are known to be reduced readily by common hydrides such as lithium aluminiumhydride (Scheme 3).[39,40]

An excess of selenium was added to a solution of **1** in either liquid ammonia or THF. The green reaction mixture was stirred at $-60\,°C$ for one hour, after which it was left to warm up to room temperature under stirring. The products were analysed *via* NMR spectroscopy and XRD analysis. The ^{77}Se NMR spectrum of the reaction mixture shows multiple new resonances in the range of 266–749 ppm, the strongest a singlet at 295 ppm (Figure S6). The green colour and the range of chemical shift is
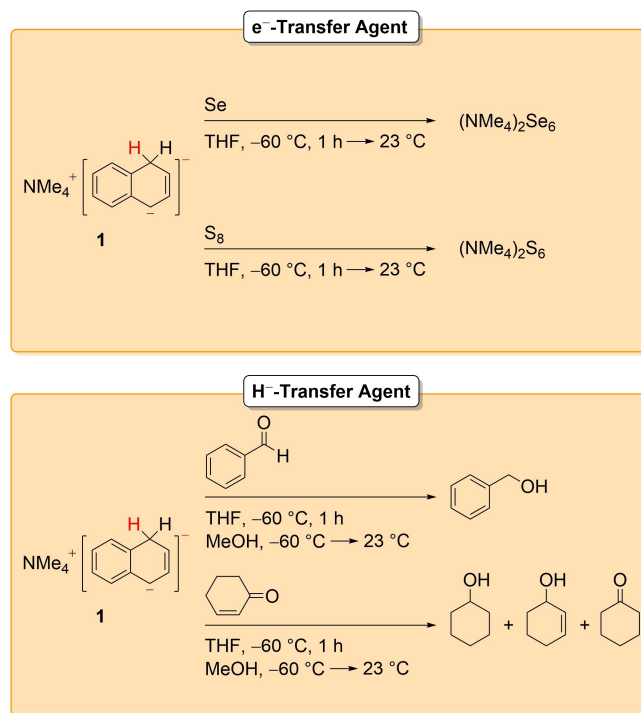
Scheme 3. Reactivity of **1** as a reducing (top) and hydride transfer agent (bottom).

typical for anionic polyselenides $[Se_x]^{2-}$, however, assigning the resonances unambiguously is not possible without further analysis. Taking the integral ratios of the resonances into consideration does not provide any further information to specify the chain length of the polyselenides. The chemical shifts and line widths are strongly dependent on the respective negative charge densities on the selenium centres which in return are highly influenced by solvent affects and atom exchange in the polychalcogenide. Warming the reaction mixture to room temperature could have led to subsequent disproportionation reactions of higher reduced $[Se_x]^{2-}$-species. The acquisition of NMR spectra at room temperature of higher polyselenides $[Se_x]^{2-}$ with $x = 3–11$ can result in the lack of resonances due to fast exchange mechanisms of the selenium nuclei.[41,42]

Crystallisation attempts of the reaction mixture yielded single crystals of $(NMe_4)_2Se_6$ suitable for XRD analysis (see Supporting Information for more details).[43] Adding **1** in an excess of 5 eq to elemental selenium proceeding analogously with the hope of obtaining a fully reduced selenide dianion, resulted in identical spectroscopical observations at room temperature. Storing the reaction mixture at $-60\,°C$ for 8 h followed by crystallisation attempts at $-75\,°C$ did not yield any crystals suitable for XRD analysis.

The reactions were repeated in analogous manner with elemental sulphur. Warming up the mixtures and crystallisation attempts at room temperature yielded orange blocks which were identified as $(NMe_4)_2S_6$ *via* X-ray diffraction analysis (see Supporting Information for more details). No further reaction products were isolated.

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Both of the hexachalcogenides crystallise in the space group *P*2/*c* and have been reported previously, albeit due to the lower measurement temperature of 105 K the unit cells are slightly contracted compared to the lattice parameters in the literature.[43,44] The isolation of tetramethylammonium hexaselenide and hexasulphide, confirm **1** as a reducing agent, however, as suggested by the relative energy of the HOMO of **1** compared to the energies of the SOMO and HOMO of the radical naphthalide or the dianion respectively, **1** is expected to be a milder reducing agent. Isolation of the hexachalcogenides as an intermediate species in the full reduction path from elemental selenium to the monoselenide is in line with this. **1** displays a tamed reduction potential compared to the naphthalide anion or reduction by elemental alkali metals which allows for higher reaction control and selective formation of the hexachalcogenides.

In order to explore the ability of **1** acting as a hydride transfer agent, a solution of **1** in THF was added to stoichiometric amounts of freshly distilled benzaldehyde at −60 °C. After stirring the reaction mixture for one hour, methanol was added to quench any residual reactivity before exposure to air or moisture. The mixture was allowed to warm to room temperature, followed by extraction with water, diethylether, toluene and *n*-hexane. Each organic phase was examined *via* GC-MS which confirmed the successful reduction of benzaldehyde to benzyl alcohol (Figure 5). The solvent peak appears after 4.33 min, whereas the reaction product is detected after 11.79 min. The mass spectrum displays the typical fragmentation pattern for benzyl alcohol with the molecular ion appearing at 108 Da. Without the trapping of reaction intermediates, it is challenging to determine irrevocably whether a reaction occurs *via* one-electron reduction followed by protonation, or through hydride-transfer. However, the reaction of **1** with benzaldehyde and subsequent addition of methanol leading to benzyl alcohol as the main product suggests **1** effectively acting as a hydride-transfer agent.

The reaction of 2-cyclohexen-1-one with a solution of **1** in THF with subsequent addition of methanol, could either lead to the reduction of the keto-group, the unsaturated alkene or the reduction of these functionalities.[39] Synthesis was performed analogously to the reaction with benzaldehyde, however, analysis of the reaction products *via* GC-MS did not indicate successful reduction reactions but showed the unreacted substrate (Figure S9).

Conclusions

In summary, we have kinetically trapped and isolated the first Birch intermediate which was observed in 1939 and postulated in 1965 as a transient species. The reaction of sodium, tetramethylammonium chloride and naphthalene at −60 °C in liquid ammonia leads to the formation of tetramethylammonium hydronaphthalide (**1**), an intermediate in the reduction and hydrogenation reaction of naphthalene to 1,2/1,4-dihydronaphthalene. **1** was fully characterised *via* XRD analysis, homo- and heteronuclear NMR, UV-visible and Raman spectroscopy.
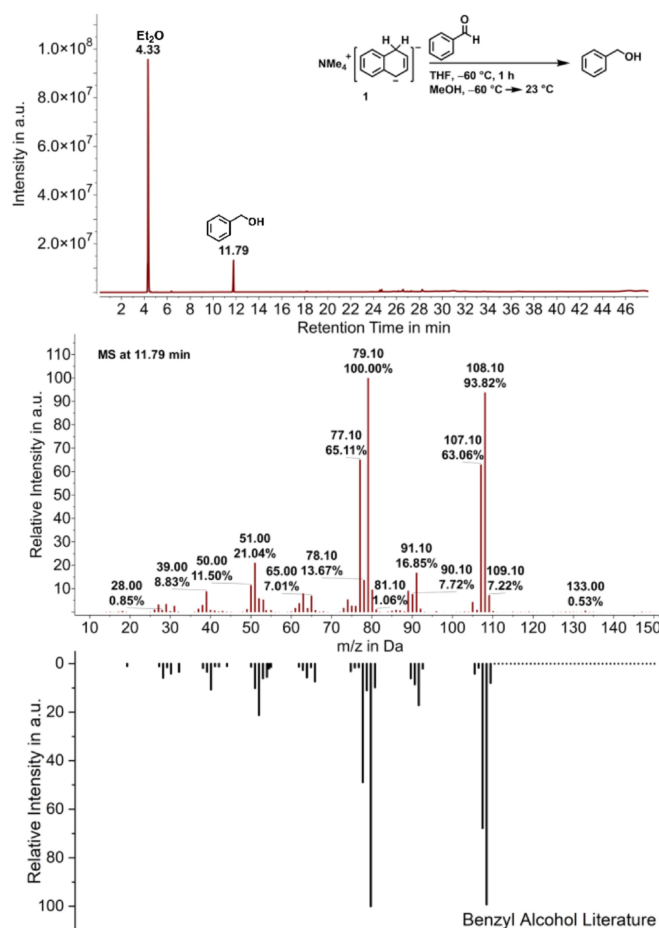

Figure 5. GC-MS trace (top) and MS-spectrum (bottom) of the reaction products of the reaction of **1** with benzaldehyde (red) compared with the mass spectrum of benzyl alcohol taken from literature (black).[45]

The experimental data was supported with DFT calculations confirming the structure and the charge localisation of the anion. A solution of **1** in the common organic solvent THF enables facile handling for further reactions. The reactivity of **1** was examined as an electron as well as a hydride transfer agent. Selenium and sulphur were both successfully reduced to form $(NMe_4)_2Se_6$ and $(NMe_4)_2S_6$, respectively. Additionally, **1** effectively underwent hydride transfer in the reduction of benzaldehyde to benzyl alcohol. The reduced reduction potential of **1** compared to that of the naphthalide anion or elemental alkali metals allow for higher reaction control and milder reductions, such as the selective formation of the hexachalcogenides.

Further investigations will aim at understanding the reaction pathway to the formation of the anion of **1** as well as include more extensive explorations of its reduction potential. Varying the counter ion might pose a viable handle for tuning its solubility and reactivity as a reducing agent. Future work will continue examiningammonia as a solvent at low temperatures, with the potential to stabilise and isolate further transient species which have been illusive to the chemistry community thus far.

Supporting Information Summary

Additional supporting information can be found online in the Supporting Information section at the end of this article.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Cambridge Crystallographic Database at https://www.ccdc.cam.ac.uk/, reference number 2330028.

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