Lithium and magnesium complexes of *ortho*-dimethylarsinoaniline and a novel insertion of dimethylsilanone into an Mg–N bond—molecular structures of $[\{Li(\mu^2:\eta^1\text{-}NHC_6H_4AsMe_2)(thf)_2\}_2]$ and the insertion product $[\{Mg_2(\mu^2:\eta^1\text{-}NHC_6H_4AsMe_2)_2(\mu^3:\eta^3\text{-}OSiMe_2\text{-}NC_6H_4AsMe_2)(thf)\}_2]$

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Treatment of *ortho*-dimethylarsinoaniline ($NASH_2$) with 1.0 equivalents of $LiBu^t$ or 0.5 equivalents of $MgBu_2$ in tetrahydrofuran affords the complexes $[\{Li(NASH)(thf)_2\}_2]$ (**1**) and $[Mg(NASH)_2(thf)_{1.5}]$ (**2**) ($NASH = NHC_6H_4AsMe_2$-2). Both complexes have been characterised spectroscopically. The crystal structure determination of **1** reveals a centrosymmetric dimeric structure with an Li_2N_2 central unit that does not exhibit arsino–lithium donor interactions. Compound **2** reacts with dimethylsilicone grease to yield the unexpected complex $[\{Mg_2(\mu^2:\eta^1\text{-}NHC_6H_4AsMe_2)_2(\mu^3:\eta^3\text{-}OSiMe_2NC_6H_4AsMe_2)(thf)\}_2]$ (**3**), *via* the novel and unprecedented insertion of a dimethylsilanone fragment into an Mg–N bond. Compound **3** is tetranuclear with a 12-membered $Mg_4N_6O_2$ double stacked cube centre that has Mg atoms residing at alternate corners of each cube. The arsino functionalities of the modified η^3-bound ligands co-ordinate to Mg atoms on the vertices.

1 Introduction

The fundamental importance of group 1 and 2 metal-amido complexes as synthetic reagents in inorganic chemistry and as strong Brønsted bases or nucleophiles in organic synthesis[1] has led to considerable advances in the field of metal amide chemistry.[2] In contrast to the actively investigated area of amidolithium chemistry, relatively less attention has been paid to amidomagnesium species.[2] As a result, there is a dearth of structural data pertaining to amidomagnesium complexes when compared to their amidolithium congeners. This is surprising given that magnesium often resembles lithium in terms of its chemical reactivity. In addition, knowledge of the structure of metal-amido species is important, as this allows the synthetic chemist to tailor syntheses or transformations utilising them.

Since the synthesis of *o*-dimethylarsinoaniline ($NASH_2$) and its diphenyl analogue (*o*-diphenylarsinoaniline) in 1970,[3] complexes of these novel ligands have not been reported. This contrasts with the wealth of structural and spectroscopic data concerning complexes of *o*-dimethylarsino-*N*,*N*-dimethylaniline reported by Peloso *et al.* during the 70's and 80's.[4] Given the presence of a soft arsino donor moiety, and hence the potentially chelating nature of NASH, we were eager to synthesise lithium and magnesium NASH complexes and demonstrate their utility in inorganic synthesis. Herein, we report the synthesis of the first NASH complexes, $[\{Li(NASH)(thf)_2\}_2]$ (**1**), $[Mg(NASH)_2(thf)_{1.5}]$ (**2**), and disclose the crystal structure of the novel Mg–N insertion product $[\{Mg_2(\mu^2:\eta^1\text{-}NHC_6H_4AsMe_2)_2\ (\mu^3:\eta^3\text{-}OSiMe_2NC_6H_4AsMe_2)(thf)\}_2]$ (**3**), originally formed from the serendipitous reaction of **2** with dimethylsilicone grease.

2 Experimental

o-Dimethylarsinoaniline ($NASH_2$) was prepared by a literature procedure.[3] $LiBu^t$ and $MgBu_2$ (1.7 and 1.0 M solutions in hexane and heptane, respectively) were purchased from Aldrich and used as received. High vacuum silicone grease was obtained from Dow Corning. Tetrahydrofuran and hexane were dried over sodium, then freshly distilled from sodium–benzophenone. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity argon or dinitrogen in flame-dried glassware. Infrared spectra were recorded from Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^1H NMR spectra were recorded at 300.13 MHz and ^{13}C NMR spectra were recorded at 75.46 MHz using a Bruker BZH 300/52 spectrometer with a Varian console. Chemical shifts were referenced to the residual ^1H or ^{13}C resonances of the solvent used (C_6D_6). Mass spectra were recorded on a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon and are uncorrected.

2.1 Preparation of $[\{Li(\mu^2:\eta^1\text{-}NASH)(thf)_2\}_2]$ (1)

tert-Butyllithium (1.7 M in hexane, 2.15 cm^3, 3.65 mmol) was added dropwise to a solution of $NASH_2$ (1.0 cm^3, 3.65 mmol) in THF (10 cm^3) at −30 °C. The resulting clear light brown solution was then stirred for 2 h at room temperature, whereupon the volatiles were removed *in vacuo* to yield a light yellow solid. This was washed with cold (− 30 °C) hexane (*ca.* 5 cm^3) and recrystallised from THF (< 2 cm^3) to yield the title

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compound as light yellow/brown prisms (1.05 g, 83%), m.p. 43 °C, decomp. 127 °C. ^{1}H NMR (300.1 MHz, C_6D_6, 300 K): δ 1.10 (br s, 16H, thf), 1.24 [s, 12H, As(CH_3)$_2$], 3.33 (br s, 2H, NH), 3.41 (br s, 16H, thf), 6.56–7.23 (mult, 8H, aromatics). ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 9.8 [s, As(CH_3)$_2$], 25.5 (s, thf), 68.0 (s, thf), 127.3, 127.5, 127.9, 128.2, 129.9, 131.0 (s, aromatics). MS (APCI): m/z (%) 198 [($NASH_2$)H^+, 100], 204 [$(MH-4thf)^+$, 34], 276 [$(MH-3thf)^+$, 7]. IR (Nujol) ν/cm^{-1}: 835m, 907m, 1045s, 1178m, 1250s, 1301s br, 1378s, 1450s, 1573m sh, 3235w br, 3380w br.

2.2 Preparation of [Mg(NASH)$_2$(thf)$_{1.5}$] (2)

Di-*n*-butylmagnesium (1.0 M in heptane, 1.45 cm^3, 1.45 mmol) was added dropwise to a solution of $NASH_2$ (0.79 cm^3, 2.89 mmol) in THF (5 cm^3) at -60 °C. The resulting light yellow solution was stirred at this sustained low temperature for 2 h and then warmed to room temperature. Stirring was continued for a further 3 h, whereupon volatiles were removed *in vacuo* and the residue washed with hexane (10 cm^3) to yield the title compound as a fine microcrystalline powder (0.72 g, 95%), m.p. 148 °C. ^{1}H NMR (300.1 MHz, C_6D_6, 300 K): δ 0.91 [s, 12H, As(CH_3)$_2$], 1.21 (br s, 6H, thf), 3.27 (br s, 6H, thf), 3.34 (br s, 2H, NH), 6.50–7.00 (mult, 8H, aromatics). ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 9.6 [s, As(CH_3)$_2$], 24.0 (s, thf), 70.7 (s, thf), 114.9, 117.2, 118.3, 131.0, 150.0, 159.0 (s, aromatics). MS (APCI): m/z (%) 198 [($NASH_2$)H^+, 22], 209 [$(MH_2-1.5\ thf)^{2+}$, 9], 220 [Mg(NASH)$^+$, 100], 418 [$(MH-1.5\ thf)^+$, 9]. IR (Nujol) ν/cm^{-1}: 707m, 840m, 892m, 1112m sh, 1286s br, 1460s, 1614s sh, 3360m br, 3457m br, 3713m sh.

2.3 Preparation of [{Mg$_2$(μ^2:η^1-NASH)$_2$(μ^3:η^3-OSiMe$_2$-NC$_6$H$_4$AsMe$_2$)(thf)}$_2$] (3)

(a) As for the preparation of **2**. The reaction mixture was warmed to room temperature and concentrated *in vacuo* to *ca.* 4 cm^3. The resultant solution was layered with hexane (10 cm^3) containing traces of dimethylsilicone grease and left overnight. This yielded the title compound as light yellow blocks (0.09 g, 16% by Mg) which were separated manually from microcrystalline **2**, m.p. 172 °C.

(b) Silicone grease (0.03 g, 0.40 mmol by $SiMe_2O$) was added as a dilute solution (10 cm^3 THF) to a solution of **2** (0.50 g, 0.95 mmol) in tetrahydrofuran (30 cm^3) at -30 °C. The solution was warmed to ambient temperature, stirred overnight and concentrated *in vacuo* (*ca.* 2 cm^3). Storage at -20 °C yielded **3** as large colourless blocks [0.21 g, 67% by ($SiMe_2O$)$_n$], m.p. 175 °C. ^{1}H NMR (300.1 MHz, C_6D_6, 300 K): δ 0.35 [s, 12H, OSi(CH_3)$_2$], 1.06 [s, 12H, As(CH_3)$_2$Si], 1.12 [s, 24H, As(CH_3)$_2$], 1.21 (br s, 8H, thf), 3.26 (br s, 8H, thf), 3.86 (br s, 4H, NH), 6.43–7.16 (mult, 24H, aromatics). ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 4.8 [s, Si(CH_3)$_2$], 7.9 (s, $AsMe_2$), 8.65 (s, $AsMe_2Si$), 25.6 (s, thf), 67.9 (s, thf), 114.5, 117.5, 118.3, 118.6, 119.9, 129.5, 130.5, 130.8, 131.1, 131.3, 159.4, 160.1 (s, aromatics). MS (APCI): m/z (%) 198 [($NASH_2$)H^+, 100], 254 [$NASSiMe_2^+$, 18], 492 [$(1.5-NASH)^+$, 62]. IR (Nujol) ν/cm^{-1}: 743s, 825m, 861m, 953m, 1025m, 1158m, 1194s, 1224s, 1245s, 1276s, 1332s, 1583s, 1608w, 3268m br.

2.4 Collection of X-ray diffraction data, solution and refinement of the structures

For compounds (**1**) and (**3**) hemispheres of data were collected (capillary sealed specimens) at room temperature on a Bruker SMART CCD diffractometer using the omega scan mode with total reflections and unique data listed in Table 1. Data sets were corrected for absorption using the program SADABS.[5] The structures were solved using direct methods and refined on F^2 using SHELXL97-2[6] using X-SEED[7] as an interface. All non-hydrogen atoms were located and were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (riding model) and were not refined. For compound (**1**), the carbon atoms on the thf molecule were disordered. These were successfully modelled and refined. Crystal data, a summary of data collection and positional parameters appear below, while selected bond distances and angles appear in the figure captions.

Crystal data for compound 1. $C_{16}H_{27}AsLiNO_2$, $M = 347.25$, triclinic, $a = 9.223(14)$, $b = 9.965(14)$, $c = 10.775(16)$ Å, $\alpha = 83.41(3)$, $\beta = 74.61(3)$, $\gamma = 86.59(3)$°, $U = 948(2)$ Å^3, $T = 296$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-Kα) = 1.8 mm^{-1}, 3929 reflections measured, 2545 unique ($R_{int} = 0.089$) which were used in all calculations. The final $R[I > 2\sigma(I)]$ was 0.094 and $wR(F^2)$ was 0.267 (all data).

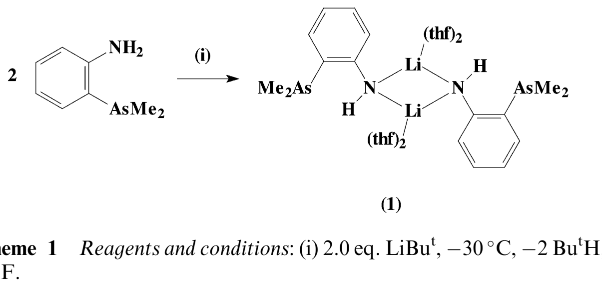
Crystal data for compound 3. $C_{60}H_{92}As_6Mg_4N_6O_4Si_2$, $M = 1564.34$, monoclinic, $a = 11.7997(11)$, $b = 18.7061(17)$, $c = 20.367(2)$ Å, $\beta = 103.910(2)$°, $U = 4363.6(7)$ Å^3, $T = 296$ K, space group $P2_1/c$ (no. 14), $Z = 2$, μ(Mo-Kα) = 2.36 mm^{-1}, 19 635 reflections measured, 6219 unique ($R_{int} = 0.076$) which were used in all calculations. The final $R[I > 2\sigma(I)]$ was 0.056 and $wR(F^2)$ was 0.16 (all data).

CCDC reference numbers 173732 and 173733. See http://www.rsc.org/suppdata/nj/b1/b108503b/ for crystallographic data in CIF or other electronic format.

3 Discussion

Lithiation of *ortho*-dimethylarsinoaniline ($NASH_2$) with one equivalent of LiBu^t in tetrahydrofuran at -30 °C rapidly formed a clear brown solution (Scheme 1). Crystallisation of the product afforded large light yellow prisms of [{Li(μ^2:η^1-NASH)(thf)$_2$}$_2$] (**1**) in high yield. Compound **1** is a thermally robust material (decomposition 127 °C) with a surprisingly low melting point of 43 °C. The ^{1}H NMR spectrum displays a resonance for the As(CH_3)$_2$ protons at 1.24 ppm which is downfield of that for the free ligand (0.91 ppm). The broad N–H resonance occurs at 3.33 ppm, upfield of that for $NASH_2$ (3.49 ppm), whilst the ^{13}C NMR spectrum of **1** is consistent with the proposed composition. Peaks in the APCI mass spectrum can be attributed to the protonated $NASH_2$ ligand (m/z 198), the protonated Li(NASH) subunit (m/z 204) and its mono-solvated protonated analogue Li(NASH)(thf) (m/z 276). The FTIR spectrum displays a broad N–H stretching mode at 3235 and 3380 cm^{-1} (free ligand; 3350br, 3441br cm^{-1}).

The molecular structure of **1** is depicted in Fig. 1. The molecule is dimeric and resides on a crystallographic inversion centre with an Li_2N_2 core unit. In the solid-state, **1** exists without co-ordination of the arsino moiety to the lithium centre. This is not unexpected, due to the preferential co-ordination of THF to the hard acceptor lithium atom. The central unit exists as a distorted square [N(1)–Li(1)–N(1)′ 104.1°, Li(1)′–N(1)–Li(1) 75.9°] with bond lengths of 2.064 Å



(1)

Scheme 1 *Reagents and conditions*: (i) 2.0 eq. LiBu^t, -30 °C, -2 Bu^{t}H, THF.

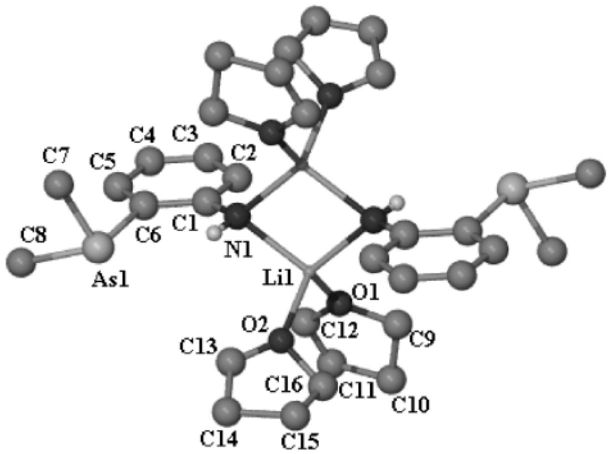
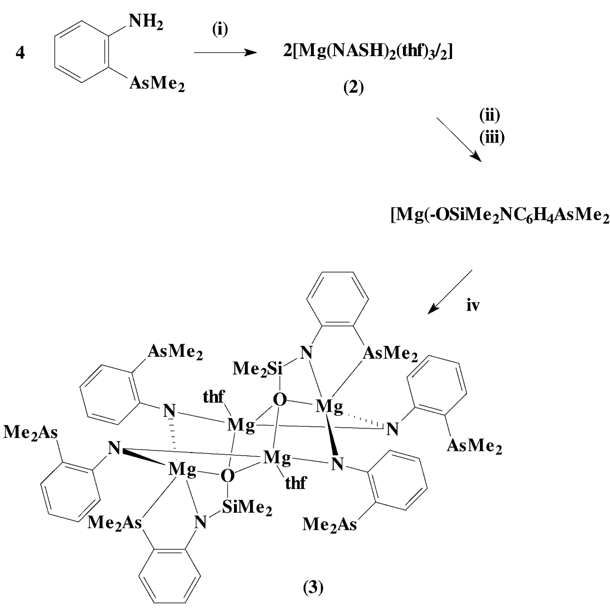


Fig. 1 Molecular structure of the centrosymmetric dimer of [{Li(η^1-NASH)(thf)$_2$}$_2$] (**1**). Selected bond lengths [Å] and angles [°]; Li(1)–O(1) 1.944(16), Li(1)–O(2) 1.960(17), Li(1)–N(1) 2.073(14), Li(1)–N(1)#1 2.054(17), Li(1)–Li(1)#1 2.54(3); C(6)–As(1)–C(7) 102.7(13), C(6)–As(1)–C(8) 104.1(9), C(7)–As(1)–C(8) 86.0(14), O(1)–Li(1)–N(1) 115.5(7), O(1)–Li(1)–N(1)#1 108.9(8), O(1)–Li(1)–O(2) 104.7(8), O(2)–Li(1)–N(1) 105.6(7), O(2)–Li(1)–N(1)#1 118.5(7), Li(1)–N(1)–Li(1)#1 75.9(7). Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y+2$, $-z+1$.



Scheme 2 *Reagents and conditions*: (i) 2.0 eq. $MgBu_2$, −60 °C, −4 BuH, THF; (ii) 2.0 eq. "$SiMe_2O$", −30 °C; (iii) −2 $NASH_2$; (iv) 4 eq. **2**.

(av. Li–N) that are slightly shorter than that of the mean structurally characterised Li–N bonds at 2.082 Å.[8] The phenyl groups organise themselves such that the arsino moiety is directed away from the central unit and, hence, does not participate in donation to the metal. This is as expected on electropositivity grounds. Accordingly, the co-ordination sphere of the lithium is satisfied by donation of the hard THF donor. This renders each lithium centre four co-ordinate with a distorted tetrahedral geometry [O(1)–Li(1)–O(2) 104.7°, N(1)–Li(1)–N(1)′ 104.1°]. Lastly, the placement of the *o*-arsinophenyl groups causes an unexpected inequivalence of the THF donors, thereby compounding distortion about the lithium centres [O(1)–Li(1)–N(1)′ 108.9°, O(2)–Li(1)–N(1)′ 118.5°].

To address the paucity of structurally characterised amidomagnesium complexes, the preparation of a magnesium analogue of **1** was attempted. Treatment of $NASH_2$ with half an equivalent of $MgBu_2$ in tetrahydrofuran at −60 °C formed a light yellow solution that when concentrated yielded the compound [Mg(NASH)$_2$(thf)$_{1.5}$] (**2**) in near quantitative yield (95%) (Scheme 2). Compound **2** is a thermally robust solid with a melting point of 148 °C. The ^{1}H NMR spectrum of **2** displays an arsino methyl proton resonance at 0.91 ppm that is identical to that for the free ligand and therefore upfield of the corresponding resonance in **1**. The N–H resonance at 3.34 ppm closely matches the analogous resonance for **1** (3.33 ppm) and as such is also downfield of that for non-deprotonated $NASH_2$. The ^{13}C NMR spectrum of **2** is unexceptional; the arsino methyls resonate at 9.6 ppm (9.8 ppm for **1**), with several aromatic singlets between 114.9 and 159.0 ppm, which match the distribution of those for $NASH_2$. The APCI mass spectrum displays peaks attributable to the protonated ligand (m/z 198), the doubly protonated non-solvated monomeric ion (m/z 209), [magnesium(NASH)]$^+$ (m/z 220) and the protonated non-solvated monomer ion (m/z 418). In addition, several broad stretches that could be assigned to the N–H bond of **2** were observed in the FTIR spectrum at 3360, 3457 and 3717 cm^{-1} ($NASH_2$: 3350br, 3441br cm^{-1}).

The co-ordination mode of NASH in **2**, *i.e.* whether the arsino moiety is involved in ligation, could not be evaluated without structural data. To this end the crystallisation of **2** was attempted. The lessened electropositivity of magnesium relative to lithium led us to believe that chelation was possible. The recrystallisation of **2** was attempted by the slow diffusion of hexane into a saturated tetrahydrofuran solution of **2**. During crystallisation a small amount of a complex that characterised differently by spectroscopy to **2** was formed as large colourless blocks. These crystals were separated manually from the bulk material and examined by X-ray diffraction. The compound formed was [{Mg_2(μ^2:η^1-$NHC_6H_4AsMe_2$)$_2$(μ^3:η^3-$OSiMe_2N$-$C_6H_4AsMe_2$)(thf)}$_2$] (**3**), indicating the novel and unprecedented insertion of a dimethylsilanone fragment into an Mg–N bond (Scheme 2). The repeated formation of **3** frustrated the structural characterisation of **2**, and hence the co-ordination of NASH in **2** could not be identified unequivocally. Furthermore, when grease was rigorously excluded from preceding steps in the crystallisation of **2**, only material of insufficient quality for a single crystal structure determination was obtained. An intentional synthesis of **3** was subsequently undertaken (Scheme 2). Treatment of a tetrahydrofuran solution of **2** with a third of an equivalent of silicone grease (based on $SiMe_2O$) heavily diluted in tetrahydrofuran led to moderate yields of a crystalline material after concentration and storage at −20 °C. An examination of the ^{1}H and ^{13}C NMR data confirmed this material to be **3**. In addition, resonances attributable to $NASH_2$ were also observed in spectra of the remnant reaction mixture. On this basis the reaction pathway presented in Scheme 2 is proposed. Recent examples of Li–N dimethylsilanone insertion intimate that the modified ligand complex can potentially undergo further reaction with complexed 'un-modified' ligand to eliminate lithium oxide and yield an N–Me_2Si–N bridged ligand which can go on to form larger and more elaborate cage structures.[9h] The preclusion of magnesium oxide formation indicated by the absence of any precipitation in the intentional synthesis of **3** infers that this mechanism does not operate in the transformation of **2** to **3**. However, we cannot conclude that the advent of dimethylsilanone insertion takes place either before or after the aggregation that results in the formation of **3**. Indeed, as the exact solution behaviour of **2** is not fully known, or its solid-state structure elucidated, the extent of aggregation in **2** cannot be defined. Hence, although Scheme 2 depicts insertion prior to aggregate formation of **3**, insertion may occur to **2** should it be of greater than mononuclearity in solution.

Compound **3** is a remarkably stable material in the solid state, with a melting point of 172–175 °C. The ^{1}H NMR spectrum displays a singlet at 0.35 ppm attributable to the dimethylsilanone group of **3**, a broad singlet at 3.86 ppm for the N–H resonances of the unmodified ligands, and a multiplet of aromatic resonances between 6.43 and 7.16 ppm. Interestingly, the two arsino methyl types resonate at 1.06 [$As(CH_3)_2$: Si] and 1.12 ppm [$As(CH_3)_2$: non Si], downfield of the parent compound **2** (0.91 ppm). The ^{13}C NMR spectrum is unexceptional and complicated by the two ligand types. Of note is the resonance attributable to the $SiMe_2$ unit of the modified ligand at 4.8 ppm. The FTIR spectrum of **3** shows a broad absorption at 3268 cm^{-1} which can be assigned to the N–H stretching mode of the unmodified NASH ligands. The APCI-MS of **3** does not show the molecular ion, due to its mass (beyond the scope of conditions employed), however, the protonated $NASH_2$ ligand was identified (*m*/*z* 198), as were the silylated ligand $NASSiMe_2^+$ (*m*/*z* 254) and the non-solvated monomer minus an NASH ligand (*m*/*z* 492).

The asymmetric unit of **3** (Fig. 2) consists of one $OSiMe_2NC_6H_4AsMe_2$ ligand, two NASH ligands and two magnesium atoms, one of which is co-ordinated by a single tetrahydrofuran. The central unit of **3** is expectedly more complex than that of **1**. It exists as a centrosymmetric dimer in which the four magnesium atoms sit on opposing corners of two 'face-joined' stacked cubes. In combination with the nitrogen and oxygen atoms, this leads to the formation of a rectangular prism. Co-ordination of the arsino moieties of the 'non-inserted' NASH ligands is precluded by the preferential co-ordination of the two modified ligands that demonstrate η^3-bonding. The arsino co-ordination of these ligands to magnesium atoms upon the vertices seems to result from increased conformational dexterity rather than an electronic preference of the ligand. Steric buttressing of the phenylene backbones also mitigates against NASH arsino co-ordination. Similarly, the modification of NASH, and subsequent arsine co-ordination, result in contraction of the arsenic–*ipso*-carbon bond from 1.968 (unmodified ligands) to 1.919 Å, however, the comparable length of the analogous bond in **1** (1.914 Å) suggests this is coincidental. The rectangular prismatic geometry of **3** is distorted such that the angles N(2)–Mg(2)–N(1) and Mg(1)′–O(1)–Mg(1) are on average 105.3 and 96.24°, respectively. However, the bond lengths N(1)–Mg(2) and O(1)–Mg(1) are almost equivalent at 2.069 and 2.054 Å, leading to a pseudo double cube structure. These bond lengths compare favourably to the mean of those crystallographically characterised (Mg–N 2.137, Mg–O 2.076 Å).[8] The comparative shortening is apparently a consequence of aggregate strain. The two differing magnesium environments display distorted trigonal bipyramidal [Mg(1), O(1)′–Mg(1)′–O(1) 83.76°] and heavily distorted tetrahedral [Mg(2), N(1)′–Mg(2)–N(2) 74.7°] geometries. Interestingly, the Mg(2)–As(3) bond length of 2.757 Å is longer than that of the only other structurally characterised example of an Mg–As bond (2.594 Å av.).[10]

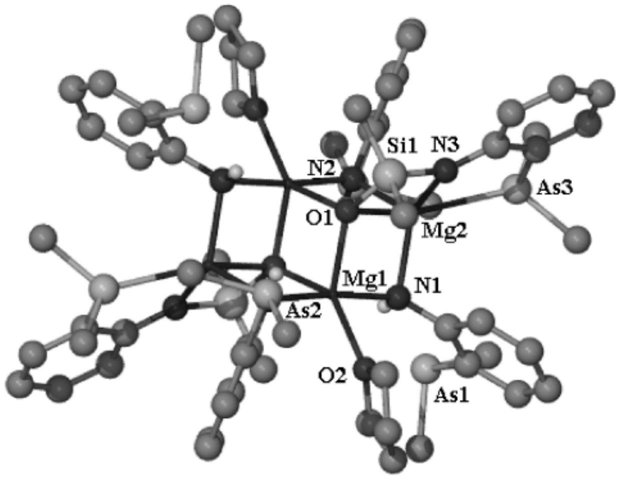


Fig. 2 Molecular structure of the tetranuclear [$\{Mg_2(\eta^1\text{-}NHC_6H_4AsMe_2)_2(\eta^3\text{-}OSiMe_2NC_6H_4AsMe_2)(thf)\}_2$] (**3**). Selected bond lengths [Å] and angles [°]; Mg(1)–O(1) 2.074(4), Mg(1)–O(1)#1 2.054(4), Mg(1)–O(2) 2.141(4), Mg(1)–N(1) 2.148(5), Mg(1)–N(2) 2.176(5), Mg(2)–O(1) 2.250(4), Mg(2)–N(1)#1 2.065(5), Mg(2)–N(2) 2.072(5), Mg(2)–N(3) 2.030(5), Mg(2)–As(3) 2.757(2), Mg(1)–Mg(1)#1 3.074(4), Mg(1)–Mg(2)#1 3.056(3), Mg(2)–Mg(1)#1 3.056(3), Si(1)–O(1) 1.656(4), Si(1)–N(3) 1.704(5); O(1)–Mg(1)–O(1)#1 83.76(15), O(1)–Mg(1)–O(2) 141.16(18), O(2)–Mg(1)–O(1)#1 135.07(18), O(1)–Mg(1)–N(1) 93.90(18), O(1)–Mg(1)–N(2) 89.82(16), O(1)#1–Mg(1)–N(1) 89.70(18), O(1)#1–Mg(1)–N(2) 95.02(17), O(2)–Mg(1)–N(1) 88.05(18), O(2)–Mg(1)–N(2) 86.34(18), N(1)–Mg(1)–N(2) 174.3(2), Mg(1)–O(1)–Mg(1)#1 96.24(15), Mg(1)–N(1)–Mg(2)#1 93.0(2), Mg(1)–O(1)–Mg(2) 89.88(14), Mg(1)#1–O(1)–Mg(2) 90.35(14), O(1)–Mg(2)–N(1)#1 86.69(18), O(1)–Mg(2)–N(2) 87.88(16), O(1)–Mg(2)–N(3) 73.17(17), O(1)–Mg(2)–As(3) 151.01(12), N(1)#1–Mg(2)–N(2) 105.3(2), N(1)#1–Mg(2)–N(3) 126.1(2), N(1)#1–Mg(2)–As(3) 109.67(15), N(2)–Mg(2)–N(3) 122.7(2), N(2)–Mg(2)–As(3) 109.43(15), N(3)–Mg(2)–As(3) 77.88(15). Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z$.

4 Conclusion

Structurally characterised examples of silicone grease insertion, *i.e.* Me_2SiO, Me_2Si or $O(Me_2SiO)_n$, number 9 in the literature.[9] Compound **3** extends this catalogue to amidomagnesium compounds. The syntheses of **1**–**3** mark the first co-ordination complexes of NASH. Complex **2** exemplifies the ease with which an $SiOMe_2$ fragment may be inserted into a metal-amido bond. The preparation of lithium and magnesium complexes of NASH has encouraged us to investigate their synthetic utility. The outcome of these studies will form the basis of forthcoming publications.

Acknowledgements

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References and notes

1 (*a*) M. Majewski and D. M. Gleave, *J. Organomet. Chem.*, 1994, **470**, 1 and references therein; (*b*) B. J. Wakefield, *Organolithium Methods*, Academic Press, New York, 1988; (*c*) A. M. Sapsa and P. v. R. Schleyer, in *Lithium Chemistry: A Theoretical and Experimental Overview*, ed. P. v. R. Schleyer, Wiley-Interscience, New York, 1995; (*d*) M. Gray, M. Tinkl and V. Snieckus, in *Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford 2nd, 1995, vol. 11, p. 1; (*e*) C. H. Heathcock, in *Comprehensive Carbanion Chemistry*, ed. E. Buncel and T. Durst, Elsevier, New York, 1980, vol. B, ch. 4.

2 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood Ltd., Chichester, 1980.

3 B. Chiswell and K. A. Verall, *J. Prakt. Chem.*, 1970, **312**, 751.

4 (*a*) A. J. Peloso, *J. Chem. Soc., Dalton Trans.*, 1981, 2429; (*b*) A. Peloso and L. Volponi, *J. Chem. Soc., Dalton Trans.*, 1974, 278; (*c*) A. Peloso and L. Volponi, *J. Chem. Soc., Dalton Trans.*, 1976, 923; (*d*) A. Peloso and L. Volponi, *J. Chem. Soc., Dalton Trans.*, 1977, 2356; (*e*) A. Peloso and L. Volponi, *J. Chem. Soc., Dalton Trans.*, 1979, 952; (*f*) A. Peloso, *J. Chem. Soc., Dalton Trans.*, 1979, 2033.

5 R. H. Blessing, *Acta. Crystallogr., Sect. A*, 1995, **51**, 33.

6 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

7 L. J. Barbour, X-SEED, Crystallographic Interface, University of Missouri-Columbia, MO, USA, 1999.

8 Mean bond lengths derived from those in the Cambridge Structural Database.

9 Insertion: (*a*) X. G. Zhou, Z. Huang, R. F. Cai, L. B. Zhang, Y. J. Liu and C.Y. Duan, *Synth. React. Inorg. Met.-Org. Chem.*, 2000, **30**, 649; (*b*) X. G. Zhou, Z. Huang, R. F. Cai, L. B. Zhang, L. X. Zhang and X. Y. Huang, *Organometallics*, 1999, **18**, 4128; (*c*) H. Bock, M. Sievert, C. L. Bogdan, B. O. Kolbesen and A. Wittershagen, *Organometallics*, 1999, **18**, 2387; (*d*) X. G. Zhou, W. W. Ma, Z. E. Huang, R. F. Cai, X. Z. You and X. Y. Huang, *J. Organomet. Chem.*, 1997, **546**, 309; (*e*) H. G. Zhou, H. Z. Ma, X. Y. Huang and X. Z. You, *J. Chem. Soc., Chem. Commun.*, 1995, 2483; (*f*) R. A. Jones, S. U. Koschmieder, J. L. Atwood and S. G. Bott, *J. Chem. Soc., Chem. Commun.*, 1992, 726; (*g*) C. Jones, P. C. Junk, S. G. Leary and N. A. Smithies, *J. Chem. Soc., Dalton Trans.*, 2000, 3186; (*h*) C. Jones, P. C. Junk and N. A. Smithies, *J. Organomet. Chem.*, 2000, **607**, 105; (*i*) D. A. Edwards, R. M. Harker, M. F. Mahon and K. C. Molloy, *J. Chem. Soc., Dalton Trans.*, 1997, 3509; (*j*) D. M. Smith, C.-W. Park and J. A. Ibers, *Inorg. Chem.*, 1997, **36**, 3798; (*k*) T. I. Gountchev and T. D. Tilley, *Organometallics*, 1999, **18**, 2896. Adventitious inclusion of $(Me_2SiO)_7$ silyl crown ether: (*l*) M. R. Churchill, C. H. Lake, S.-H. L. Chao and O. T. Beachley, Jr, *J. Chem. Soc., Chem. Commun.*, 1993, 1577; (*m*) C. Eaborn, P. B. Hitchcock, K. Izod and J. D. Smith, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2679.

10 M. Westerhausen and A. Pfitzner, *J. Organomet. Chem.*, 1995, **487**, 187.