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Hydride encapsulation in s-block metal inverse crown chemistry

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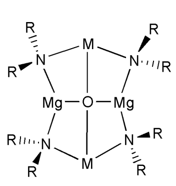
A new category of 'inverse crown' complex has been established through the synthesis of the disodium–dimagnesium diisopropylamide $[Na_2Mg_2\{N(Pr^i)_2\}_4(\mu\text{-}H)_2\cdot(toluene)_2]$, the first such complex to exhibit hydride encapsulation, a non-planar octagonal 'host' ring or solvent stabilisation.

The recent discovery[1] that ferrocene can be regioselectively deprotonated four times by the encapsulating action of a 16-membered tetrasodium–tetramagnesium amide ring provides the most powerful demonstration to date of the special synergic chemistry that can be unleashed when an alkali metal amide is coupled together with its magnesium (or zinc) congener in the same molecular environment. This arene-encapsulation reaction represents the latest development hitherto in the emerging phenomenon of 'inverse crown' chemistry.[2] One of the sub-divisions within this area, the so called 'inverse crown ethers'[3] take their name from a topological (inverse) relationship with conventional crown ether complexes: the metal-based host rings are Lewis acidic (cationic), and their oxygen-based core occupants are Lewis basic (anionic). The generalized structure of an inverse crown ether is illustrated by **1**. Independent of whether the alkali metal constituent (M) is Li, Na or K, the host ring comprises eight atoms, arranged in NMNMg sections. Prior to the work reported herein, these 8-membered heterobimetallic ring systems have all had in common (i) planarity; (ii) amide linking atoms based on either 1,1,1,3,3,3-hexamethyldisilazide (HMDS) or 2,2,6,6-tetramethylpiperidide (TMP) ligands; (iii) an oxide or peroxide guest lodged in the central cavity; and (iv) no contact with solvating ligands. In this paper we report a novel new addition to this family in $[Na_2Mg_2\{N(Pr^i)_2\}_4(\mu\text{-}H)_2\cdot(toluene)_2]$, **2**, the first example of a 'hydride-encapsulated' inverse crown ether complex. The extent of its novelty can be gauged by the fact that it displays none of the aforementioned features. Furthermore, while uncertainty remains as to the precise mechanism/s involved in the oxide- and peroxide-encapsulated analogues, the formation of **2** can be rationalised by a β-hydride elimination pathway.

Complex **2**† is best prepared by heating to reflux for about 1 h, a 1 : 1 : 3 stoichiometric mixture of *n*-butylsodium, *n,sec*-dibutylmagnesium and diisopropylamine in neat toluene or a mixed hydrocarbon/toluene solution, using an inert-atmosphere protocol throughout. The presence of **2** is easily discerned from the hydrido resonance in its ^1H NMR spectrum, the chemical shift of which (3.70 ppm in $C_6D_5CD_3$ solution) is close to that reported for the Mg–(μ-H)–Al resonances in a series of anthracene-derived magnesium aluminates[4] (range, 2.90–2.73 ppm in d_8-THF solution).



1

The 8-membered ring within the centrosymmetric structure of **2**‡ (Fig. 1) sits in a chair conformation. Defined by N1Na1N1, the chair-back is tilted at an angle of 153.5(2)° with respect to the strictly planar N1Mg1N···N1Mg1N1 chair-seat. H^- ions occupy the chair-seat in a $(MgH)_2$ planar ring which itself leans towards the chair-back making an angle of 79.6(13)° with the seat. Covering the 'head- and foot-rest' positions, toluene molecules solvate the Na cations to complete the structure. The Pr^i substituents directly facing each other across the chair-seat, are eclipsed. Only the Mg atoms bind strongly to the H^- ions, at a distance [1.89(2) Å] closely resembling that for the corresponding bonds in $[\{(C_5Me_5)_2Ti(\mu\text{-}H)_2\}_2Mg]$[5] (mean value 1.88 Å). This continues the pattern observed previously throughout the inverse crown family,[2] namely that the positioning of the encapsulated guest is dictated by the placement of the Mg atoms within the host ring. The shortest Na···H separation distance in **2** at 2.68(3) Å, is significantly longer than that found in both NaH (2.44 Å)[6] and $[(Ph_3CO)_3Al(\mu\text{-}H)Na\cdot(THF)_3]$ (2.177 Å).[7] Two amide N atoms complete the highly distorted tetrahedral coordination of the Mg atom (mean bond angle 107.39°; range 79.8–133.16°) at a distance [2.065(18) Å] comparable to that (mean 2.023 Å) in the aforementioned ferrocenyl inverse crown $[Na_4Mg_4[N(Pr^i)_2]_8\{(C_5H_3)_2Fe\}]$ **3**. There is slightly more variation between the structures in the N–Mg–N bond angles [*i.e.*, 133.16(11)° in **2**; 138.5° (mean) in **3**]. However, significant differences do occur in the N–Na–N bond angles [132.08(10)° in **2** *cf.* 129.46 and 150.43° (mean 139.94°) in **3**] and in the Na–N–Mg bond angles [88.29(7)° in **2** *cf.* range in **3**, 78.35–93.70°]. It is this angular flexibility, associated with the weaker, more electrostatic Na–N bonding [distance in **2**, 2.4807(18) Å], which permits different ring sizes (*i.e.*, 8- or 16-membered) of the same mixed-metal amide composition. In **2** the toluene molecule binds asymmetrically to the Na atom making three relatively short contact distances [to the *ipso*-C, 3.157(4) Å, to two *ortho*-C, 3.275(3) Å]; the Na···centroid distance is 3.208 Å, but all other distances exceed 3.5 Å. Such π-solvation is a new feature for a metal atom within a host inverse crown ring. Here it compensates for the absence of any significant Na–guest interaction (*cf.* the M–O bonds in **1**).

On its own magnesium diisopropylamide is known to undergo a thermally induced hydride elimination from one of its

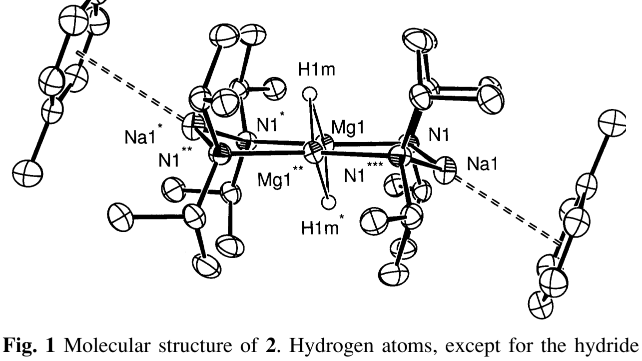


Fig. 1 Molecular structure of **2**. Hydrogen atoms, except for the hydride ions, are omitted for clarity. $^* = 1 - x, -y, z$; $^{**} = 1 - x, -y, -z$; $^{***} = x, y, -z$.

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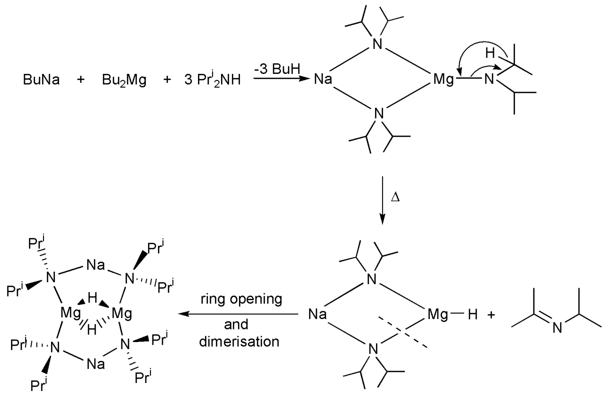

Scheme 1

β-C atoms, which in turn can be exploited to reduce aldehydes or ketones to alcohols.[8] One can postulate a similar intramolecular β-hydride transfer pathway (Scheme 1) to rationalise the formation of **2**. The concomitant loss of the imine $Me_2C{=}NPr^i$, leads to an attenuation of the steric crowding about the Mg atom, thus clearing the way for dimerisation. Therefore the idea of a preformed host ring encapsulating a guest represents a formalism in this particular case, as the final structure is strictly built from a monomeric unit containing half of the 'host ring' and one 'guest' anion. However, such a pathway cannot apply generally (or indeed at all) in inverse crown complexes based on HMDS or TMP linkers as neither possess β-C–H bonds. Having such potentially cleavable β-C–H bonds, the diisopropylamido system is offered a choice of two distinct reaction pathways: β-hydride elimination/encapsulation or arene deprotonation/encapsulation (by analogy with the twofold-deprotonated arene in $[Na_4Mg_2(TMP)_6(C_6H_3CH_3)]^2$). The production of **2** with its intact toluene molecules implies that the former encapsulation process is kinetically favoured over the latter. With regard to the alternative possibility that the β-hydride elimination process occurs from a butyl group on the metal alkyl reagents, this can be ruled out unequivocally as **2** can also be prepared from a mixture of the pure sodium amide and magnesium bis(amide) reagents (i.e., made separately and isolated prior to combining, with the absence of butyl groups confirmed by NMR studies).

Since **2** is both a bulky amide and molecular hydride it may be endowed with useful deprotonating and/or reducing powers.[9] With respect to the former, there is the intriguing possibility that it plays a part (as an unseen intermediate) in the fourfold regioselective deprotonation of ferrocene which ultimately leads to **3**. Future work will explore these ideas.

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Notes and references

† Complex **2** forms as non-pyrophoric, colourless needles, which effervesce on exposure to air. Isolated yields of first batches are typically 25%, reflecting the high arene-solubility of the crystals. Mp: decompose from about 136 °C. ^1H NMR (400.13 MHz, $C_6D_5CD_3$, 300 K): δ 3.70 (2H, s, Mg–H), 3.17 (8H, m, Me_2CH), 1.19 (48H, d, Me_2CH). ^{13}C NMR (100.62 MHz, $C_6D_5CD_3$, 300 K); δ 49.51 (Me_2CH), 27.72 (Me_2CH). The complex readily loses toluene upon isolation, leading to variable microanalysis results.

‡ *Crystal data* for **2**: $C_{38}H_{74}Mg_2N_4Na_2$, M_r = 681.61, orthorhombic, space group *Pnnm*, a = 9.9353(4), b = 12.480(5), c = 17.314(9) Å, V = 2089.71(16) $Å^3$, Z = 2, D_c = 1.083 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, μ = 0.108 mm^{-1}, T = 123 K; 11817 reflections were collected, 1912 were unique, R_{int} = 0.069; final refinement to convergence of F^2 with all non-H atoms anisotropic, the hydride atom isotropic and all other H atoms in calculated positions gave R = 0.0479 (F, 1355 obs, data only) and R_w = 0.1146 (F^2, all data), GOF = 1.096, 119 refined parameters, residual electron density, max. and min. 0.186 and –0.197 e $Å^{-3}$.

CCDC reference number 173092. See http://www.rsc.org/suppdata/cc/b1/b110117j/ for crystallographic data in CIF or other electronic format.

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