1,8-Bis(silylamido)naphthalene Complexes of Magnesium and Zinc Synthesised Through Alkane Elimination Reactions

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Abstract

The reactions between magnesium or zinc alkyls and 1,8-bis(triorganosilyl)diaminonaphthalenes afford the 1,8-bis(triorganosilyl)diamidonaphthalene complexes with elimination of alkanes. The reaction between $1,8\text{-}C_{10}H_6(NSiMePh_2H)_2$ and one or two equivalents of Mg^nBu_2 affords two complexes with differing coordination environments for the magnesium; the reaction between $1,8\text{-}C_{10}H_6(NSiMePh_2H)_2$ and Mg^nBu_2 in a 1:1 ratio affords $1,8\text{-}C_{10}H_6(NSiMePh_2)_2\{Mg(THF)_2\}$ (**1**), which features a single magnesium centre bridging both ligand nitrogen donors, whilst treatment of $1,8\text{-}C_{10}H_6(NSiR_3H)_2$ ($R_3 = MePh_2$, $^iPr_3$) with two equivalents of Mg^nBu_2 affords the bimetallic complexes $1,8\text{-}C_{10}H_6(NSiR_3)_2\{^nBuMg(THF)\}_2$ ($R_3 = MePh_2$ **2**, $R_3 = {}^iPr_3$ **3**), which feature four-membered Mg_2N_2 rings. Similarly, $1,8\text{-}C_{10}H_6(NSi^iPr_3)_2\{MeMg(THF)\}_2$ (**4**) and $1,8\text{-}C_{10}H_6(NSiMePh_2)_2\{ZnMe\}_2$ (**5**) are formed through reactions with the proligands and two equivalents of MMe_2 (M = Mg, Zn). The reaction between $1,8\text{-}C_{10}H_6(NSiMePh_2H)_2$ and two equivalents of MeMgX affords the bimetallic complexes $1,8\text{-}C_{10}H_6(NSiMePh_2)_2(XMgOEt_2)_2$ (X = Br **6**; X = I **7**). Very small amounts of $[1,8\text{-}C_{10}H_6(NSiMePh_2)_2\{IMg(OEt_2)\}]_2$ (**8**), formed through the coupling of two diamidonaphthalene ligands at the 4-position with concomitant dearomatisation of one of the naphthyl arene rings, were also isolated from a solution of **7**.

Introduction

Sterically demanding, bidentate amido ligands have been the subject of intense research interest for some time,[1] with examples of their compounds spanning the whole Periodic Table.[2] Such complexes have found applications in catalysis,[3,4] and from a fundamental perspective these ligands have afforded the isolation and subsequent characterisation of a number of low-coordinate species with unusual metal-metal bonding interactions. Key examples include the quintuply-bonded Cr complex featuring an amidopicoline ligand,[5] and the first Mg(I) complexes, which incorporated the bulky guanidinate $[(Dipp)N]_2C(N^iPr_2)^-$ and β-diketiminate $[(Dipp)NC(Me)]_2CH^-$ (Dipp = 2,6-diisopropylphenyl) ligands.[6]

Through the incorporation of a naphthalene framework into the backbone of amido ligands, an increased degree of structural rigidity is added, as well as a large amount of steric bulk. These properties have seen 1,8-diamidonaphthalene ligands used in the stabilisation of lanthanoid metal complexes.[7] Additional steric bulk can be achieved through further modification to include sterically demanding silyl groups, and the resulting 1,8-bis(silylamido)naphthalene ligands have been utilised in the isolation of a number of main group complexes, including with lithium,[8-11] mixed metal compounds,[8,9] Group 13,[12-15] tin,[12,16,17] and bismuth.[18,19] Examples of transition metal complexes featuring these bidentate ligands have come from our research group[20,21] and from others who have developed Ti and Zr complexes which are promising olefin polymerisation catalysts.[13,22-24]

During our investigations with the use of the $[1,8-C_{10}H_6(NSiR_3)_2]^{2-}$ (R = Me, ^{i}Pr) ligands in the isolation of amido complexes of Mn(II), Fe(II), and Zn(II) we isolated a number of complexes resulting from the incorporation of LiCl(THF)$_n$ moieties into the structures.[20] Given the synthetic utility of alkyl-containing precursors in the formation of homoleptic and heteroleptic Group 2 complexes,[25] we have been investigating the use of this methodology to synthesise homobimetallic magnesium and zinc complexes featuring 1,8-bis(silylamido)naphthalene ligands. Herein we

present the use of 1,8-bis(silylamido)naphthalene ligands featuring the $-Si^iPr_3$ and $-SiMePh_2$ groups in the synthesis of monometallic and bimetallic complexes of magnesium, along with a bimetallic zinc complex, through alkane elimination reactions between the proligands and either Grignards or dialkyl complexes.

Experimental Section

All manipulations were performed under an argon or dinitrogen atmosphere using standard Schlenk line and glove box techniques. Hexane was dried by passing through a column of activated alumina, whilst toluene, diethyl ether and THF were purified *via* distillation over potassium, NaK and Na/benzophenone, respectively, and all solvents were degassed and saturated with argon prior to use. All solvents were stored in ampoules over potassium mirrors, with the exception of THF which was stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 (Goss) was dried, distilled over potassium and degassed with three freeze-pump-thaw cycles, whilst THF-d_8 was dried over CaH$_2$, distilled and then degassed with three freeze-pump-thaw cycles prior to use. Proligands $\mathbf{L^1H_2}$ and $\mathbf{L^2H_2}$ [$\mathbf{L^1H_2}$ = 1,8-C$_{10}$H$_6$(NSi^{i}Pr$_3$H)$_2$, $\mathbf{L^2H_2}$ = 1,8-C$_{10}$H$_6$(NSiMePh$_2$H)$_2$] and MgMe$_2$ were prepared using modified literature methods.[11,26] MeMgI(OEt$_2$)$_{1.5}$ was synthesised by refluxing activated magnesium with MeI in diethyl ether. Di(*n*-butyl)magnesium was obtained as a 1.0 M solution in heptane (Aldrich); solvent was removed *in vacuo*, and the compound was used as a solid. All other compounds were used as received. IR spectra were recorded as Nujol mulls on KBr discs using a Bruker Tensor 27 FTIR spectrometer. Elemental microanalyses were performed by Mr Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK. Mass spectrometry was performed by Dr Mick Cooper at the University of Nottingham. ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy was performed using Bruker DPX300, DPX400, AV400 and AV(III)400 spectrometers. Chemical shifts are quoted in ppm relative to TMS. Yields refer to purified products and are not optimised.

Synthesis of 1,8-$C_{10}H_6(NSiMePh_2)_2\{Mg(THF)_2\}$ (1)

A solution of **L^{2}H$_2$** (0.70 g, 1.3 mmol) in THF (25 mL), was added dropwise to a solution of di(n-butyl)magnesium (0.25 g, 1.8 mmol) in THF (25 mL) at −78 °C. After addition was complete, the golden-coloured solution was allowed to warm slowly to room temperature and stirred for 48 hours. Removal of the solvent *in vacuo* yielded a golden-coloured glassy solid. The solid was dissolved in toluene (10 mL), and on addition of hexane (10 mL), a golden-yellow microcrystalline sample of **1** precipitated out of solution. Storage of the saturated filtrate at −30 °C yielded colourless crystals of **1** suitable for analysis by single crystal X-ray diffraction. Yield: 0.75 g (80 %). ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): δ = 0.79 (s, 6H, Si(CH_3)), 0.86 (m, 8H, O(CH$_2$CH_2)$_2$), 3.07 (m, 8H, O(CH_2CH$_2$)$_2$), 6.85 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2 Hz, 2H, *2,7*-$C_{10}H_6$), 6.94 (t, $^3J_{H,H}$ = 8 Hz, 2H, *3,6*-$C_{10}H_6$), 7.18 (dd, J = 8 Hz, J = 2 Hz, 2H, *4,5*-$C_{10}H_6$), 7.54-7.59 (m, 12H, o- and p-Si(C$_6H_5$)$_2$), 7.94 ppm (m, 8H, *m*-Si(C$_6H_5$)$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, 298 K, C_6D_6): δ = 0.5 (Si(CH_3)), 24.6 (O(CH$_2$CH_2)$_2$), 63.4 (O(CH_2CH$_2$)$_2$), 117.4 (*2,7*-$C_{10}H_6$-CH), 118.9 (*4,5*-$C_{10}H_6$-CH), 125.2 (*9*-$C_{10}H_6$-C), 128.4 (*3,6*-$C_{10}H_6$-CH), 128.6 (*o*-Si(C$_6H_5$)$_2$-CH), 134.8 (*p*-Si(C$_6H_5$)$_2$-CH), 135.4 (*m*-Si(C$_6H_5$)$_2$-CH), 139.8 (*10*-$C_{10}H_6$-C), 143.1 (*i*-Si(C$_6H_5$)$_2$-C), 156.9 ppm (*1,8*-$C_{10}H_6$-CN). ^{29}Si{^{1}H} NMR (79.49 MHz, 298 K, C_6D_6): δ = −19.9 ppm. IR (Nujol mull): v/cm^{-1} = 3064 w, 3037 w, 2361 w, 1959 w, 1888 w, 1821 w, 1583 md, 1542 st, 1502 md, 1420 st, 1365 w, 1299 st, 1278 st, 1262 st, 1243 st, 1166 w, 1104 w, 1069 st, 1037 st, 916 st, 868 md, 832 md, 779 md, 760 md, 705 st, 640 w, 625 w, 500 md, 454 st. Anal. Calcd. for $C_{44}H_{48}MgN_2O_2Si_2$: C 73.67, H 6.74, N 3.91; found: C 73.69, H 6.65, N 3.82 %.

Synthesis of 1,8-$C_{10}H_6(NSiR_3)_2\{^nBuMg(THF)\}_2$ R$_3$ = MePh$_2$ (2), R$_3$ = ^{i}Pr$_3$ (3)

A solution of **L²H₂** (0.70 g, 1.3 mmol) in THF (25 mL), was added dropwise to a solution of Mg^{n}Bu₂ (0.35 g, 2.5 mmol) in THF (25 mL) at −78 °C. After addition was complete, the reaction was stirred at ambient temperature for 6 hours, producing a pale brown solution. This mixture was then heated to 50 °C and stirred at this temperature for 16 hours, producing an orange/brown solution. When the reaction had cooled to room temperature, the solvent was removed *in vacuo* to give a golden-yellow solid, which was extracted with toluene (10 mL). Storage of the saturated toluene solution at −30 °C yielded colourless crystals of 1,8-C₁₀H₆(NSiMePh₂)₂{^{n}BuMg(THF)}₂ (**2**) suitable for single crystal X-ray diffraction. Data for 1,8-C₁₀H₆(NSiMePh₂)₂{^{n}BuMg(THF)}₂ (**2**). Yield: 0.87 g (94 %). ¹H NMR (400.13 MHz, 298 K, C₆D₆): δ = 0.26 (m, 4H, MgC*H*₂CH₂CH₂CH₃), 0.98 (m, 8H, O(CH₂C*H*₂)₂), 1.10-1.15 (m, 8H, (MgCH₂C*H*₂C*H*₂CH₃), 1.37 (s, 6H, Si(C*H*₃)), 1.65 (m, 6H, (MgCH₂CH₂CH₂C*H*₃), 3.19 (m, 8H, O(C*H*₂CH₂)₂), 6.81 (t, *J* = 8 Hz, 2H, *3,6*-C₁₀*H*₆), 6.96 (dd, *J* = 7 Hz, *J* = 1.2 Hz, 2H, *2,7*-C₁₀*H*₆), 7.47 (dd, *J* = 7 Hz, *J* = 1.2 Hz, 2H, *4,5*-C₁₀*H*₆), 7.61 (dd, *J* = 7 Hz, *J* = 1.6 Hz, 12H, *o*- and *p*-Si(C₆*H*₅)₂), 7.99-8.01 ppm (m, 8H, *m*-Si(C₆*H*₅)₂). ¹³C{¹H} NMR (100.61 MHz, 298 K, C₆D₆): δ = 2.1 (Si(*C*H₃)), 14.0 (Mg*C*H₂CH₂CH₂CH₃), 14.8 (MgCH₂*C*H₂CH₂CH₃), 25.2 (O(CH₂*C*H₂)₂), 32.7 (MgCH₂CH₂*C*H₂CH₃), 33.4 (MgCH₂CH₂CH₂*C*H₃), 69.9 (O(*C*H₂CH₂)₂), 119.8 (*2,7*-C₁₀H₆-*C*H), 121.1 (*4,5*-C₁₀H₆-*C*H), 121.7 (*9*-C₁₀H₆-*C*), 126.4 (*3,6*-C₁₀H₆-*C*H), 128.5 (*o*-SiC₆H₅-*C*H), 129.7 (*p*-SiC₆H₅-*C*H), 136.0 (*m*-Si(C₆H₅)₂-*C*H), 139.8 (*10*-C₁₀H₆-*C*) 143.6 (*i*-Si(C₆H₅)₂-*C*), 152.6 ppm (*1,8*-C₁₀H₆-*C*N). ²⁹Si{¹H} NMR (79.49 MHz, 298 K, C₆D₆): δ = −12.1 ppm. IR (Nujol mull): v/cm⁻¹ = 3048 w, 2360 w, 1558 md, 1426 md, 1255 st, 1108 st, 1051 st, 869 md, 798 st, 740 md, 701 md, 501 w, 463 w. Anal. Calcd. for C₅₂H₆₆Mg₂N₂O₂Si₂: C 72.97, H 7.77, N 3.27; found: C 73.02, H 7.95, 3.67 %. Data for 1,8-C₁₀H₆(NSi^{i}Pr₃)₂{^{n}BuMg(THF)}₂ (**3**). Synthesised from **L¹H₂** (0.30 g, 0.64 mmol) and di(n-butyl)magnesium (0.19 g, 1.40 mmol). Yield: 0.38 g (67 %). ¹H NMR (400.13 MHz, 298 K, C₆D₆): δ = −0.03 (m, 4H, MgC*H*₂CH₂CH₂CH₃), 0.21 (t, 4H, MgCH₂C*H*₂CH₂CH₃), 0.89 (m, 8H, O(C*H*₂CH₂)₂), 1.05 (t, 4H, MgCH₂CH₂C*H*₂CH₃), 1.14 (m, 6H, MgCH₂CH₂CH₂C*H*₃), 1.35 (d, ³$J_{H,H}$ = 7.5 Hz, 36H, Si(CH(C*H*₃)₂)₃), 1.67 (sept, 6H,

Si(CH(CH$_3$)$_2$)$_3$), 2.99 (m, 8H, O(CH$_2$CH_2)$_2$), 6.90 (d, J = 8 Hz, 2H, $2,7$-C$_{10}$$H_6$), 6.99 (d, J = 8 Hz,

2H, $4,5$-C$_{10}$$H_6$), 7.08 ppm (t, 2H, J = 8 Hz, $3,6$-C$_{10}$$H_6$). ^{13}C{^{1}H} NMR (100.61 MHz, 298 K, C$_6$D$_6$):

δ = 12.6 (MgCH$_2$CH$_2$CH$_2$CH$_3$), 14.6 (MgCH$_2$CH$_2$CH$_2$CH$_3$), 15.4 (Si(CH(CH$_3$)$_2$)$_3$), 21.0

(Si(CH(CH$_3$)$_2$)$_3$), 25.2 (O(CH$_2$$CH_2$)$_2$), 30.2 (MgCH$_2$$CH_2CH_2CH_3$), 32.2 (MgCH$_2CH_2$$CH_2CH_3$),

70.2 (O(CH$_2$CH$_2$)$_2$), 119.9 ($2,7$-C$_{10}$H$_6$-CH), 121.5 ($4,5$-C$_{10}$H$_6$-C), 124.2 (9-C$_{10}$H$_6$-C), 126.8 ($3,6$-

C$_{10}$H$_6$-CH), 140.0 (10-C$_{10}$H$_6$-C), 151.2 ppm ($1,8$-C$_{10}$H$_6$-CN). ^{29}Si{^{1}H} NMR (79.49 MHz, 298 K,

C$_6$D$_6$): δ = 5.9 ppm. IR (Nujol mull): v/cm^{-1} = 2029 w, 1959 w, 1561 md, 1538 md, 1428 w, 1417

w, 1302 w, 1269 md, 1257 md, 1218 w, 1204 w, 1172 w, 1161 w, 1038 st, 1016 md, 916 w, 900

md, 883 md, 849 md, 804 w, 760 w, 741 md, 666 w, 652 w, 627 w, 532 w, 522 w, 467 w. Anal.

Calcd. for C$_{44}$H$_{82}$Mg$_2$N$_2$O$_2$Si$_2$: C 68.11, H 10.65, N 3.61; found: C 67.83, H 10.53, N 3.55 %.

Synthesis of 1,8-C$_{10}$H$_6$(NSi^{i}Pr$_3$)$_2${MeMg(THF)}$_2$ (4)

A solution of MgMe$_2$ (0.08 g, 1.40 mmol) in THF (20 mL) was added dropwise to a solution of

L^{1}H$_2$ (0.30 g, 0.64 mmol) in THF (20 mL) at −78 °C. After addition was complete, the reaction

mixture was then allowed to warm slowly to room temperature and stirred for 16 hours. The solvent

was then removed *in vacuo* and the solid was extracted with hexane (10 mL). Storage at −30 °C

caused precipitation of the product, which was isolated *via* filtration and dried further to afford **4**

as a golden-coloured solid. Single crystals of **4** were obtained *via* slow cooling of the concentrated

hexane solution to −30 °C. Yield: 0.32 g (72 %). ^{1}H NMR (400.13 MHz, 298 K, C$_6$D$_6$): δ = −0.75

(s, 6H, MgCH_3), 1.00 (m, 8H, O(CH_2CH$_2$)$_2$), 1.36 (d, J = 7 Hz, 36H, Si(CH(CH_3)$_2$)$_3$), 1.76 (sept,

6H, Si(CH(CH$_3$)$_2$)$_3$), 2.97 (m, 8H, O(CH$_2$CH_2)$_2$), 7.02 (d, J = 8 Hz, 2H, $2,7$-C$_{10}$$H_6$), 7.08 (t, 2H, J

= 8 Hz, $3,6$-C$_{10}$$H_6$), 7.14 ppm (d, J = 8 Hz, 2H, $4,5$-C$_{10}$$H_6$). ^{13}C{^{1}H} NMR (100.61 MHz, 298 K,

C$_6$D$_6$): δ = −7.7 (MgCH$_3$), 15.1 (Si(CH(CH$_3$)$_2$)$_3$), 21.0 (Si(CH(CH$_3$)$_2$)$_3$), 25.5 (O(CH$_2$$CH_2$)$_2$), 69.5

(O(CH$_2$CH$_2$)$_2$), 119.6 ($2,7$-C$_{10}$H$_6$-CH), 121.1 ($4,5$-C$_{10}$H$_6$-CH), 124.3 (9-C$_{10}$H$_6$-C), 126.8 ($3,6$-

C$_{10}$H$_6$-CH), 140.1 (10-C$_{10}$H$_6$-C), 152.0 ppm ($1,8$-C$_{10}$H$_6$-CN). ^{29}Si{^{1}H} NMR (79.49 MHz, 298 K,

C_6D_6): δ = 6.3 ppm. IR (Nujol mull): v/cm^{-1} = 3052 w, 1959 w, 1899 w, 1596 w, 1557 st, 1506 w, 1427 md, 1301 w, 1259 md, 1203 st, 1171 md, 1121 md, 1112 md, 1036 st, 1016 st, 930 w, 916 md, 886 md, 864 md, 842 st, 824 md, 795 md, 763 md, 737 md, 650 md, 624 md, 553 w, 522 md, 441 w. Anal. Calcd. for $C_{38}H_{70}Mg_2N_2O_2Si_2$: C 65.98, H 10.20, N 4.05; found: C 66.00, H 9.99, N 4.12 %.

Synthesis of 1,8-$C_{10}H_6$(NSiMePh$_2$)$_2${ZnMe}$_2$ (5)

A solution of ZnMe$_2$ in toluene (1.2 M, 3 mL, 3.6 mmol) was added to a solution of **L^{2}H$_2$** (0.30 g, 0.55 mmol) in toluene (20 mL) at 0 °C with stirring. The resulting mixture was heated to reflux overnight, after which all the solvent was removed *in vacuo* and toluene was added (*ca.* 10 mL). This was heated until a clear golden solution was formed, and single crystals of **5** suitable for X-ray diffraction were grown from this solution after slow cooling to 5 °C (0.27 g, 71%). ^{1}H NMR (300.13 MHz, 298 K C_6D_6): δ = –0.31 (s, 6H, Me), 0.30 (s, 6H, Si(C*H*$_3$)), 6.89 (t, 2H, *J* = 8 Hz, *3,6*-C$_{10}$*H*$_6$), 7.12 (d, *J* = 8 Hz, 2H, *2,7*-C$_{10}$*H*$_6$), 7.25 (d, *J* = 8 Hz, 2H, *4,5*-C$_{10}$*H*$_6$), 7.30-7.32 (m, 12H, *o*- and *p*-Si(C$_6$*H$_5$*)$_2$), 7.96-7.99 ppm (br m, 8H, *m*-Si(C$_6$*H$_5$*)$_2$). ^{13}C{^{1}H} NMR (100.63 MHz, 298 K, C_6D_6): δ = –2.04 (SiMe$_3$), 22.0 (Me), 121.9 (*2,7*-C$_{10}$H$_6$-*C*H), 126.6 (*4,5*-C$_{10}$H$_6$-*C*H), 127.7 (*9*-C$_{10}$H$_6$-*C*), 128.9 (*3,6*-C$_{10}$H$_6$-*C*H), 129.9 (*o*-SiC$_6$H$_5$-*C*H), 130.6 (*p*-SiC$_6$H$_5$-*C*H), 135.9 (*m*-Si(C$_6$H$_5$)$_2$-*C*H), 136.9 (*10*-C$_{10}$H$_6$-*C*), 138.5 (*i*-Si(C$_6$H$_5$)$_2$-*C*), 144.3 ppm (*1,8*-C$_{10}$H$_6$-*C*N). ^{29}Si{^{1}H} NMR (79.49 MHz, 298 K, C_6D_6): δ = –5.2 ppm. IR (Nujol mull): v/cm^{-1} = 2601 (st), 1959 (wk), 1566 (wk), 1541 (wk), 1513 (st), 1365 (wk), 1292 (wk), 1262 (wk), 1125 (wk), 1064 (wk), 1026 (wk), 886 (wk), 863 (wk), 810 (st), 782 (wk), 761 (wk), 748 (st), 630 (wk), 589 (wk), 521 (wk). EI-MS: M$^+$ ion not present, fragment ion peaks observed at *m/z* 612 [M-ZnMe$_2$, 20%]$^+$, 443 [M-ZnMe$_2$-MePh$_2$, 8%]$^+$, Anal. Calcd for $C_{38}H_{38}N_2Si_2Zn_2$: C, 64.31; H, 5.40; N, 3.95. Found: C, 63.97; H, 5.19; N, 4.08 %.

Synthesis of 1,8-C$_{10}$H$_6$(NSiMePh$_2$)$_2$(BrMgOEt$_2$)$_2$ (6)

A solution of **L^{2}H$_2$** (0.30 g, 0.55 mmol) in diethyl ether (20 mL) was added dropwise to a solution of methylmagnesium bromide (3.0 M in diethyl ether, 0.36 mL, 1.09 mmol) in diethyl ether (20 mL) at −78 °C. After addition was complete, the reaction mixture was allowed to warm slowly to room temperature and stirred for 16 hours. The golden-coloured solution was then filtered to remove unreacted material. Storage of the saturated diethyl ether solution at 4 °C yielded colourless crystals of **6** suitable for single crystal X-ray diffraction studies. Yield: 0.17 g (34 %); ^{1}H NMR (400.13 MHz, 298 K, C$_6$D$_6$/THF-d_8): δ = −0.55 (s, 6H, Si(CH_3)), 1.23 (t, 12H, O(CH$_2$CH_3)$_2$), 3.38 (q, 8H, O(CH_2CH$_3$)$_2$), 6.90 (t, J = 8 Hz, 2H, $3,6$-C$_{10}$$H_6$), 7.06 (d, J = 8 Hz, 2H, $2,7$-C$_{10}$$H_6$), 7.16 (d, J = 8 Hz, 2H, $4,5$-C$_{10}$$H_6$), 7.62 (m, 12H, o- and p-Si(C$_6$$H_5$)$_2$), 8.00 ppm (m, 8H, m-Si(C$_6$$H_5$)$_2$).^{13}C{^{1}H} NMR (100.61 MHz, 298 K, C$_6$D$_6$/THF-d_8): δ = 4.2 (Si(CH_3)), 15.9 (O(CH$_2$$CH_3$)$_2$), 66.2 (O($CH_2CH_3$)$_2$), 117.9 ($2,7$-C$_{10}H_6$-$C$H), 119.4 ($4,5$-C$_{10}H_6$-$C$H), 120.7 ($9$-C$_{10}H_6$-$C$) 126.6 ($3,6$-C$_{10}H_6$-$C$H), 129.0 ($o$-SiC$_6H_5$-$C$H), 129.7 ($p$-SiC$_6H_5$-$C$H), 136.5 ($m$-SiC$_6H_5$-$C$H), 139.8 ($10$-C$_{10}H_6$-$C$), 143.7 ($i$-SiC$_6H_5$-$C$), 151.5 ppm ($1,8$-C$_{10}H_6$-$C$N). ^{29}Si{^{1}H} NMR (79.49 MHz, 298 K, C$_6$D$_6$/THF-d_8): δ = 0.0 ppm. IR (Nujol mull): v/cm^{-1} = 3065 w, 3046 w, 1568 w, 1427 w, 1311 w, 1254 st, 1102 w, 1088 md, 1038 md, 995 st, 886 w, 854 md, 828 w, 807 md, 785 md, 774 w, 642 w, 506 md. Anal. Calcd. for C$_{44}$H$_{52}$Br$_2$Mg$_2$N$_2$O$_2$Si$_2$: C 58.36, H 5.79, N 3.09; found C 58.28, H 5.72, N 3.13 %.

Synthesis of 1,8-C$_{10}$H$_6$(NSiMePh$_2$)$_2$(IMgOEt$_2$)$_2$ (7)

A solution of **L^{2}H$_2$** (0.30 g, 0.55 mmol) in diethyl ether (30 mL) was added dropwise to a solution of methylmagnesium iodide (0.34 g, 1.23 mmol) in diethyl ether (20 mL) at −78 °C. After addition was complete, the reaction mixture was allowed to warm slowly to room temperature and stirred

for 16 hours. The golden-coloured solution was then filtered to remove unreacted material. Storage of the saturated diethyl ether solution at room temperature yielded colourless crystals suitable for study by single crystal X-ray diffraction. The crystals were dried *in vacuo*, affording 1,8-$C_{10}H_6(NSiMePh_2)_2(IMgOEt_2)_2$ (**7**) which was used for spectroscopic characterisation. Initial attempts to crystallise **7** instead resulted in the isolation of a few crystals of [1,8-$C_{10}H_6(NSiMePh_2)_2\{IMg(OEt_2)\}]_2$ (**8**). Yield of **7**: 0.15 g (27 %); ^{1}H NMR (400.13 MHz, 298 K, C_6D_6/THF-d_8): δ = −0.63 (s, 6H, Si(C*H₃*)), 1.19 (t, 12H, O(CH₂C*H₃*)₂), 3.38 (q, 8H, O(C*H₂*CH₃)₂), 6.90 (t, *J* = 8 Hz, 2H, *3,6*-$C_{10}H_6$), 7.03 (d, *J* = 8 Hz, 2H, *2,7*-$C_{10}H_6$), 7.16 (dd, *J* = 8 Hz, *J* = 2 Hz, 2H, *4,5*-$C_{10}H_6$), 7.34-7.96 (m, 12H, *o*- and *p*-Si(C_6H_5)₂), 8.03 ppm (m, 8H, *m*-Si(C_6H_5)₂). ^{13}C{^{1}H} NMR (100.61 MHz, 298 K, C_6D_6/THF-d_8): δ = 3.3 (Si(*C*H₃)), 15.9 (O(CH₂*C*H₃)₂), 66.3 (O(*C*H₂CH₃)₂), 117.8 (*2,7*-$C_{10}H_6$-*C*H), 119.4 (*4,5*-$C_{10}H_6$-*C*H), 120.1 (*9*-$C_{10}H_6$-*C*), 125.7 (*3,6*-$C_{10}H_6$-*C*H), 128.9 (*o*-SiC₆H₅-*C*H), 129.6 (*p*-SiC₆H₅-*C*H), 136.0 (*m*-Si(C_6H_5)₂-*C*H), 139.7 (*10*-$C_{10}H_6$-*C*), 143.6 (*i*-Si(C_6H_5)₂-*C*), 157.5 ppm (*1,8*-$C_{10}H_6$-*C*N). ^{29}Si{^{1}H} NMR (79.49 MHz, 298 K, C_6D_6/THF-d_8): δ = −20.0 ppm. IR (Nujol mull): *v*/cm[-1] = 3046 w, 2726 w, 2671 w, 1562 md, 1427 md, 1310 w, 1246 st, 1107 md, 1039 md, 998 w, 890 w, 859 md, 828 w, 796 md, 698 md, 638 w, 510 md, 463 w. Anal. Calcd. for $C_{44}H_{52}I_2Mg_2N_2O_2Si_2$: C 52.87, H 5.24, N 2.80; found C 53.01, H 5.27, N 2.77 %.

Crystallographic Procedures

Crystals were mounted on MicroMounts™ (MiTeGen) using YR1800 perfluoropolyether oil and cooled rapidly to 90 or 120 K in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device.[27] Data for **L₂H₂** (120 K), **1** (90 K), **4** (120 K), **5** (90 K) and **7** (90 K) were collected on a Rigaku Oxford Diffraction SuperNova diffractometer, equipped with a mirror-monochromated Cu-*K*α source (λ = 1.5418 Å) and data for **2**, **6** and **8** were collected on a Bruker SMART APEX diffractometer (90 K) equipped with graphite-monochromated Mo-*K*α source (λ =

0.71073 Å). Programs used were CrysAlisPro[28] (control and integration) and Bruker AXS SMART[29] (control), and Bruker AXS SAINT[29] (integration), and SHELXS,[30] SHELXL[30] and OLEX2[31] (structure solution, structure refinement and molecular graphics, respectively). CCDC-1531494-1531501 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **L^2H_2**: $C_{36}H_{34}N_2Si_2$, M_r 550.83, $0.47 \times 0.10 \times 0.09$ mm^3, triclinic, space group P-1 (No. 2), $a = 9.8529(5)$, $b = 12.7192(7)$, $c = 12.8221(8)$ Å, $\alpha = 100.086(5)$, $\beta = 92.916(4)$, $\gamma = 106.819(5)°$, $V = 1505.55(15)$ Å^3, $Z = 2$, $D_{calc} = 1.215$ g cm^{-3}, $\mu = 1.268$ mm^{-1}, CuKα radiation, 1.54184 Å, $T = 120$ K. 9878 reflections measured (5860 unique, $R_{int} = 0.023$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give $wR_2 = 0.1344$ for all data and $R_1 = 0.0480$ for 5860 reflections with $I > 2\sigma(I)$, GooF = 1.08 for 369 parameters. Min. and max. residual electron densities –0.32 and 0.57 e/Å^3.

Crystal data for **1**: $C_{44}H_{48}MgN_2O_2Si_2$, M_r 717.33, $0.03 \times 0.09 \times 0.16$ mm^3, triclinic, P-1 (No. 2), $a = 8.6851(9)$, $b = 11.9556(8)$, $c = 20.1125(13)$ Å, $\alpha = 75.089(6)$, $\beta = 80.260(7)$, $\gamma = 72.972(8)°$, $V = 1919.6(3)$ Å^3, $Z = 2$, $D_{calc} = 1.241$ g cm^{-3}, $\mu = 1.301$ mm^{-1}, CuKα radiation, 1.54184 Å, $T = 90$ K. 12398 reflections measured (6694 unique, $R_{int} = 0.126$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give $wR_2 = 0.2775$ for all data and $R_1 = 0.1128$ for 6694 reflections with $I > 2\sigma(I)$, GooF = 1.11 for 462 parameters. Min. and max. residual electron densities –0.56 and 0.93 e/Å^3. Unfortunately, the crystal of **1** used for X-ray diffraction was low quality, and consequently the resulting data set obtained for **1** was of poor quality.

Crystal data for **2**: $C_{52}H_{66}Mg_2N_2O_2Si_2$, M_r = 855.86, 0.07 x 0.07 x 0.14 mm^3, monoclinic, Space group $C2/c$ (No. 15), a = 20.089(5), b = 10.280(3), c = 24.015(6) Å, β = 105.207(5)°, V = 4786(2) Å^3, Z = 4, D_{calc} = 1.188 g cm^{-3}, μ = 0.142 mm^{-1}, MoKα radiation, 0.71073 Å, T = 90 K. 11463 reflections measured (4162 unique, R_{int} = 0.079). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give wR_2 = 0.2109 for all data and R_1 = 0.0984 for 4162 reflections with $I > 2\sigma(I)$, GooF = 1.15 for 274 parameters. Min. and max. residual electron densities –0.47 and 0.59 e/Å^3.

Crystal data for **4**: $C_{38}H_{70}Mg_2N_2O_2Si_2$, M_r = 691.76, 0.15 x 0.21 x 0.61 mm^3, orthorhombic, space group $Pbca$ (No. 61), a = 14.4729(5), b = 17.2445(6), c = 32.0382(9) Å, V = 7996.0(5) Å^3, Z = 8, D_{calc} = 1.149 g cm^{-3}, μ = 1.358 mm^{-1}, CuKα radiation, 1.54184 Å, T = 120 K. 21583 reflections measured (7994 unique, R_{int} = 0.051). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give wR_2 = 0.1211 for all data and R_1 = 0.0428 for 7994 reflections with $I > 2\sigma(I)$, GooF = 1.04 for 448 parameters. Min. and max. residual electron densities –0.31 and 0.43 e/Å^3.

Crystal data for **5**: $C_{38}H_{38}N_2Si_2Zn_2$, M_r = 709.62, 0.05 x 0.10 x 0.14 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 9.9259(3), b = 16.7724(4), c = 20.3979(5) Å, β = 96.839(2)°, V = 3371.70(15) Å^3, Z = 4, D_{calc} = 1.398 g cm^{-3}, μ = 2.646 mm^{-1}, CuKα radiation, 1.54184 Å, 90 K. 13642 reflections measured (6643 unique, R_{int} = 0.040). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give wR_2 = 0.1048 for all data and R_1 = 0.0382 for 6643 reflections with $I > 2\sigma(I)$, GooF = 1.04 for 401 parameters. Min. and max. residual electron densities –0.55 and 0.81 e/Å^3.

Crystal data for **6**: $C_{44}H_{52}Br_2Mg_2N_2O_2Si_2$, $M_r = 905.49$, 0.15 x 0.21 x 0.61 mm^3, monoclinic, space group $C2/c$ (No. 15), $a = 14.345(4)$, $b = 14.986(4)$, $c = 19.710(6)$ Å, $\beta = 90.481(5)°$, $V = 4237(2)$ Å^3, $Z = 4$, $D_{calc} = 1.419$ g cm^{-3}, $\mu = 2.038$ mm^{-1}, MoKα radiation, 0.71073 Å, $T = 90$ K. 11769 reflections measured (4584 unique, $R_{int} = 0.037$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give $wR_2 = 0.1267$ for all data and $R_1 = 0.0505$ for 4584 reflections with $I > 2\sigma(I)$, GooF = 1.12 for 248 parameters. Min. and max. residual electron densities -1.09 and 0.98 e/Å^3.

Crystal data for **7**: $C_{44}H_{52}I_2Mg_2N_2O_2Si_2$, $M_r = 999.47$, 0.37 x 0.39 x 0.51 mm^3, monoclinic, space group $C2/c$ (No. 15), $a = 20.2536(7)$, $b = 10.1900(3)$, $c = 21.7038(7)$ Å, $\beta = 93.943(3)°$, $V = 4468.7(2)$ Å^3, $Z = 4$, $D_{calc} = 1.486$ g cm^{-3}, $\mu = 12.129$ mm^{-1}, CuKα radiation, 1.54184 Å, 90 K. 29315 reflections measured (4528 unique, $R_{int} = 0.073$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give $wR_2 = 0.1473$ for all data and $R_1 = 0.0502$ for 4528 reflections with $I > 2\sigma(I)$, GooF = 1.07 for 248 parameters. Min. and max. residual electron densities -1.34 and 1.72 e/Å^3.

Crystal data for **8**: $C_{80}H_{84}I_2Mg_2N_4O_2Si_4 \cdot C_4H_{10}O$, $M_r = 1622.41$, 0.03 x 0.04 x 0.05 mm^3, triclinic, space group P-1 (No. 2), $a = 10.827(2)$, $b = 13.846(3)$, $c = 14.987(3)$ Å, $\alpha = 69.427(3)$, $\beta = 75.353(4)$, $\gamma = 85.388(4)°$, $V = 2035.0(7)$ Å^3, $Z = 1$, $D_{calc} = 1.324$ g cm^{-3}, $\mu = 0.896$ mm^{-1}, MoKα radiation, 0.71073 Å, $T = 90$ K. 17889 reflections measured (9167 unique, $R_{int} = 0.060$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give $wR_2 = 0.1385$ for all data and $R_1 = 0.0838$ for 9167 reflections with $I > 2\sigma(I)$, GooF = 1.20 for 530 parameters. Min. and max. residual electron densities -1.10 and 0.52 e/Å^3.

Results and Discussion

Proligands L^1H_2 and L^2H_2 [L^1H_2 = 1,8-$C_{10}H_6(NSi^iPr_3H)_2$, L^2H_2 = 1,8-$C_{10}H_6(NSiMePh_2H)_2$] were synthesised according to modified literature procedures.[11] Single crystals of L^2H_2 were obtained *via* the slow cooling of a saturated hexane solution to –30 °C. The crystal structure of L^2H_2 is shown in Figure 1, along with relevant bond lengths and angles. The structure of L^2H_2 features two differing Si–N bonds [Si(1)–N(1) = 1.7420(17) Å, Si(2)–N(2) = 1.7303(18) Å], and concurrent with this one C–N bond is shorter than the other [C(1)–N(1) = 1.437(2) Å, C(9)–N(2) = 1.390(3) Å]. These values are in the ranges reported by Roesky *et al.* for L^1H_2.[12] There is also an intramolecular hydrogen bond [H(2)···N(1) = 2.06(3) Å, N(2)–H(2)···N(1) = 144(2)°], and the two SiMePh$_2$ units are staggered with respect to each other, leading to a C(11)–Si(1)···Si(2)–C(24) torsion angle of 128.27(11)°. In L^2H_2 the naphthyl backbone is not planar, with the two rings twisted in a "figure of 8" pattern in which they are offset by *ca.* 2.5°. The two silicon atoms are also offset from the plane of the naphthyl rings, with both protruding in the same direction, with Si(1) and Si(2) sitting out of the mean plane of the rings by 0.97 Å and 0.51 Å, respectively.
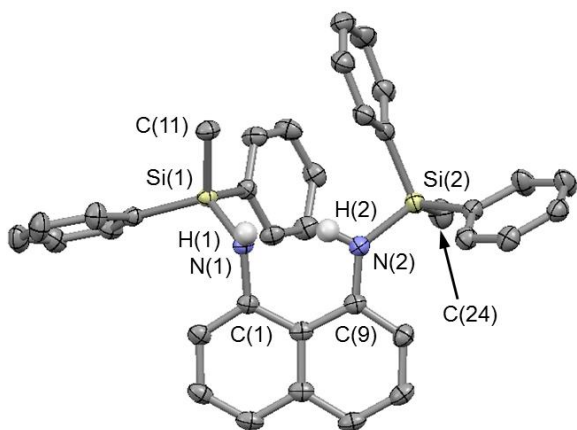
Figure 1. Molecular structure of L^2H_2 with displacement ellipsoids set at 50% probability level. With the exception of H(1) and H(2) all hydrogen atoms have been omitted for clarity. Relevant bond lengths (Å) and angles (°): N(1)–H(1) 0.864, N(2)–H(2) 0.843, Si(1)–N(1) 1.7420(17), Si(2)–N(2) 1.7303(18), C(1)–N(1) 1.437(2), C(9)–N(2) 1.390(3), H(2)···N(1) 2.06(3), N(2)–H(2)···N(1) 144(2), C(11)–Si(1)···Si(2)–C(24) torsion angle 128.27(11).

The reaction between **L¹H₂** or **L²H₂** and alkylmetal reagents afforded complexes **1-7** with concomitant evolution of the corresponding alkane (Scheme 1). In the case of the reaction between **L²H₂** and methylmagnesium iodide a small amount of crystalline material which was found to be $[1,8-C_{10}H_6(NSiMePh_2)_2\{IMg(OEt_2)\}]_2$ (**8**), was also isolated, and will be discussed below.
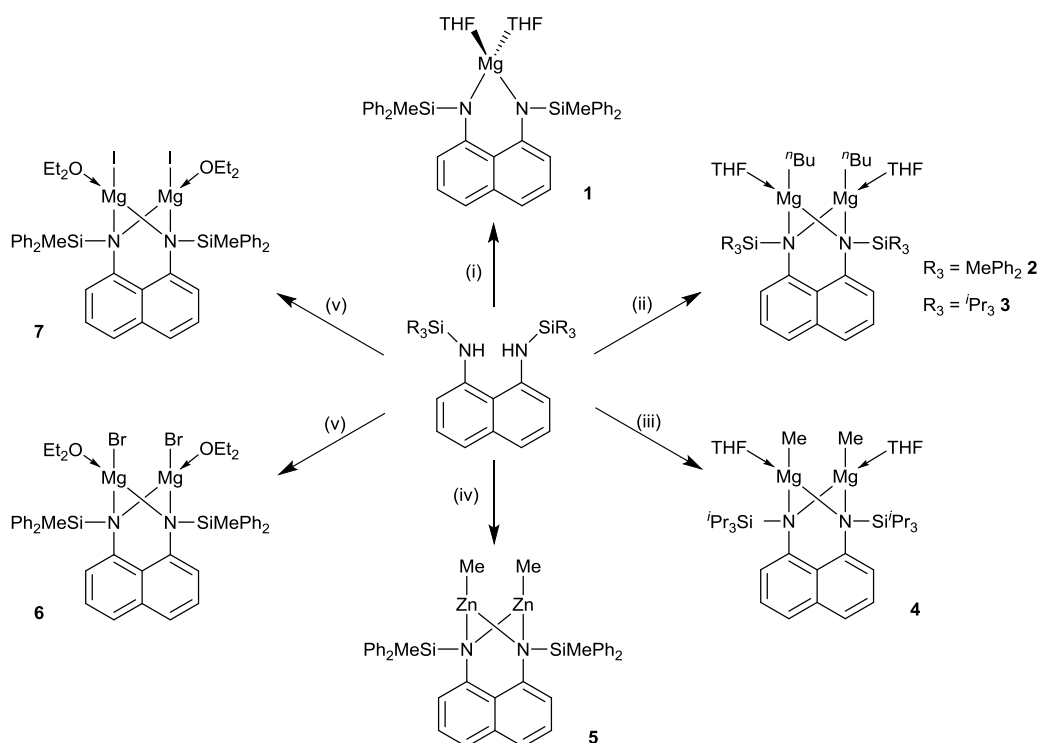
Scheme 1. Synthesis of complexes **1-7**. *Reagents and Conditions:* (i) 1.4 eq. Mg^{n}Bu₂, THF, −78 °C → room temperature, 48 hours, −2 eq. ^{n}BuH. (ii) 2 eq. Mg^{n}Bu₂, THF, −78 °C → room temperature, 16 hours, −2 eq. ^{n}BuH. (iii) 2 eq. MgMe₂, THF, −78 °C → room temperature, 16 hours, −2 eq. MeH. (iv) x/s ZnMe₂, toluene, 0 °C → reflux, 16 hours, −2 eq. MeH. (v) 2 eq. MeMgX (X = Br **6**, I **7**), diethyl ether, −78 °C → room temperature, 16 hours, −2 eq. MeH.

The reaction between **L²H₂** and 1.4 equivalents of di(*n*-butyl)magnesium in THF at −78 °C with slow warming to room temperature affords $1,8-C_{10}H_6(NSiMePh_2)_2Mg(THF)_2$ (**1**) (Scheme 1) in good yield. **1** has been characterised by NMR spectroscopy, elemental microanalysis and IR

spectroscopy, which support the proposed formulation. Single crystals of suitable quality for X-ray diffraction studies were obtained by storage of a saturated solution in a mixture of toluene/hexane at −30 °C. The solid state structure of **1** is shown in Figure 2. The quality of the data obtained for **1** was poor, so the discussion of the crystal structure will be limited to its connectivity. The structure of **1** contains a single magnesium atom coordinated to both nitrogen atoms of the dianionic ligand, as well as two THF solvent molecules, placing the metal centre in a distorted tetrahedral environment. The structure features a non-planar six-membered ring in a distorted half-chair conformation, containing three naphthalene carbon atoms, the two amido nitrogen atoms, and a magnesium atom, in a binding motif which has been previously seen in complexes of boron,[12] aluminium,[14] indium,[15] tin,[12,16] titanium,[13,23,24,32,33] zirconium,[10,13,22] and bismuth.[18,19] The two MePh$_2$ units are staggered, in an *anti*-conformation to one another.
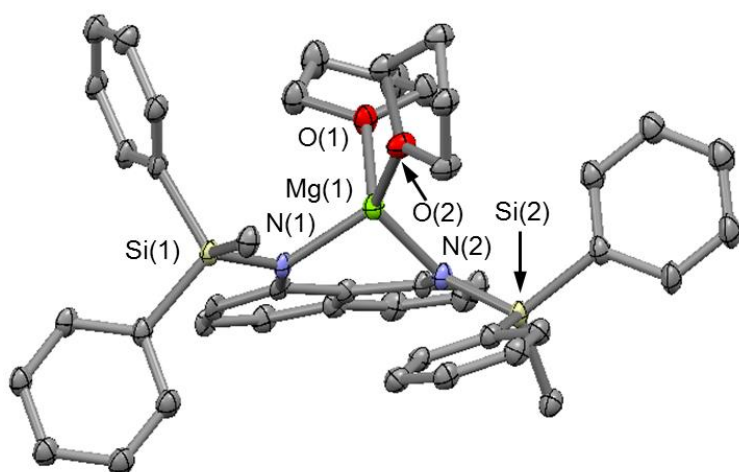
Figure 2. Molecular structure of **1** with displacement ellipsoids set at 50% probability level. All hydrogen atoms have been omitted for clarity.

Alkylmagnesium diamidonaphthalene complexes were synthesised by treating the relevant proligand with two equivalents of the diorganomagnesium (Mg^{n}Bu$_2$ or MgMe$_2$) in THF affording 1,8-C$_{10}$H$_6$(NSiR$_3$)$_2${^{n}BuMg(THF)}$_2$ [R$_3$ = MePh$_2$ (**2**), R$_3$ = ^{i}Pr$_3$ (**3**)] or 1,8-

C$_{10}$H$_6$(NSi^{i}Pr$_3$)$_2${MeMg(THF)}$_2$ (**4**), as shown in Scheme 1. The related solvent-free methylzinc diamidonaphthalene complex 1,8-C$_{10}$H$_6$(NSiMePh$_2$)$_2${ZnMe}$_2$ (**5**) was synthesised by the reaction of **L^{1}H$_2$** with excess ZnMe$_2$ in toluene. These complexes have been characterised by multinuclear NMR spectroscopy, IR spectroscopy and elemental microanalysis, and in the case of **5** by mass spectrometry, which supports the proposed formula. Single crystals of **2**, **4** and **5** of suitable quality for X-ray diffraction study were obtained *via* slow cooling of saturated solution in either hexane or toluene. The structures of these complexes can be found in Figures 3-5, along with relevant bond lengths and angles.
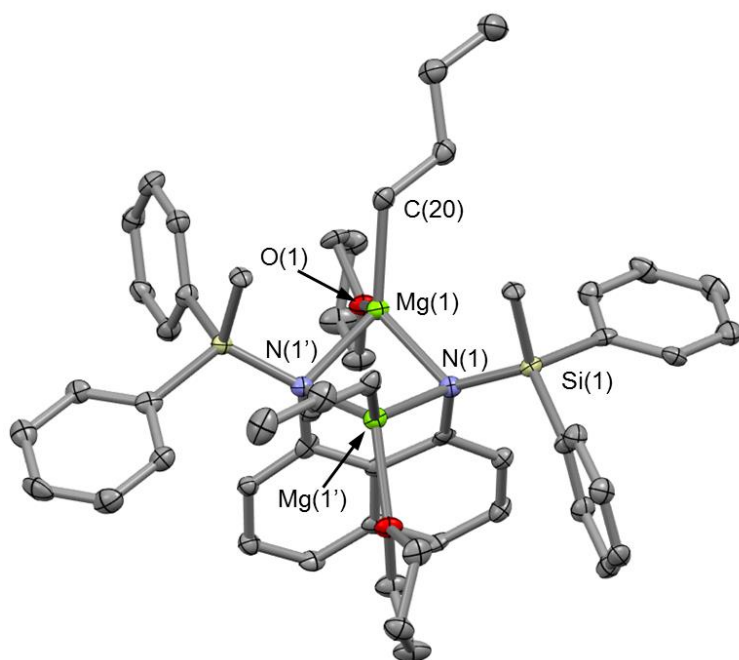
Figure 3. Molecular structure of **2** with displacement ellipsoids set at 50% probability level. All hydrogen atoms have been omitted for clarity. Relevant bond lengths (Å) and angles (°): Mg(1)–N(1) 2.169(5), Mg(1)–N(1') 2.129(5), Si(1)–N(1) 1.749(4), Mg(1)–C(20) 2.161(7), Mg(1)–O(1) 2.084(4), N(1)–Mg(1)–N(1') 81.69(18), Mg(1)–N(1)–Mg(1') 89.64(17). Symmetry elements used to generate equivalent atoms: ' = –*x*, *y*, ½–*z*.

The solid state structures of **2** and **4** (Figures 3 and 4, respectively) both feature two magnesium cations, each bound to two nitrogen atoms, one alkyl ligand and one THF moiety, leading to distorted tetrahedral geometries for the metals. These bonding arrangements place the two nitrogen atoms in distorted tetrahedral environments, with the coordinated solvent molecule perpendicular to the least-squares mean plane through the naphthyl ligand backbone. The structures also feature two six-membered cyclometallate rings, each containing three naphthalene carbon atoms, the two amido nitrogen atoms, and a metal atom. Due to both rings sharing five of the six atoms, they are not planar. Related complex **5** features two zinc cations bridging the two amido nitrogen atoms and a methyl group, leading to trigonal planar metal centres [Σ angles around Zn(1) and Zn(2) = 359.0(2)° and 359.2(2)°, respectively]. These M_2N_2 motifs have been observed in homobimetallic[8,9,11,13,16] and heterobimetallic[8,9,20] complexes. The M_2N_2 rings in **2**, **4** and **5** are non-planar (sums of the inner angles are 342.6°, 346.0°, and 342.7°, respectively), a geometry which is enforced by the rigidity of the naphthyl framework.
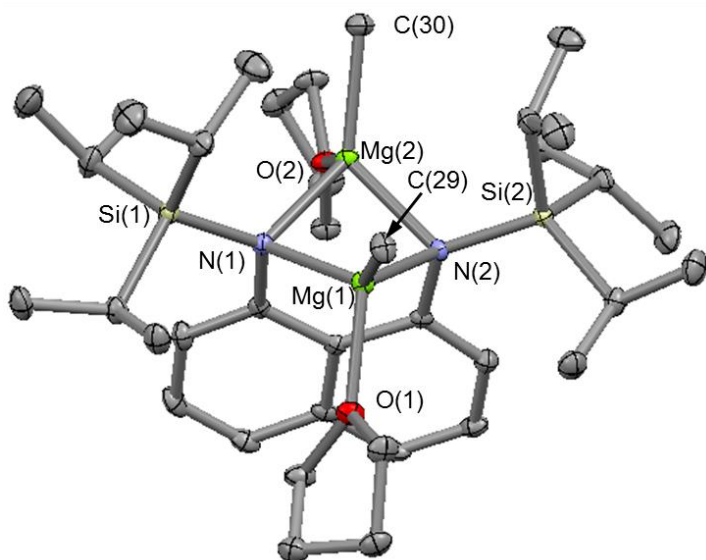
Figure 4. Molecular structure of **4** with displacement ellipsoids set at 50% probability level. All hydrogen atoms have been omitted for clarity. Relevant bond lengths (Å) and angles (°): Mg(1)–N(1) 2.1331(12), Mg(1)–N(2) 2.1358(12), Mg(2)–N(1) 2.1816(12), Mg(2)–N(2) 2.1566(12), Si(1)–N(1) 1.7769(12), Si(2)–N(2) 1.7745(12), Mg(1)–O(1) 2.0987(12), Mg(2)–O(2) 2.1042(12),

Mg(1)–C(29) 2.1399(15), Mg(2)–C(30) 2.1434(17), Mg(1)···Mg(2) 3.0529(9), N(1)–Mg(1)–N(2) 83.43(5), N(1)–Mg(2)–N(2) 81.81(5), Mg(1)–N(1)–Mg(2) 90.07(5), Mg(1)–N(2)–Mg(2) 90.67(5).

The Mg–N bonds in **4** are within a relatively wide range, in which the Mg(2)–N bonds are longer than the Mg(1)–N [Mg(1)–N(1) 2.1331(12), Mg(1)–N(2) 2.1358(12), Mg(2)–N(1) 2.1816(12), Mg(2)–N(2) 2.1566(12) Å], with Mg(2)–N(1) being particularly elongated. These distances, with the exception of that for Mg(2)–N(2), are within the range of other magnesium amidonaphthalenes [2.031(6)-2.150(3) Å].[9,34] As in **4**, there is also asymmetry in the Zn–N bond distances in **5** [Zn–N distances in the range 2.036(2)-2.074(2) Å] (Figure 5); these are within the range reported for related zinc complexes [2.002(3)-2.074(7) Å].[20,34-36] The metal···metal distances in **4** and **5** are 3.0529(9) and 2.859(5) Å, respectively, which are significantly less than the sum of the van der Waals radii for these elements (4.4 Å for Mg···Mg and 4.2 Å for Zn···Zn).[37] The solid state structure of **5** is similar to those for the magnesium complexes, featuring two zinc units bridging between the diamidonaphthalene ligand, but the metals are free of coordinating solvent, leading to a three-coordinate, distorted trigonal planar geometry.
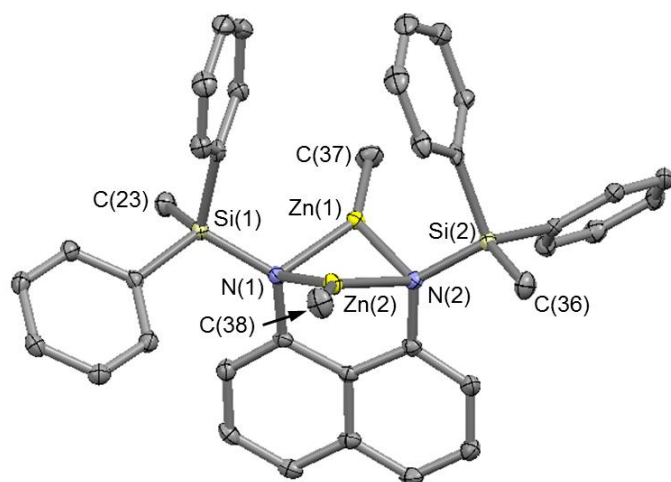
Figure 5. Molecular structure of **5** with displacement ellipsoids set at 50% probability level, with hydrogen atoms omitted for clarity. Relevant bond lengths (Å) and angles (°): Zn(1)–N(1) 2.064(2), Zn(1)–N(2) 2.038(2), Zn(2)–N(1) 2.036(2), Zn(2)–N(2) 2.074(2), Si(1)–N(1) 1.752(2), Si(2)–N(2)

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1.745(2), Zn(1)–C(37) 1.931(3), Zn(2)–C(38) 1.948(3), Zn(1)···Zn(2) 2.859(5), N(1)–Zn(1)–N(2) 83.18(8), N(1)–Zn(2)–N(2) 82.96(8), Zn(1)–N(1)–Zn(2) 88.45(8), Zn(1)–N(2)–Zn(2) 88.14(8).

The reaction between **L²H₂** and two equivalents of MeMgX in diethyl ether afforded the magnesium halide complexes 1,8-$C_{10}H_6(NSiMePh_2)_2(XMgOEt_2)_2$ (X = Br, **6**, Figure 6; X = I, **7**;) in moderate isolated yields with concomitant formation of two equivalents of methane, as illustrated in Scheme 1. Complexes **6** and **7** have been characterised by multinuclear NMR spectroscopy, IR spectroscopy and elemental microanalysis, which supports the proposed formula. These complexes feature two Mg(X)OEt₂ (X = Br, I) units, which is in contrast to Gade's 1,8-$C_{10}H_6(NSiMePh_2)_2Li(THF)Mg(Br)THF$, where even in the presence of excess $MgBr_2(OEt_2)$ only the mixed-metal amide could be obtained from the salt metathesis reactions.[9] The ¹H and ¹³C{¹H} NMR spectra of both **6** and **7** in C_6D_6/THF-d_8 solution exhibit one resonance for the methyl group in the SiMePh₂ moiety, suggesting that they are monomeric in solution. Single crystals of **6** and **7** suitable for study by X-ray diffraction were obtained from the storage of saturated diethyl ether solutions of these complexes at 4 °C or room temperature, respectively. Complexes **6** and **7** both feature two magnesium cations, each bound to two nitrogen atoms, one halide and one diethyl ether ligand.
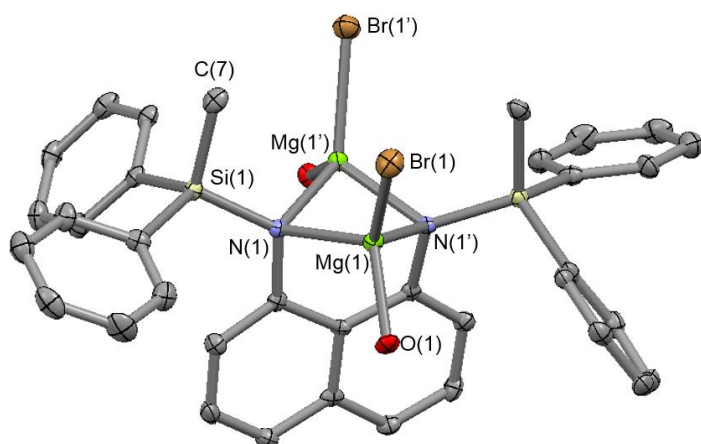
Figure 6. Molecular structure of **6** with displacement ellipsoids set at 50% probability level, with hydrogen atoms and the diethyl ether alkyl chains omitted for clarity. The structure of **7** is analogous. Relevant bond lengths (Å) and angles (°) for **6** [with analogous parameters for **7** in square brackets]: Mg(1)–N(1) 2.097(3) [2.110(4)], Mg(1)–N(1') 2.126(3) [2.131(4)], Mg(1)–X(1) 2.4388(16) (X = Br) [2.6898(14) (X = I)], Si(1)–N(1) 1.756(3) [1.749(4)], Mg(1)–O(1) 2.033(3) [2.042(3)], Mg(1)···Mg(1') 2.980(3) [3.040(2)], N(1)–Mg(1)–N(1') 83.15(13) [82.92(14)], Mg(1)–N(1)–Mg(1') 89.49(12) [91.57(14)]. Symmetry elements used to generate equivalent atoms: ' = 1–x, y, ½–z.

The Mg–Br bonds in **6** [Mg(1)–Br(1) = 2.4388(16) Å] are significantly shorter than that for 1,8-$C_{10}H_6$(NSiMePh$_2$)$_2$Li(THF)Mg(Br)THF [2.469(3) Å], which features a Mg–Br···Li interaction in the solid state.[9] The Mg–I distances [Mg(1)–I(1) = 2.6898(13) Å] are at the shorter end of the scale when compared to species containing six-membered cyclometallate rings [Mg−I distances range from 2.6722(15)-2.8271(11) Å].[38,39]

The Mg–N bonds in **6** [2.097(3), 2.126(3) Å] and **7** [2.110(4), 2.131(4) Å] occupy a narrower range than in **4**. Acute N–Mg–N angles are seen for **4** [83.43(5), 81.81(5)°], **6** [83.15(13)°] and **7** [82.92(14)°], which is due to the rigidity of the diamidonaphthalene moiety, again enforced by the ligand, and there is no difference in this angle on changing from bromide (**6**) to iodide (**7**). The naphthyl moieties display a slight deviation from planarity, with the angle between the fused rings being in the range 2.56-3.62°. Shorter Mg···Mg distances are observed for **6** [3.030(4) Å] and **7** [2.980(3) Å] compared to the methyl complex **4** [3.0529(9) Å].

The M$_2$N$_2$ rings are significantly deviated from planarity, the geometry within the bimetallic complexes is enforced by the rigidity of the naphthyl framework. The sums of the inner angles in these rings for **4-7** are 346.0°, 342.7°, 345.3° and 349.0°, and the corresponding dihedral angles

between the planes defined by the M–N–M moieties in these rings: 41.0°, 45.0°, 41.8° and 36.6°, respectively.

In **5**, one of the phenyl rings of the SiMePh$_2$ moieties is oriented approximately perpendicular to the least-squares mean plane through the M$_2$N$_2$ moiety. Conversely, in **6** and **7** the methyl groups of the SiMePh$_2$ moieties are in this orientation (perpendicular to the best mean plane created by the M$_2$N$_2$ moiety), which is presumably to avoid unfavourable steric interactions between the two phenyl rings and the magnesium-bound halides. However, close inspection of the crystal structures of **6** and **7** reveal that this orientation also allows close approach of the methyl groups to the halide ligands, and a C–H···X interaction. For **6** H(7A)···Br(1') = 2.78 Å, C(7)–H(7A)···Br(1') = 157.1°; H(7B)···Br(1) = 2.96 Å, C(7)–H(7B)···Br(1) = 147.3°, and for **7** H(7A)···I(1') = 3.02 Å, C(7)–H(7A)···I(1') = 159.3°; H(7C)···I(1) = 3.07 Å, C(7)–H(7C)···I(1) = 145.6°. In **4** the Si^{i}Pr$_3$ groups deviate by *ca.* 18° from an eclipsed conformation.

Initial attempts to crystallise **7** from a saturated solution in diethyl ether at 4 °C instead resulted in the isolation of a very small number of crystals of [1,8-C$_{10}$H$_6$(NSiMePh$_2$)$_2${IMg(OEt$_2$)}]$_2$ (**8**). These crystals are extremely sensitive and immediately decomposed after X-ray diffraction studies were completed; multiple attempts to isolate this product again have been unsuccessful. The solid state structure of **8** is shown in Figure 7, along with relevant bond distances and angles, and indicates that two of the diamidonaphthalene ligands have coupled together at the 4-position with concomitant dearomatisation of one of the naphthyl arene rings. The magnesium cations in **8** are in a distorted tetrahedral environment, and are bound to two nitrogen atoms, an iodide and a diethyl ether. Although a mechanism for this coupling has yet to be elucidated, the bis(imino)acenapthene ligand, 2,6-diisopropylphenyl-substituted diimine (BIAN), has been shown to activate in the analogous position to our naphthalene ligand with concomitant dearomatisation in the reaction between Ae{CH(SiMe$_3$)$_2$}$_2$THF$_2$ (Ae = Mg, Ca, Sr) and BIAN,[40] and a magnesium complex has been shown to mediate a C–C coupling reaction, in

this case of benzothiazole.[41] In addition, 1,4,5,8-tetrakis(guanidino)naphthalene compounds have been coupled and dearomatised using iodine.[42] Furthermore, the catalysis of this cross-coupling by trace amounts of a late transition metal contaminant *e.g.* palladium cannot be disregarded.[43]
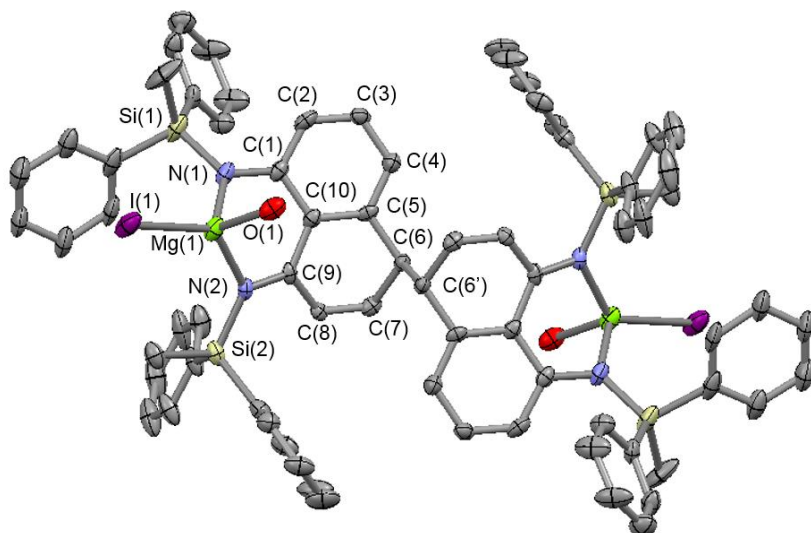

Figure 7. Molecular structure of **8** with displacement ellipsoids set at 50% probability level, with hydrogen atoms, the diethyl ether alkyl chains and the lattice diethyl ether molecule omitted for clarity. Relevant bond lengths (Å) and angles (°): Mg(1)–N(1) 2.000(5), Mg(1)–N(2) 2.104(5), Mg(1)–I(1) 2.682(2), Mg(1)–O(1) 2.071(5), N(1)–C(1) 1.365(7), N(2)–C(9) 1.328(7), C(6)–C(6') 1.586(10), C(6)–C(7) 1.494(8), C(7)–C(8) 1.330(8), C(8)–C(9) 1.479(8), N(1)–Mg(1)–N(2) 89.9(2). Symmetry elements used to generate equivalent atoms: ' = –*x*, 2–*y*, –*z*.

Complex **8** features a non-planar C(5)-C(10) ring which is non-aromatic and adopts a boat conformation; two of the carbon atoms in the ring are sp^2 hybridised, intimating a remaining degree of conjugation and the presence of a double bond. The angles around where the ring folding occurs are 117.0(5)° [C(5)–C(10)–C(9)], 110.8(5)° [C(5)–C(6)–C(7)] and 115.3(5)° [C(8)–C(9)–C(10)]. The two non-planar rings are bound to one another at the C(6) position, which, together with a proton, places these carbon atoms in a distorted tetrahedral geometry; the long C(6)–C(6') bond [1.586(10) Å][44] is likely caused by steric repulsion. A clearer view of these effects is shown in

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Figure 8. The other ring of the naphthalene remains planar, and forms a plane with C(6) and C(9) of the folded ring, resulting in a fold angle of 35.5(3)°. Closer examination of the bonding in the non-aromatic ring of the ligand suggests the presence of an α,β-unsaturated imine. The N–C bond connected to this ring is slightly shorter than that on the aromatic ring [N(2)–C(9) = 1.328(7) Å, N(1)–C(1) = 1.365(7) Å], as well as a short C–C bond in the ring [C(7)–C(8) = 1.330(8) Å], which both intimate increased bond order (Figure 9). These bond distances and the pattern of N=C–C=C–C bonds match those in similar complexes which contain conjugated imines,[15,45] although the difference in N–C distances is smaller in **8**.
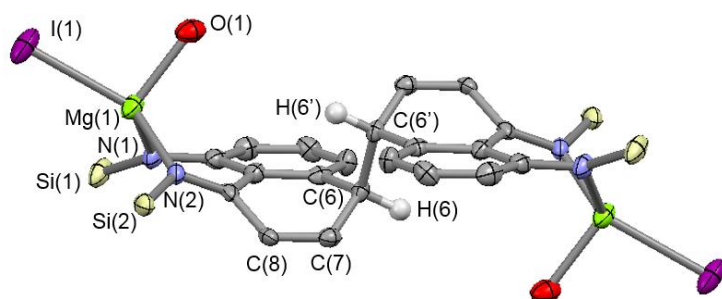
Figure 8. Backbone folding and magnesium coordination in **8** (' = –x, 2–y, –z). Displacement ellipsoids modelled at 50% probability. With the exception of H(6) and H(6'), hydrogen atoms are omitted for clarity, as are silyl substituents and magnesium-bound diethyl ether alkyl chains.
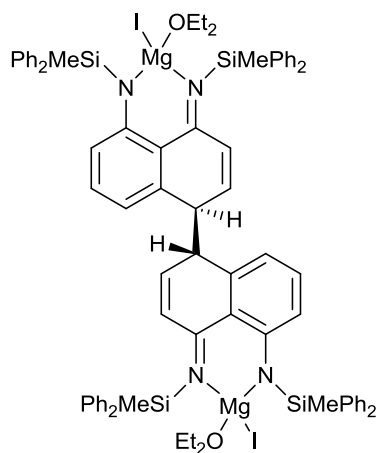
Figure 9. Suggested bonding in compound **8**.

In **8** the Mg–N distances differ significantly [Mg(1)−N(1) = 2.000(5) Å, Mg(1)−N(2) = 2.104(5) Å]. Differences in M–N bond distances have also been observed in other monometallic complexes featuring a diamidonaphthalene backbone,[46] the shorter Mg–N distance is in the range of those reported in complexes containing six-membered cyclometallate rings [Mg−N distances range from 1.990(2) Å to 2.049(4) Å].[38,39] The formally assigned dative N→Mg bond in **8** is similar in length to the Mg−N bonds in (btmgn)MgBr$_2$ (btmgn = 2,8-bis(tetramethylguanidino)naphthalene), a monometallic magnesium naphthalene complex featuring imino nitrogen donors,[34] as well as those in other complexes featuring coordinating imines.[47,48] Significant differences between Mg–N distances have also been previously observed in complexes featuring a classic amido Mg−N σ-bond and a dative N→Mg interaction.[47,49,50]

Conclusions

Alkane elimination reactions between magnesium or zinc alkyl compounds and 1,8-bis(triorganosilyl)diaminonaphthalenes provide very versatile methods for the synthesis of the 1,8-bis(triorganosilyl)diamidonaphthalene complexes. Changing the reaction stoichiometry conveniently affords the mono- or bimetallic systems, leading to differing coordination environments for the magnesium centres. The homobimetallic magnesium and zinc complexes feature distorted four-membered M$_2$N$_2$ rings, this coordination environment enforced by the rigidity of the amidonaphthyl moiety. The reaction between **L^{2}H$_2$** and Grignard reagents affords the homobimetallic complexes 1,8-C$_{10}$H$_6$(NSiMePh$_2$)$_2$(XMgOEt$_2$)$_2$ (X = Br, I), which have proven inaccessible *via* salt elimination methodology.[9] In the case of the iodide complex, very small amounts of crystals of [1,8-C$_{10}$H$_6$(NSiMePh$_2$)$_2${IMg(OEt$_2$)}]$_2$, where two of the diamidonaphthalene ligands have coupled together at the 4-position, with concomitant dearomatisation of one of the naphthyl arene rings were also isolated.

Acknowledgements

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